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KINETIC AND MECHANISTIC INVESTIGATION OF REDUCTIVE DECHLORINATION AT IRON SURFACES

by

Tie Li

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMICAL AND ENVIRONMENTAL ENGINEERING
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2002
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Tie Li entitled *Kinetic and Mechanistic Investigation of Reductive Dechlorination at Iron Surfaces* and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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DEDICATION

To Dahai, my wife, for your love and support.

To Mom and Dad, for your understanding, faith, and encouragement.
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ABSTRACT

The long-term performance of zero-valent iron for reductive dechlorination of trichloroethylene (TCE) and perchloroethylene (PCE) was investigated. The effects of elapsed time, mass transfer limitations, influent halocarbon concentration, and water chemistry on reductive dechlorination rates were studied in a series of column reactors. Dechlorination rates were pseudo-first order in reactant concentration for submillimolar halocarbon concentrations. With increasing elapsed time, reaction rates deviated from pseudo-first order behavior due to reactive site saturation, and increased iron surface passivation towards the influent end of each column. Measurements of iron corrosion rates in nitrate and chloride solutions showed that nitrate contributed to increased iron surface passivation and decreased rates of iron corrosion. Corrosion current measurements indicated that halocarbon reduction on fresh iron surfaces was cathodically controlled, whereas on aged iron surfaces, iron corrosion was anodically controlled. The decrease in TCE reaction rates over time can be attributed to anodic control of iron corrosion, and not to increasing reactant mass transfer limitations associated with diffusion through porous corrosion products. The disparity between amperometrically measured reaction rates and those measured in the column reactor indicated that halocarbon reduction may occur via direct electron transfer or may occur indirectly through reaction with atomic hydrogen absorbed on the iron surface.

The kinetics, reaction mechanisms, and current efficiencies for electrochemical reduction of TCE and CT were investigated using flow-through, iron electrode reactors,
and with amperometric measurements of reduction rates. Typical reduction half-lives for TCE and CT in the iron reactor were 9.4 and 3.7 minutes, respectively. The addition of palladium as an electrocatalyst at a level of 1 mg-Pd per square meter of electrode surface area increased the reaction rates by a factor of three. Comparisons of amperometrically measured current efficiencies with those measured in the flow-through reactors, and the weak effect of electrode potential on TCE reaction rates, indicated that the primary pathway for TCE reduction by iron and palladized iron electrodes was indirect, and involves atomic hydrogen as the reducing agent. For CT, similar amperometric and analytically measured current efficiencies indicated that the primary mechanism for CT reduction is direct electron transfer.

Chronoamperometry (CA) and chronopotentiometry (CP) analyses were used to determine the kinetics of CT and TCE reduction by a rotating disk electrode in solutions of constant halocarbon concentration. The transfer coefficient for CT was independent of temperature, while that for TCE was temperature dependent. This indicated that CT reduction was limited by the rate of electron transfer. The temperature dependent transfer coefficient for TCE indicated that its reduction was limited by chemical dependent factors, and not by the rate of electron transfer. In accord with a rate limiting mechanism involving an electron transfer reaction, the apparent activation energy ($E_a$) for CT reduction was found to decrease with decreasing electrode potential. Conversely, the $E_a$ for TCE reduction showed a slight increase with decreasing electrode potential, supporting the conclusion that its reaction rate was not limited by the rate of electron transfer.
CHAPTER 1

INTRODUCTION

1.1 Introduction

Chlorinated organic compounds are prevalent groundwater contaminants due to their widespread use as industrial solvents during the past several decades. Water contaminated with chlorinated organic compounds is of significant health concern since most commonly used halocarbons are identified or suspected carcinogens, mutagens or teratogens. Removal of chlorinated organic compounds from contaminated groundwaters and industrial waste streams is a ubiquitous environmental problem. There are an estimated 400,000 contaminated sites that are scheduled for cleanup over the next few decades in the United States.

Presently employed remediation technologies include adsorption by activated carbon and air stripping. While these methods are effective for removing the halocarbons from the aqueous phase, they only transfer the contaminants from water to another medium, which then requires treatment or disposal.

In recent years, there has been increasing interest in developing destructive treatment methods for removing chlorinated organic compounds from aqueous waste streams and contaminated groundwaters. Reductive dechlorination at metal surfaces, which transforms halocarbons into their non-chlorinated analogs and chloride ions, has been extensively investigated as a method to remove halocarbons from aqueous solutions.
The use of zerovalent metals for reductive dechlorination has been a very active research area since Gillham and O’Hannesin (1) proposed that metallic iron filings could be utilized in passive ground water remediation schemes (2-5).

Zerovalent iron (ZVI) (6) has been found to be effective at mediating the reductive dechlorination of halocarbons in aqueous systems. Full and pilot scale ZVI remedial systems have been installed at more than twenty field sites in the United States and Canada (7). However, reductive dechlorination with zerovalent iron filings is too slow to be employed in above ground canister treatment systems, and is subject to declining performance due to the buildup of a protective iron (hydr)oxide passivating layer at the reactive surface (8).

The long-term performance of ZVI remedial systems depends on the continued effectiveness of the iron to serve as an electron donor. The current-voltage relationship for redox reactions involving a corroding iron electrode can be described by a form of the Butler-Volmer equation (9) as:

$$i = i_{corr} \left[ e^{-\beta_c (E - E_{corr})} - e^{\beta_a (E - E_{corr})} \right]$$

where $i$ is the net current density, $i_{corr}$ is the corrosion current density, $E$ is the electrode potential, $E_{corr}$ is the free corrosion potential, and $\beta_c$ and $\beta_a$ are the cathodic and anodic Tafel slopes, respectively. Under open circuit conditions where the electrode potential is equal to $E_{corr}$, $i$ is equal to zero, and the corrosion rate of the electrode is equal to $i_{corr}$. At electrode potentials sufficiently above or below $E_{corr}$, equation 1 indicates that a plot of log $i$ versus $E$ will be linear. The linear regions of the polarization profiles have slopes equal to $\beta_a$ and $\beta_c$, and are known as the anodic and cathodic Tafel regions. The $i_{corr}$
under open circuit conditions can be determined graphically by extrapolating the anodic and cathodic Tafel slopes to their point of intersection at $E_{corr}$ \(10\).

Under open circuit conditions, the overall rate of iron corrosion may be limited by either the anodic or cathodic half-cell reactions. For corrosion of ZVI by aqueous TCE in anaerobic solutions, the anodic reaction is given by:

\[
Fe \rightarrow Fe^{2+} + 2e^- \quad (2)
\]

while the cathodic reactions when ethene is the product may be expressed as:

\[
H_2O + H^- + 2e^- \rightarrow H_2 + OH^- \quad (3)
\]

\[
C_2HCl_3 + 3H^- + 6e^- \rightarrow C_2H_4 + 3Cl^- \quad (4)
\]

If the aggregate rate of the anodic reactions is slower than the potential rate of the cathodic reactions, corrosion of the iron is anodically controlled \(11\). Under anodically controlled conditions, the rate at which oxidants are able to accept electrons is faster than the rate at which the iron is able to release electrons. In contrast, cathodically controlled corrosion occurs when the rate at which oxidants are able to accept electrons is slower than the rate at which the iron is able to release electrons. The relative magnitude of $\beta_a$ and $\beta_c$ indicate whether the anodic or cathodic reactions are limiting the overall rate of iron corrosion. For example, when $\beta_c > \beta_a$, corrosion of the iron is anodically controlled. The condition of the iron surfaces, and the polarizing ability of potential oxidants, determine whether iron corrosion is anodically or cathodically controlled.

The potential problems associated with ZVI groundwater treatment include dissolution of the iron, formation of oxide coatings on the iron surface (surface passivation), and slow reaction kinetics. For above ground treatment systems cathodic
polarization of iron could be used to protect iron from corrosion and enhance the rates of reductive dechlorination.

There are both direct and indirect mechanisms for halocarbon reduction by zerovalent metals. Direct reduction may occur by electron tunneling, or by formation of a chemisorption complex of the organic compound with surface metal atoms (12). Electron tunneling may occur to halocarbons that are physically adsorbed at the zerovalent metal surface, or to halocarbons that are separated from the surface by adsorbed water or iron corrosion products (10, 13). Indirect reduction of organic compounds involves atomic hydrogen. Atomic hydrogen absorbed at the metal surface may reduce organic compounds through the formation of chemisorbed hydride complexes (12). This mechanism is fast on metals with low hydrogen overpotentials, such as platinum and palladium, but is much slower on metals with high hydrogen overpotentials, such as iron (12). Indirect evidence has also been presented that Fe\(^{2+}\) may contribute to halocarbon reduction (14).

1.2 Research Objectives

The overall objective of this research was to investigate the kinetics, pathways, reaction mechanisms and rate-limiting factors for reductive dechlorination at iron surfaces with or without externally applied potentials. TCE, perchloroethylene (PCE) and carbon tetrachloride (CT) were chosen for the target compounds because they are typical examples of chlorinated alkenes and chlorinated alkanes in contaminated groundwater. The understanding of reaction mechanisms and rate-limiting factors is
essential in successful development of feasible and cost effective treatment methods for removing chlorinated organic compounds from aqueous solutions.

1.3 Dissertation Outline

This dissertation consists of seven chapters. Following the Chapter 1 Introduction is a literature review of relevant research in Chapter 2. Chapter 3 and Chapter 4 describe the column studies and electrochemical analysis on the kinetics, long-term effectiveness, and the rate controlling mechanisms of reductive dechlorination on fresh and aged iron surfaces. Both chapters have been published in the journal of Environmental Science and Technology (ES&T). Chapter 5 is also a published manuscript that investigates the kinetics, mechanisms, and current efficiencies for electrochemical reduction of TCE and CT using flow-through iron and palladized iron electrode reactors. In Chapter 6 a rotating disk electrode reactor was used to determine temperature dependence of the electron transfer coefficient and potential dependence of the apparent activation energies for both TCE and CT reduction. Chapter 7 summarizes the findings and conclusions throughout this dissertation research.

1.4 References


CHAPTER 2

LITERATURE REVIEW

2.1 Zerovalent Iron for Reductive Dechlorination

The use of ZVI for in situ remediation of ground water contaminated with chlorinated organic compounds has received considerable attention in recent years. Iron and other base metals, such as zinc and magnesium, have been found to be effective at mediating the reductive dehalogenation of chlorinated organic compounds in aqueous systems (7-6). Full and pilot scale ZVI remedial systems have been installed at more than twenty field sites in the United States and Canada (7).

2.1.1 Kinetic study

Many investigators have observed first order kinetics for degradation of chlorinated organic compound by zerovalent iron in aqueous systems (8-11). Matheson and Tratnyek (4) also found a linear relationship between average iron specific surface area and observed first order rate constant. Deviation from first order kinetics for halocarbon reduction by zerovalent iron were reported as well (12, 13). Wust et al (13) applied a combined zero- and first-order kinetic model in describing the degradation of TCE and cis-DCE with zerovalent iron. Johnson et al (12) found that “first order” rate cosntants for CT disapperance decreased with increasing initial CT concentration and attributed this change to saturation of reactive sites.
A modified Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model was adapted by Arnold and Roberts to describe iron surface mediated reductive chlorination of chlorinated ethylene and acetylene (14). The LHHW model assumes that the activity of the surface towards adsorption, desorption, or surface reaction is independent of the surface coverage (15). However, the iron surfaces contain both anodic sites where iron become oxidized and cathodic sites where chlorinated solvents get reduced. Therefore, the number of potentially cathodic sites available for halocarbon reduction would actually decrease with increasing halocarbon concentration.

Reaction rates for most chlorinated compounds of environmental relevance have been determined in short-term laboratory testing using both batch and column reactors (16). Reported reaction rates are highly variable among different investigators (16). This variability can be attributed to differences in experimental conditions and to differences in iron type and specific surface area. Among all the rate affecting factors, the type of iron appears to be the most significant determinant of reaction rates. Even when reaction rates are normalized for the specific surface area of the iron, and are measured under the same experimental conditions, reaction rates for a particular compound have been observed to vary by up to three orders of magnitude between different types of iron (17).

Early investigations recognized that the condition of the iron surfaces also has a profound impact on reaction rates, and early batch testing was often performed on acid washed iron filings in order to achieve a repeatable initial surface condition (4). Several investigations in batch systems have observed that reaction rates are initially first order in reactant concentration, but deviate from first order behavior with increasing elapsed time.
Declining reaction rates with time have been attributed to increasing mass transfer limitations through surface associated oxide layers (1) and to anodic control of iron corrosion (18). X-ray diffraction analyses from field and column tests indicate that the passivating layer on iron filings consists of an inner layer of magnetite (Fe3O4) with an outer coating of maghemite (γ-Fe2O3) (11, 18).

The effects of solution chemistry on rates of reductive dechlorination have been investigated in several short-term laboratory studies, with sometimes conflicting results between different investigators. In some investigations, halocarbon reduction rates have been found to be highly pH dependent (1, 19), with up to a ten-fold increase in reaction rates accompanying a decrease of two pH units (20), while other investigators have reported minimal pH effects on reaction rates (17). These conflicting pH effects may be due to differences in buffering agents, some of which have been found to reduce rates of iron corrosion via a specific adsorption mechanism (10, 21). Conflicting results have also been reported on the effects of chloride ions on dechlorination rates. Some investigations have found up to a factor of three increase in carbon tetrachloride (CT) reduction rates with increases in chloride concentration (22), while other investigations have reported that chloride ions reduce rates of halocarbon reduction (3). Nitrate ions may also significantly affect halocarbon reduction rates by competing for electrons with the chlorinated compounds (2, 23).

Rates of reductive dechlorination for one and two carbon compounds have been correlated with several halocarbon properties, including the equilibrium potentials for one and two electron transfer reactions (24, 25). Generally, iron mediated dechlorination
rates for homologous compounds increase with increasing degree of halogenation. For example, recent review articles using data compiled from a variety of published sources have reported that PCE reaction rates are approximately five times faster than those for TCE, which in turn are 3-60 times faster than those for the three dichloroethylene isomers (16, 24). However, this trend has not been observed in all studies. For example, Burris et al. (8) reported that reaction rates for TCE and PCE were similar in short-term batch testing. This disparity from previously reported trends was attributed to possible mass transfer limitations and greater adsorption of PCE to nonreactive sites. Increasing dechlorination rates with decreasing degree of halogenation have been observed for chlorinated ethenes in bimetallic iron-palladium systems (26) and for reduction by supported palladium catalysts (27, 28).

2.1.2 Byproduct and pathways

Reductive dehalogenation reactions are generally divided into two categories (29): hydrogenolysis (replacement of a halogen by a hydrogen) and reductive elimination (in which two halide ions are released).

Chloro-alkene Reduction

Senzaki and Kumagai (30) found that the predominant TCE reduction products in iron powder column experiments were ethylene and ethane, with minor amounts of methane and acetylene. Orth and Gillham (9) conducted column experiments using electrolytic iron powder with TCE and found the products to be ethylene and ethane, with minor amounts of vinyl chloride (VC), 1,1-DCE, cis-DCE, trans-DCE, methane, propene, propane, butane, and 1-butene. Acetylene was not determined. Schreier and Reinhard
examined the transformation of PCE in batch systems using iron powder and observed only TCE, ethene, and ethane as products.

Orth and Gillham (9) proposed that a cumulative six electron transfer occurs to yield ethylene while the TCE molecule, or rather the organic carbon from the original TCE molecule, was still adsorbed to the iron surface. Schreier and Reinhard (5) proposed that sequential hydrogenolysis of PCE (PCE→TCE→cis-DCE→VC→ethene) may occur as well as unspecified side reactions to yield their observed products. The reported presence of acetylene (30) is not accounted for in either of the above proposed reaction mechanisms.

Roberts et al. (29) have recently shown that reduction of vicinal polychlorinated ethylenes by zero-valent metals can occur via a β-elimination mechanism in addition to the more conventionally proposed sequential hydrogenolysis pathway. The reduction of cis- and trans-DCE by zero-valent iron was shown to directly yield acetylene by reductive β-elimination. The reduction of PCE by zerovalent zinc also produced a significant amount of acetylene under conditions in which lesser-halogenated products such as cis-DCE are relatively stable. The reductive β-elimination of TCE and PCE would yield chloroacetylene and dichloroacetylene, respectively. The resulting chloroacetylene then undergoes hydrogenolysis to form acetylene, which may then be further reduced to ethene or ethane. Figure 1 summarizes possible TCE reduction pathways proposed by investigators (5, 29, 30).
Figure 1. TCE Reaction Pathways
Chloro-alkane Reduction

Matheson and Tratnyek (4) conducted a detailed study of CT degradation by ZVI. They found that conversion to chloroform typically accounted for about 70% of the CT degraded and the appearance of methylene chloride typically accounted for about 50% of the chloroform lost (4). Methylene chloride disappearance was only apparent after several months. No formation of chloromethane, methane, or coupling products like hexachloroethane were detected. Their results indicate that the dominant degradative pathway for chlorinated methanes in anaerobic Fe-H₂O systems is sequential hydrogenolysis and that the rates become much less favorable with each successive dechlorination step.

Reductive elimination was also suggested to be the second reaction pathway for CT degradation by iron (29, 31, 32). Both hydrogenolysis and reductive elimination pathways are initiated by dissociative electron transfer to give trichloromethyl radical and chloride ion as described by equation 1 (33).

\[
\text{CCl}_3 + e^- \rightarrow \cdot\text{CCl}_3 + \text{Cl}^-
\]  

(1)

In hydrogenolysis, the trichloromethyl radical is reduced to chloroform, which may undergo further hydrogenolysis to give dichloromethane. Liu (34) conducted the mechanistic study of CT reduction in mixtures of organic solvents and water. He was able to capture trichloromethyl radicals with a spin trap N-tert-butyl-α-phenylnitone (PNB) and provided direct evidence for the free radical mechanisms. In reductive elimination, the trichloromethyl radical undergoes a second dissociative electron transfer to form dichlorocarbene, which is hydrolyzed to give HCl and CO (35, 36). Balko and
Tratnyek (32) have found that photogenerated conduction band electrons do degrade CT and shift the product distribution to more completely dechlorinated products that are indicative of the reductive elimination pathway with a dichlorocarbene intermediate. In Figure 2 both hydrogenolysis and reductive elimination pathways are described for CT reduction.

**Figure 2. CT Reaction Pathways**

2.2 Bimetal Catalyst and Palladium-Hydrogen System

2.2.1 Bimetallic Catalyst

Transition metal bimetallic catalysts have been utilized to promote halocarbon degradation in several studies (37-40). Muftikian et al (37) have shown that TCE, 1,1-DCE, cis and trans-DCE, and PCE were rapidly hydrodechlorinated to ethane in a few minute on a Pd/Fe bimetallic surface. The chloroalkanes, CCl₄, CHCl₃, and CH₂Cl₂, were also dechlorinated to methane on the Pd/Fe surface (37).
Neurath et al (39) studied the feasibility of degradation of various chlorinated phenols (CPs), dichlorobenzenes (CBs), and PCBs with palladized iron in laboratory batch and flow-through model systems. They contributed the initial rapid loss of tri-, tetra- and penta- chlorophenols to adsorption to the palladized iron surface (39). The degradation rate of chlorophenols increased with the amount of Pd used, the surface area of Fe/Pd complex, and the cosolvent concentration (acetone, isopropanol, methanol). Analysis of the surface film on the Fe⁰/Pd⁰ reductant by X-ray photo spectroscopy (XPS) indicated that all Pd atoms were in the zerovalent state and all the Fe atoms in the surface film were in Fe²⁺ and/or Fe³⁺ states (39).

Nickel-plated granular iron has been tested for the acceleration of halocarbon degradation (40). When the nickel was enhancing the rate of TCE reduction, only ethane was observed as the daughter product. After 250 pore volumes, the rate enhancing effect of Ni on TCE reduction had disappeared and cis-DCE and vinyl chloride were produced. Muftikian et al. (38) has also found that prolonged exposure of Pd/Fe surface to a saturated solution of aqueous TCE resulted in the growth of a hydroxylated iron oxide film that deactivated the Pd/Fe surface.

2.2.2 Palladium-Hydrogen System

Supported palladium catalysts and a hydrogen source have also been shown to be effective in the treatment of halocarbons in the aqueous phase (23, 28, 41–45). Work on aqueous phase hydrodechlorination in columns with supported Pd was first reported by Yu (41). The gas feed consisted of pure hydrogen, and the liquid stream consisted of water containing 100-190 mg/L of 1,1,2-TCA or TCE. The trickling bed reactor
contained 31 mg of 1% w/w Pd on carbon particles. The steady-state reaction rate constants were 2.4/hr for 1,1,2-TCA and 6.0/hr for TCE. Catalyst deactivation was observed. The reaction rate constant for TCA dropped from its initial value of 7.14/hr to a constant value of 2.4/hr after 10 hours of operation. The deactivation was attributed to chloride poisoning, which has been observed in the gas phase (46).

Munakata et al. (42) utilized an upflow packed column filled with 0.1-2.0 g of 1% w/w Pd on alumina catalyst for reductive dechlorination of TCE in the aqueous phase. The influent TCE concentrations ranged from 1.5 to 25 mg/L. Hydrogen was supplied by purging the influent water with hydrogen gas and pressurizing it to 0.5 atm. With an average residence time of approximately one minute, TCE was >99% removed with an average first order rate constant of 436/hr and no noticeable decrease in activity over 5 months. The addition of 44 mg/L of nitrate to the influent water decreased TCE removal to 52%. Carbon dioxide (purged into the influent water supply with 90% H2/10% CO2 gas mixture) was shown to completely deactivate the catalyst after 13 days. However, the carbonate-deactivated catalyst was recovered to its original activity through exposure to a high temperature vacuum followed by oxygen.

In Lowry and Reinhard’s study (28), palladium supported on alumina and unsupported palladium filings were used in a flow through reactor to dehalogenate chlorinated, fluorinated, and brominated hydrocarbons. Reaction rates increased with decreasing degree of halogenation with DCE > TCE > PCE. Methylene chloride, 1,1-DCA and 1,2-DCA were nonreactive. Complete TCE conversion to ethane occurred in a
single interaction with the catalyst surface. CT was transformed to methane and ethane, indicating a free radical mechanism (28).

McNab and Ruiz (43) developed a two-stage treatment column for reductive dehalogenation of dissolved chlorinated aliphatics. The first stage consists of an electrolyzer cell which generates hydrogen by electrolyzing the influent water. The second stage contains a catalyst bed of palladium metal supported on alumina beads. Removal efficiencies greater than 95% were achieved for PCE, TCE, 1,1-DCE, and CT with residence times on the order of 2 minutes (43). Dissolved oxygen present in solution did not completely inhibit reduction of the chlorinated hydrocarbons on the catalyst (43).

2.3 Electrochemical Reduction of Halocarbons

Electrochemical reduction of halogenated aliphatic and aromatic compounds has been attempted by many investigators (31, 47-53). Overall the rate of halocarbon reduction was controlled by electrode kinetics or mass transport limitations (51). The electrode kinetics were found to be a function of electrode potential, electrode materials, and halocarbon type (31, 47, 48, 50).

2.3.1 Electrode Material

Different electrode materials have been tested in different electrochemical studies (30, 45-51). A silver cathode was used to reduce CT by Criddle and McCarty (31). CT was reduced to chloroform and to trace amounts of carbon monoxide. At $-0.71$ V SHE, some of the CT that was removed was converted to CF ($\sim15\%$). According to a chloride
balance, the non-CF products must be completely dechlorinated. At -0.93 V SHE, reduction to CF accounted for only ~6% of the CT transformation, while reduction to formate accounted for ~75% (31).

Other investigators have attempted electrochemical reduction of chlorocarbons using palladium supported on carbon and graphite cathodes (49, 52, 53). Although rapid dechlorination rates have been achieved with palladium coated cathodes, the effectiveness of the catalyst is short-lived. Several investigators have reported declining reaction rates over time due to loss of palladium from the electrode (52, 53). Cheng et al. (49) used a solid palladium cathode to eliminate the problem of palladium flaking off the electrode surface but found that the palladium gauze electrode was ineffective for chlorophenol reduction, despite rapid reaction rates by palladium supported on carbon and graphite (49). Sonoyama and Sakata (50) compared the efficiencies for chloroform decomposition by electrochemical reduction at various metal-impregnated carbon fiber electrodes (CFE). They reported that silver impregnated carbon fiber yielded the fastest kinetics. An oxide-free iron electrode was used to study the kinetics of CT reduction by Scherer and coworkers (51). For the conditions of their study (51), the rate of CT reduction by oxide-free iron appeared to be dominated by reaction at the metal-water interface rather than by mass transfer limitations.

Liu et al. (47) studied the electrolytic reduction of CT at metal cathodes consisting of pure Ag, Al, Au, cu, Fe, Ni, Pd, and Zn. At all electrodes reaction rates were found to conform to Butler-Volmer kinetics, modified to account for mass transfer limitations. Under comparable conditions, the materials tested exhibited the following order of
reactivity: Ni>Cu>Pd>Fe>Au>Ag>Zn>Al. Based on electrode efficiency (ratio of current for dehalogenation to total current), the electrode materials were ordered Zn>Cu>Fe>Ni (47). The electrode efficiency was found to be inversely proportional to the material-dependent exchange current density for hydrogen evolution (47).

2.3.2 Electrode Kinetics

First-order kinetics are often reported in electrochemical studies for chlorocarbon reduction (47-49, 51, 53). Liu and coworkers observed that the kinetics were first-order with respect to halocarbon concentration (47, 48). A linear free energy relationship (LFER) was developed between potential-dependent rate constants for chlorinated aliphatic compounds and their minimum carbon-chlorine bond dissociation energies. The chlorinated ethenes reacted much faster than predicted from bond enthalpy calculations and the alkane-based correlation, suggesting that alkenes are not transformed via the same mechanism as the chlorinated alkanes (48). At a fixed cathode potential, reaction rate constants were directly related to the degree of chlorine substitution of the target compound (48).

Cheng et al. (49) compared pseudo-first-order rate constants for the disappearance of 4-chlorophenol with different electrode materials. The normalized rate constants with respect to surface area for the palladized electrodes were observed to follow the trend: carbon cloth > graphite rod > iron wire (49). In a kinetic study of CT reduction with an iron electrode (51), the first-order heterogeneous rate constant ($k_{CT}$) was measured to be $2.3 \times 10^{-5} \text{ cm s}^{-1}$ at open circuit potential. This $k_{CT}$ value was 10 times greater than the
average reduction rate constant for previously reported batch and column experiments performed with granular iron (51).

2.3.3 Electron Transfer Mechanisms

There are two possible mechanisms responsible for electron transfer reactions (54): outer-sphere and inner-sphere electron transfer reactions. An outer-sphere reaction involves only e⁻ transfer, no bonds are broken or formed, and a catalyst plays no role. Transfer coefficients for an electron transfer reaction are defined as the fraction of the total applied electrical energy that is used for changing the activation energy of the reaction (55). Transfer coefficients should be independent of temperature for an outer-sphere mechanism (54). In an inner-sphere electron transfer reaction, the breaking of bond, a molecular rearrangement, or chemisorption of the reactant to the electrode surface may be rate determining. For an inner-sphere reaction, an effective transfer coefficient may be defined, but it may depend on temperature (54).

Reduction of oxidants at metal surfaces may occur through direct and indirect electron transfer reactions (56). Direct reduction may occur by electron tunneling, or by formation of a chemisorption complex of the organic compound with the iron surface (56). Electron tunneling may occur to halocarbons that are physically adsorbed at the iron surface, or to halocarbons that are separated from the iron surface by one or more layers of adsorbed water. Brewster (56) has also proposed an indirect reduction mechanism, which involves the formation of hydride complexes with atomic hydrogen adsorbed to the surface of the iron. Arnold and Roberts postulated that reduction of TCE
at zerovalent iron surfaces involves di-sigma bond formation between the carbon atoms on TCE and iron atoms (14).

2.4 References


5 Schreier, C. G.; Reinhard, M. *Chemosphere* 1994 29, 1743.


44 Schreier, C. G.; Reinhard, M. *Chemosphere*. 1995, 31 (6), 3475.


CHAPTER 3

INVESTIGATION OF THE LONG-TERM PERFORMANCE OF ZEROVALENT IRON FOR REDUCTIVE DECHLORINATION OF TRICHLOROETHYLENE

3.1 Abstract

This research investigated the long-term performance of zerovalent iron for mediating the reductive dechlorination of trichloroethylene (TCE). Over a two year period, rates of TCE dechlorination in columns packed with iron filings were measured in simulated ground waters containing either 3 mM CaSO₄, 5 mM CaCl₂ or 5 mM Ca(NO₃)₂. At early elapsed times, TCE reaction rates were pseudo-first order in TCE concentration, and were independent of the solution pH. With increasing elapsed time, reaction rates deviated from pseudo-first order behavior due to reactive site saturation, and increased iron surface passivation towards the influent end of each column. The extent of passivation was dependent on both the TCE concentration and the background electrolyte solution. For most of the investigation, TCE reaction rates in 3 mM CaSO₄ and 5 mM CaCl₂ solutions were statistically identical at the 0.05 confidence level. However, TCE reaction rates in 5 mM Ca(NO₃)₂ were slower. In columns operated using chloride and sulfate containing waters, the effective half-life for TCE dechlorination increased from approximately 400 minutes after ten days elapsed, to approximately 2500 minutes after 667 days. The effective TCE half-life in the nitrate containing water increased from approximately 1500 minutes after ten days, to approximately 3500 minutes after 667 days.
days. Measurements of iron corrosion rates in nitrate and chloride solutions showed that nitrate contributed to increased iron surface passivation and decreased rates of iron corrosion. Corrosion current measurements indicated that halocarbon reduction on fresh iron surfaces was cathodically controlled, whereas on aged iron surfaces, iron corrosion was anodically controlled. Anodic control of iron corrosion contributed to the development of reactive site saturation with time, and to similar reaction rates for TCE and perchloroethylene. Passivation of the iron surfaces was found to be dependent on the adhering tendency of the corrosion products, and not on the overall mass of corrosion products in the columns. The decrease in TCE reaction rates over time can be attributed to anodic control of iron corrosion, and not to increasing reactant mass transfer limitations associated with diffusion through porous corrosion products.

3.2 Introduction

This research investigated the long-term performance of zerovalent iron (ZVI) for reductive dechlorination of trichloroethylene (TCE). The effects of elapsed time, influent halocarbon concentration, flow rate, grain scale mass transfer limitations, and water chemistry on reaction rates were investigated in laboratory column reactors over a two year period. Voltammetric analyses of halocarbon reduction by iron and magnetite coated iron electrodes were used to investigate the mechanisms controlling TCE reduction rates on fresh and aged iron surfaces.
3.2.1 Iron Mediated Dechlorination

The use of ZVI for in situ remediation of ground water contaminated with chlorinated organic compounds has received considerable attention in recent years. Iron and other base metals, such as zinc and magnesium, have been found to be effective at mediating the reductive dehalogenation of chlorinated organic compounds in aqueous systems (1-6). Full and pilot scale ZVI remedial systems have been installed at more than twenty field sites in the United States and Canada (7).

The primary pathway for TCE reduction on ZVI occurs via a β-elimination mechanism (8). This pathway involves a two electron transfer in which chlorine atoms on adjacent carbons are released as chloride ions, with the concomitant formation of a triple bond (8). The resulting chloroacetylene then undergoes hydrogenolysis to form acetylene, which may then be further reduced to ethene or ethane. The primary end products of TCE dechlorination are ethane, ethene and acetylene, with the relative speciation dependent on the reactant concentration, temperature, pH, and the condition of the iron surfaces (2,3). Chlorinated products may also be produced, but they normally account for less than 5% of the total degradation products (8,9). The most commonly observed chlorinated products, cis-1,2-dichloroethylene (DCE), 1,1-DCE, and trans-1,2-DCE are not produced by the primary reaction pathway, but are produced by an alternate reaction pathway involving sequential hydrogenolysis (10,11).

Reaction rates for most chlorinated compounds of environmental relevance have been determined in short-term laboratory testing using both batch and column reactors (12). Reported rates of dechlorination vary widely among different investigators,
primarily due to differences in the iron reactants and solution chemistries (12). The condition of the iron surfaces may also affect reaction rates. Several investigators have reported that dechlorination rates on freshly acid washed surfaces are considerably faster than those on surfaces with aged iron oxide layers (13,14).

Many factors may influence the speciation and morphology of the iron corrosion products. Under anaerobic conditions, amorphous ferrous hydroxide Fe(OH)_2 is the first corrosion product formed (15). Magnetite (Fe_3O_4) may then be formed by oxidation of Fe(OH)_2. Under neutral pH conditions, intermediate to the formation of magnetite, mixed valent Fe(II)/Fe(III) salts, known as green rusts, may form (15). Green rusts are stable only at low redox potentials, and their oxidation commonly leads to formation of maghemite (γ-Fe_2O_3) or lepidocrocite. Slow oxidation which allows dehydroxylation of the green rust phase favors maghemite formation over lepidocrocite (15). Maghemite has the same inverse spinel structure as magnetite, but contains only Fe(III). The loss of ferrous ions from the lattice maintains charge balance in the structure. Although there are cation vacancies in the lattice, maghemite formed via oxidation of magnetite is nonporous, while maghemite formed from dehydroxylation of lepidocrocite is mesoporous (15).

Spectroscopic analyses of aged iron surfaces have found that the iron becomes coated with an inner layer of magnetite and an outer layer of maghemite (10,16). Although magnetite is a semiconductor, the small band gap between its valence and conduction bands gives it an electrical conductivity close to that of metals (15).
Therefore, magnetite is not considered to be a passivating oxide. In contrast to magnetite, maghemite has a large band gap and is considered to be a passivating oxide (17,18).

The effects of solution chemistry on rates of reductive dechlorination have been investigated in several short-term laboratory studies, with sometimes conflicting results between different investigators. In some investigations, halocarbon reduction rates have been found to be highly pH dependent (1,14), with up to a ten-fold increase in reaction rates accompanying a decrease of two pH units (19), while other investigators have reported minimal pH effects on reaction rates (20). These conflicting pH effects may be due to differences in buffering agents, some of which have been found to reduce rates of iron corrosion via a specific adsorption mechanism (17,26). Conflicting results have also been reported on the effects of chloride ions on dechlorination rates. Some investigations have found up to a factor of three increase in carbon tetrachloride (CT) reduction rates with increases in chloride concentration (21), while other investigations have reported that chloride ions reduce rates of halocarbon reduction (3). Nitrate ions may also significantly affect halocarbon reduction rates by competing for electrons with the chlorinated compounds (2,22).

The long-term performance of ZVI remedial systems depends on the continued effectiveness of the iron to serve as an electron donor. Several short-term column studies of approximately two months duration (9,23,24,25), and one five month column study (26) have reported no apparent loss in reactivity with elapsed time. In some of these studies, the columns were operated at accelerated flow rates in order to simulate long-
term aging effects (24,25). This type of testing is of only limited usefulness since oxidation of the iron surfaces by chlorinated organic compounds is only one of many possible contributions to the overall aging process. Other drawbacks to accelerated flow rate testing are that the mineral type and porosity of the surface oxides are dependent on the rate of oxidation, and thus depend on the halocarbon feed rate. Therefore, long-term testing may be required to determine the long-term effectiveness of ZVI remedial systems.

3.2.2 Electrochemical Analysis

The current-voltage relationship for redox reactions involving a corroding iron electrode can be described by a form of the Butler-Volmer equation (27) as:

\[ i = i_{corr} \left[ e^{-\beta_c (E - E_{corr})} - e^{\beta_a (E - E_{corr})} \right] \]  

(1)

where \( i \) is the net current density, \( i_{corr} \) is the corrosion current density, \( E \) is the electrode potential, \( E_{corr} \) is the free corrosion potential, and \( \beta_c \) and \( \beta_a \) are the cathodic and anodic Tafel slopes, respectively. Under open circuit conditions where the electrode potential is equal to \( E_{corr} \), \( i \) is equal to zero, and the corrosion rate of the electrode is equal to \( i_{corr} \). At electrode potentials sufficiently above or below \( E_{corr} \), equation 1 indicates that a plot of log \( i \) versus \( E \) will be linear. The linear regions of the polarization profiles have slopes equal to \( \beta_a \) and \( \beta_c \), and are known as the anodic and cathodic Tafel regions. The \( i_{corr} \) under open circuit conditions can be determined graphically by extrapolating the anodic and cathodic Tafel slopes to their point of intersection at \( E_{corr} \) (27).
Under open circuit conditions, the overall rate of iron corrosion may be limited by either the anodic or cathodic half-cell reactions. For corrosion of ZVI by aqueous TCE in anaerobic solutions, the anodic reaction is given by:

$$Fe \rightarrow Fe^{2+} + 2e^-$$  \hspace{1cm} (2)

while the cathodic reactions when ethene is the product may be expressed as:

$$H_2O + H^+ + 2e^- \rightarrow H_2 + OH^-$$  \hspace{1cm} (3)

$$C_2HCl_3 + 3H^+ + 6e^- \rightarrow C_2H_4 + 3Cl^-$$  \hspace{1cm} (4)

If the aggregate rate of the anodic reactions is slower than the potential rate of the cathodic reactions, corrosion of the iron is anodically controlled (17). Under anodically controlled conditions, the rate at which oxidants are able to accept electrons is faster than the rate at which the iron is able to release electrons. In contrast, cathodically controlled corrosion occurs when the rate at which oxidants are able to accept electrons is slower than the rate at which the iron is able to release electrons. The relative magnitude of $\beta_a$ and $\beta_c$ indicate whether the anodic or cathodic reactions are limiting the overall rate of iron corrosion. For example, when $\beta_c > \beta_a$, corrosion of the iron is anodically controlled. The condition of the iron surfaces, and the polarizing ability of potential oxidants, determine whether iron corrosion is anodically or cathodically controlled.
3.3 Materials and Methods

3.3.1 Column Experiments

Iron filings obtained from Master Builders’ Supply (MBS) (Cleveland, OH) and Cercona of America (Dayton, OH) were used in the investigation. Three columns were packed with MBS GX-27 iron filings mixture and one column was packed with the Cercona material. The MBS filings had particle diameters ranging from 0.15 to 1.7 mm, with a weight average mean diameter of 0.56 mm. The Cercona iron particles were roughly spherical in shape with diameters ranging from 0.84 to 1.7 mm. The specific surface area of both materials was measured by Micromeritics (Norcross, GA) using single point nitrogen BET analysis (28). The MBS iron had a specific surface area of 0.34 m²/g, and the Cercona iron had a specific surface area of 2.0 m²/g. Since iron corrosion products often have specific surface areas in excess of 10 m²/g (29), the BET measured surface areas likely overestimate the surface area of the underlying ZVI. Both types of iron were used as received, and appeared black due to the presence of adsorbed surface oxides.

The iron reactants were packed in 50 cm long by 2.54 cm o.d., stainless steel columns fitted with three sampling ports at 8.6, 15.8, and 32 cm from the influent end. The sampling ports were welded to the columns and were sealed with silicone rubber septa. Pseudo-steady state column experiments were used to measure reaction rates and determine reaction byproducts of TCE degradation. The pore volumes and dispersivities of the MBS columns were measured using a bromide tracer test. Dispersivity values
were calculated from the axial dispersion coefficients determined from the tracer breakthrough fronts \((30)\). The pore volume of the Cercona iron column was determined gravimetrically. Hydraulic conductivity values for all columns were determined using a falling head test \((31)\).

Three laboratory simulated ground waters with a background electrolyte ionic strength of 15 mM were used in the investigation. Two columns were operated using a 3 mM solution of calcium sulfate, one column was operated using 5 mM calcium chloride, and one column was operated using 5 mM calcium nitrate. To prevent biological activity in the feed water reservoirs, 3 mM sodium azide was added to all solutions, and the reservoirs were purged with nitrogen gas to remove dissolved oxygen. Properties of the columns are summarized in Table 1.

Table 1. Summary of column packing materials and properties.

<table>
<thead>
<tr>
<th>Column</th>
<th>Material</th>
<th>Water</th>
<th>Pore Volume (ml)</th>
<th>(K) (cm/s)</th>
<th>Dispersivity (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>1</td>
<td>MBS</td>
<td>CaSO(_4)</td>
<td>83</td>
<td>86</td>
<td>0.019</td>
</tr>
<tr>
<td>2</td>
<td>MBS</td>
<td>CaCl(_2)</td>
<td>85</td>
<td>75</td>
<td>0.021</td>
</tr>
<tr>
<td>3</td>
<td>MBS</td>
<td>Ca(NO(_3))(_2)</td>
<td>88</td>
<td>80</td>
<td>0.031</td>
</tr>
<tr>
<td>4</td>
<td>Cercona</td>
<td>CaSO(_4)</td>
<td>129</td>
<td></td>
<td>0.020</td>
</tr>
</tbody>
</table>

Halocarbon concentrations in the feed water stream were controlled using a water-gas contactor consisting of 1 m of 0.25 cm o.d., silicone rubber tubing contained inside a
1 L sealed glass vessel. The water-gas contactor was purged with a carbon dioxide and nitrogen gas mixture containing the halocarbon reactants. The feed water was pumped through the silicone rubber contact tubing with peristaltic pumps (Cole Parmer, Vernon Hills, IL). Constant carbonate (3 mM) and organic compound concentrations were maintained via diffusion of the gas phase compounds through the silicone rubber tubing. Halocarbon concentrations were independent of the flow rate through the water-gas contactor, indicating that equilibrium was attained between the water and gas phases. Between the water-gas contacting vessel and the column inlet, stainless steel tubing was used to prevent compound losses and oxygen contamination.

Reactant concentrations were measured by withdrawing 100 μl aqueous samples with a 250 μL gas-tight syringe (Hamilton, Reno, NV). The aqueous samples were then injected into 1 g of pentane which was analyzed using a Hewlett Packard 5890 gas chromatograph (GC) equipped with an autosampler and electron capture detector. Chlorinated reaction byproducts, such as vinyl chloride and the three DCE isomers, were identified using a Finnigan ITD 700 GC/mass spectrometer. Nonchlorinated reaction byproducts were measured by injecting 500 μL aqueous samples into a counter-current stripping apparatus purged with nitrogen gas. The analytes stripped into the purge gas were then quantified using a molecular sieve column mounted in a SRI Instruments GC equipped with a flame ionization detector. TCE adsorption in the columns was measured using a previously described liquid chromatography technique (32). Dissolved iron and anion concentrations were determined by the Soil, Water and Plant Analysis Laboratory.
at the University of Arizona. X-ray diffraction analyses of the oxide coatings on the filings were performed by the Geosciences X-ray Diffraction Laboratory at the University of Arizona.

During the first five days of operation, the columns were operated at a flow rate of 0.5 ml/min in order to reduce the buildup of hydrogen gas produced by vigorous corrosion of the iron. For the remainder of the investigation, the flow rates were 0.06±0.02 ml/min, except where indicated. A flow rate of 0.06 ml/min corresponds to approximately one pore volume per day in the three MBS columns. For the initial 100 days, the columns were operated with only TCE in the feed stream at an influent concentration of 0.3 mM. To investigate potential diffusive mass transfer limitations, perchloroethylene (PCE) or CT was added to the feed stream after 100 days elapsed. The rationale behind adding PCE and CT was that diffusive mass transfer rates for TCE, PCE and CT would be similar due to the small (~5%) difference in their aqueous diffusion coefficients, but reaction rate differences would be much greater. Previous investigators have found that PCE reaction rates are approximately five times faster than those for TCE, while CT reaction rates are up to 100 times faster than TCE reaction rates (12). The low PCE concentration was selected so that reaction byproducts from the minor reaction pathway of sequential hydrogenolysis, which converts PCE to TCE, would not significantly affect the measurement of TCE reaction rates. To investigate the effects of high halocarbon concentrations on iron surface passivation, the TCE concentration was
increased to 7.8 mM between 326 and 467 days elapsed. The operating conditions for the columns are summarized in Table 2.

Table 2. Column operating conditions and representative effective half-life values for TCE for each operating condition

<table>
<thead>
<tr>
<th>Days Elapsed</th>
<th>Operating Conditions</th>
<th>TCE Effective Half-life (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-99°⁰</td>
<td>0.9 mM TCE</td>
<td>456±27 (98)</td>
</tr>
<tr>
<td>100-325°</td>
<td>0.9 mM TCE</td>
<td>941±100 (151)</td>
</tr>
<tr>
<td>326-467°</td>
<td>7.8 mM TCE</td>
<td>1166±187 (263)</td>
</tr>
<tr>
<td>468-667°</td>
<td>0.9 mM TCE</td>
<td>2395±464 (422)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Column</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>456±27 (98)</td>
<td>445±25 (98)</td>
<td>1549±166 (98)</td>
<td>291±22 (69)</td>
</tr>
<tr>
<td>941±100 (151)</td>
<td>503±28 (151)</td>
<td>2828±877(151)</td>
<td>450±25 (151)</td>
<td></td>
</tr>
<tr>
<td>1166±187 (263)</td>
<td>907±62 (268)</td>
<td>2419±312 (274)</td>
<td>545±38(263)</td>
<td></td>
</tr>
<tr>
<td>2395±464 (422)</td>
<td>2563±511(426)</td>
<td>3433±864 (428)</td>
<td>3939±856(352)</td>
<td></td>
</tr>
<tr>
<td>2502±266 (667)</td>
<td>2493±265 (666)</td>
<td>3507±481 (667)</td>
<td>1697±115 (586)</td>
<td></td>
</tr>
</tbody>
</table>

**Numbers in parentheses are the elapsed time in days at which each measurement was taken.**  
**b Days elapsed.**

### 3.3.2 Voltammetry Experiments

Iron corrosion rates in TCE, PCE and CT solutions were determined by Tafel analysis (27) of polarization profiles of iron wire electrodes. The polarization profiles were generated using an EG&G (Oak Ridge, TN) Model 273A potentiostat and M270 software. Corrosion rates of magnetite coated iron were also measured using Tafel analysis. The magnetite coated iron wire was prepared by heating iron wire to 650 °C under a carbon dioxide atmosphere (33). The voltammetry experiments were performed
in an EG&G three electrode microcell using a platinum wire counter electrode and a Ag/AgCl reference electrode. All electrode potentials are reported with respect to the standard hydrogen electrode (SHE).

3.4 Results and Discussion

In the absence of mass transfer limitations, steady state column experiments can be described by a one dimensional advection-dispersion equation with a first order reaction term as:

\[
\frac{dC}{dx} = \frac{D}{\Delta x^2} \frac{\partial^2 C}{\partial x^2} - kC
\]

where \(C\) is the reactant concentration, \(x\) is the coordinate of position, \(u\) is the interstitial fluid velocity, \(D\) is the dispersion coefficient, and \(k\) is the first order reaction rate constant. For steady state operation, the concentration \(C\) at any point in the column is given by:

\[
C = C_0 \exp\left[ x - \frac{\sqrt{u^2 + 4Dk}}{2D} \right]
\]

where \(C_0\) is the influent reactant concentration. For a first order reaction, dispersion will decrease the extent of reactant conversion compared to that in a plug flow reactor (30). However, where the effects of dispersion on reactant transport are small, the first order rate constant can be determined from the slope of a semilogarithmic plot of the normalized concentration \(C/C_0\) versus distance into the column, as given by:

\[
k = -u \frac{d(\ln C/C_0)}{dx}
\]
For the flow rates used in this study, reaction rate constants calculated using equations 6 and 7 differed by less than 1%. This indicates that dispersion effects on reactant conversion were minimal (34). During the first 30 days of operation, TCE reaction rates were independent of the flow rate, for all flow rates tested between 0.5 and 0.05 ml/min. This indicates that reactant diffusion across the hydrodynamic film boundary layer was fast compared to the rate of reaction, and thus, the measured rate constants were not affected by mass transfer limitations (34).

For most of the investigation, reaction rates deviated from pseudo-first order behavior, with the apparent rate constant increasing with distance into the column. If the TCE half-lives are calculated from a regression on data from all five sampling ports, the calculated half-lives underestimate the degree of reactant conversion. Therefore, the half-life \( t_{1/2} \) values reported in this study have been calculated from only the influent \( (C_0) \) and effluent \( (C_e) \) reactant concentrations, according to: \( t_{1/2} = 0.693 \theta \ln(C_0/C_e) \), where \( \theta \) is the hydraulic residence time. These \( t_{1/2} \) values are representative of the integrated reaction rates along the length of each column, and will hereafter be referred to as effective half-lives. The 95% confidence intervals shown in Tables 2 and 3 were therefore based on only the sampling error of the halocarbon concentrations and flow rates. All hydraulic residence time values were based on the initial pore volume of each column.

3.4.1 Early Time Behavior

During the early period of operation, reaction rates were pseudo-first order in reactant concentration. For the first several days, the normalized concentration profiles in
all columns were approximately linear, as illustrated in Figure 1a for column 1. The linearity of each profile at a given elapsed time indicates that the first order rate constant is uniform along the length of the column. However, the decreasing slope of the profiles in Figure 1a indicate that the reaction rate constant rapidly declines with increasing elapsed time. Although the columns had not achieved steady state operation during the first five days elapsed, the declining profile slopes with elapsed time can be attributed to decreasing \( k \) values. Good mass balances (±30%) were obtained, indicating that the decreasing slope of the concentration profiles cannot be attributed to saturation of nonreactive adsorption sites over time. Additionally, separate chromatographic experiments measuring TCE adsorption in columns packed with the iron reactants found that there was no measurable adsorption at early elapsed times of operation. However, after two years elapsed, experiments in column 1 found measurable adsorption, corresponding to a TCE retardation factor (31) of 4.2.

The declining TCE reaction rates illustrated in Figure 1a can be attributed to passivation of the iron surfaces by iron hydroxide precipitates. Iron corrosion by water and halocarbons generates ferrous and hydroxyl ions. As shown in Figure 1b for column 1, the pH at each point in the column declined with increasing elapsed time. This can be attributed to both decreasing iron reactivity, and to precipitation of iron hydroxide precipitates. During the first several days of operation, the effluent iron concentrations from all four columns were below the detection limit of 0.5 \( \mu \text{M} \). However, the rate of TCE conversion in columns 1, 2, and 4 indicates that iron corrosion should have
produced dissolved iron concentrations greater than 2.5 mM in the column effluents. Therefore, the low iron concentrations in the column effluents indicate that iron corrosion products are precipitating within the columns.

Figure 1. a) Normalized concentration profiles for TCE in column 1 operated at 0.5 ml/min; b) pH profiles for column 1 over the first five days elapsed.
At each elapsed time in Figure 1a, the reaction rate constant is uniform along the length of the column, despite pH variations. This indicates that TCE reaction rates were not dependent on the bulk solution pH. This may be explained by the fact that the surface of corroding iron is in contact with a saturated solution of hydrous ferrous oxide, which has a pH of approximately 9.5 \((17)\). Therefore, unless the solution pH is low enough to dissolve the surface hydroxide layer, the bulk solution pH should have little effect on rates of TCE reduction.

3.4.2 Iron Surface Passivation

With increasing elapsed time, the concentration profiles in all columns showed increasing deviation from first order behavior. Figure 2 compares TCE concentration profiles in columns 1, 2, and 3 after 98 days elapsed. All three profiles show increasing slope with distance into the column, indicating that the apparent first-order rate constant increases towards the effluent end of each column. This deviation from pseudo-first order behavior cannot be explained by pH effects, since the pH gradient in each column was 0.6 pH units or less. Because reaction rates were initially first order in TCE concentration, the decrease in reaction rate towards the influent end of each column must be attributed to increased iron surface passivation in that region.

Iron passivation may lead to reactive site saturation, and thus concentration dependent reaction rates. To investigate reactive site saturation, the influent TCE concentration to all columns was increased from 0.3 to 0.9 mM after 100 days elapsed. Increasing the TCE concentration resulted in increased effective half-life values in all
columns, as illustrated by the data in Table 2 at 98 and 151 days elapsed. The increase in effective half-life observed between 98 and 151 days elapsed may be attributed to both reactive site saturation associated with the increase in TCE concentration, and to increased aging of the surfaces with elapsed time.

Figure 2. Normalized TCE concentration profiles in columns 1, 2, and 3 at 98 days elapsed at a flow rate of 0.062 ml/min.

Reactive site saturation should also lead to increased effective half-life values at higher flow rates, since increasing the flow rate increases the concentration at each point in the column. The influence of flow rate on reaction rates was investigated in columns 1 and 4. The data in Table 3 compare effective half-life values for TCE and PCE at several flow rates. For TCE, increasing the flow rate from 0.075 ml/min at 224 days elapsed to 0.17 ml/min at 279 days resulted in statistically significant increases in effective half-life values in both columns, at the 0.05 confidence level. The decrease in TCE half-life in
column 1 accompanying the reduction in flow rate to 0.06 ml/min at 325 days elapsed indicates that the increase in effective half-life between 224 and 279 days was due to the increased flow rate, and not to increased aging of the iron surfaces. The statistically significant increases in effective half-life at higher flow rates confirms the presence of reactive site saturation, since dispersion effects on reaction rates were found to be negligible during the first month of operation. For PCE, the increases in effective half-life with increasing flow rate were not statistically significant at the 0.05 confidence level.

Table 3. Effective half-life values for TCE and PCE *

<table>
<thead>
<tr>
<th>Flow Rate (ml/min)</th>
<th>Column 1 TCE Effective Half-life (min)</th>
<th>Column 1 PCE Effective Half-life (min)</th>
<th>Column 4 TCE Effective Half-life (min)</th>
<th>Column 4 PCE Effective Half-life (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.075</td>
<td>933±80 (224)</td>
<td>749±74 (224)</td>
<td>410±24 (224)</td>
<td>495±32 (224)</td>
</tr>
<tr>
<td>0.13</td>
<td>1166±187 (263)</td>
<td>1499±456 (263)</td>
<td>545±38 (263)</td>
<td>639±69 (263)</td>
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<tr>
<td>0.17</td>
<td>1501±337 (279)</td>
<td>1024±240 (279)</td>
<td>719±68 (278)</td>
<td>527±58 (278)</td>
</tr>
<tr>
<td>0.060</td>
<td>876±64 (325)</td>
<td>770±68 (325)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Numbers in parentheses are the elapsed time in days at which each measurement was taken.

To investigate the effect of high halocarbon concentrations on iron surface passivation, the TCE concentration in all columns was increased to 7.8 mM between 326 and 467 days elapsed. As indicated by the data in Table 2, increasing the TCE concentration resulted in increased effective half-life values in all columns. The increase in effective half-life values can be attributed to both reactive site saturation, and to
increased iron surface passivation. To determine the contribution of increased surface passivation, the TCE concentration was changed back to 0.9 mM after 467 days elapsed. As shown in Table 2, lowering the TCE concentration did not lead to recovery of TCE reaction rates for the three MBS iron columns. However, for the Cerconia iron column, the decrease in effective half-life from 3939±856 to 1697±115 minutes was statistically significant. This difference in recovery between columns 1 and 4 suggests that iron composition influences passivation behavior.

3.4.3 Anodically Controlled Corrosion

Iron surface passivation can be attributed to the formation of an adherent oxide layer that leads to anodic control of iron corrosion. When TCE or water receive electrons at cathodic sites on the iron surfaces, anodic sites must release both electrons and ferrous ions. If the ferrous ions are hampered from entering the solution by an overlying oxide layer, the thermodynamic favorability for iron corrosion decreases due to polarization by Fe$^{2+}$ at the anodic sites (17). This increases the polarization necessary for anodic sites to release electrons, and thereby decreases the rate of halocarbon reduction. The polarization profile for a magnetite coated iron wire electrode in Figure 3 shows that the presence of an oxide coating leads to anodic control of iron corrosion in a 10 mM CaSO$_4$ solution saturated with TCE. For the magnetite coated electrode, the 0.026 decades (dec) per millivolt (mV) anodic Tafel slope was smaller than the 0.034 dec/mV cathodic Tafel slope. This indicates that the rate of iron corrosion was limited by the ability of anodic sites to release electrons and Fe$^{2+}$. 
In contrast to anodically controlled corrosion of magnetite coated iron, fresh iron corrosion by TCE was cathodically controlled. As shown by the polarization diagram in Figure 3 for the fresh iron wire electrode, the \( \beta_c \) of 0.0087 dec/mV was smaller than the \( \beta_a \) of 0.014 dec/mV. This indicates that corrosion of the fresh iron was cathodically controlled, even in solutions 100% saturated with TCE. Cathodically controlled corrosion results when the rate at which oxidants are able to accept electrons at cathodic sites is less than the rate at which anodic sites are able to release electrons. Under these conditions, halocarbon reduction rates are dependent on the properties of the organic compound.

![Figure 3. Polarization profiles for fresh iron and magnetite coated iron wire electrodes in 10 mM CaSO\(_4\) solutions saturated with TCE. The electrodes were equilibrated with each solution for one hour prior to measuring the polarization currents. Current densities are based on the measured current and the nominal geometric surface area of each electrode.](image-url)
Figure 4. Effective half-life values for TCE in columns 1, 2 and 3 over the first 100 days elapsed.

3.4.4 Water Chemistry Effects

Figure 4 compares effective half-life values for TCE in columns 1, 2 and 3 over the first 100 days of operation. For the columns operated with the chloride and sulfate waters, the decline in reaction rates was most pronounced during the first four days elapsed. For the column operated with 5 mM calcium nitrate, there was no measurable TCE dechlorination during the first three days. However, during this time, approximately 20% of the nitrate was removed by the column. This suggests that nitrate reduction inhibits TCE reduction.

Slower TCE reaction rates in the presence of nitrate may be due to competition for a limited number of electrons between nitrate and TCE, and to increased iron passivation in the presence of another oxidant. To determine if increased surface passivation
contributed to the slower TCE reaction rates in the nitrate column, corrosion current densities were measured for iron wire electrodes in 5 mM CaCl₂ and Ca(NO₃)₂ solutions saturated with TCE. Polarization diagrams for the wire electrodes and the corrosion parameters determined from them are shown in Figure 5. The data in Figure 5 show that the E\text{corr} of the iron in the nitrate solution was 10 mV greater than the E\text{corr} in the chloride solution. This might suggest a greater degree of cathodic depolarization in the presence of the oxidant, nitrate. The greater β\text{c} of 0.026 (dec/mV) in the nitrate solution compared the β\text{c} of 0.012 dec/mV in the chloride solution does indicate that nitrate was reduced by the electrode. However, the i\text{corr} in the nitrate solution was 34% smaller than in the chloride solution, despite the presence of nitrate as an oxidant. The smaller i\text{corr} shows that the iron is less reactive in the nitrate solution, indicating a greater degree of surface passivation. This passivation leads to anodic control of iron corrosion in the nitrate solution, as indicated by the smaller β\text{a} of 0.017 dec/mV compared to the β\text{c} of 0.026 dec/mV. In contrast, corrosion of the iron wire in the chloride solution was under mixed control, as indicated by the similar anodic and cathodic Tafel slopes. Nitrate solutions containing no TCE also showed smaller i\text{corr} compared to chloride solutions. This indicates that the presence of 10 mM nitrate did not lead to faster consumption of the iron reactants, but rather greater iron surface passivation.
Figure 5. Polarization diagrams for iron wire electrodes in 5 mM CaCl₂ and Ca(NO₃)₂ solutions saturated with TCE. The electrodes were equilibrated with each solution for one day prior to measuring the polarization currents. Current densities are based on the measured current and the nominal geometric surface area of each electrode.

Throughout most of the investigation, TCE reaction rates in columns 1 and 2 were statistically identical at the 0.05 confidence level. However, except at the 7.8 mM influent TCE concentration, TCE reaction rates in column 3 were slower. This indicates that chloride ions at a concentration of 10 mM do not significantly enhance TCE reaction rates compared to sulfate ions. This may be attributed to the fact that the rate enhancing effects of chloride are most pronounced at concentrations below 0.08 mM (21), whereas all columns in this investigation contained millimolar levels of chloride generated from TCE dechlorination.
3.4.5 Effects of Halocarbon Type

At most sampling points, reaction rates for TCE and PCE in all columns were statistically identical, as illustrated by the half-life data for columns 1 and 4 in Table 3. Previous reports of similar reaction rates for TCE and PCE have been attributed to grain scale mass transfer limitations (35). Although reaction rates were not limited by halocarbon diffusion across the hydrodynamic film boundary layer at the particle surfaces, they may still be limited by diffusion through a porous oxide film coating the particles. The effect of intraoxide mass transfer limitations was investigated by replacing PCE in the influent feed stream with CT at 325 days elapsed. In contrast to the behavior exhibited by TCE and PCE, which showed little or no reaction before the first sampling port in all four columns, CT was removed below the detection limit before the first port in all columns. This corresponds to more than 99.99% CT removal, and an effective half-life of less than 25 minutes. This suggests that mass transfer limitations associated with diffusion through a nonreactive oxide layer was not responsible for the similar reaction rates of TCE and PCE.

A possible explanation for similar TCE and PCE reaction rates is that reductive dechlorination of these two compounds is anodically controlled on aged iron surfaces. Tafel analyses of the magnetite coated iron electrode in TCE and PCE solutions indicated that corrosion was anodically controlled. Under conditions of anodically controlled corrosion, halocarbon dechlorination rates may be less dependent on the properties of the halocarbon than are reaction rates on fresh iron surfaces. This effect can be seen by the corrosion current data for the magnetite coated iron electrode shown in Figure 6.
Increasing the TCE concentration from 0 to 8 mM resulted in less than a 20% increase in $i_{corr}$. However, for a fresh iron wire electrode, TCE at a concentration of 6 mM increased the $i_{corr}$ by more than a factor of four compared to the blank electrolyte solution. The weak effect of TCE on the corrosion rate of the magnetite coated iron indicates that TCE did not polarize the iron sufficiently to increase its corrosion rate. The similar corrosion rates in the blank and TCE saturated solution indicate that water is the primary oxidant for magnetite coated iron.

![Figure 6](image)

**Figure 6.** Corrosion current densities for a magnetite coated iron wire electrode in 3 mM CaSO$_4$ solutions containing TCE and CT. Also shown is the corrosion current density as a function of the aqueous TCE concentration for a fresh iron wire electrode immersed in a 3 mM CaSO$_4$ electrolyte solution. Current densities are based on the measured corrosion current and the nominal geometric surface area of each electrode.

Corrosion current measurements for the magnetite coated electrode in PCE solutions gave similar $i_{corr}$ values as those for TCE. However, as shown in Figure 6, CT was able
to increase the $i_{corr}$ of the magnetite coated electrode by more than a factor of two compared to the blank electrolyte solution. This can be attributed to the ability of CT to sufficiently polarize the iron to release additional electrons. In the presence of CT, corrosion of the magnetite coated electrode was no longer anodically controlled. At all CT concentrations, the $\beta_a$ was similar to the $\beta_c$, indicating mixed control of iron corrosion. Under mixed control, the weak effect of CT on the corrosion rate at concentrations above 1.25 mM may be due to saturation of cathodic sites.

### 3.4.6 Reaction Byproducts

The reaction products from TCE reduction were similar to those reported in previous investigations, and indicated that $\beta$-elimination was the primary reaction pathway (8). Throughout the investigation, the sum of all chlorinated products accounted for less than 2% of the TCE conversion, and carbon mass balances were within ±30%. For columns 1, 2, and 4, the predominant reaction byproducts during the first month elapsed were ethylene (~60%), ethane (~25%), and acetylene (~10%). However, in column 3, acetylene accounted for more than 90% of the reaction products throughout the course of the investigation.

The predominance of acetylene can be attributed to anodic control of iron corrosion in the nitrate solution. Under anodic control, the slow rate at which electrons are released from anodic sites may allow acetylene to desorb from the surface faster than it can be reduced to ethene or ethane. This hypothesis is supported by results from the other three
columns. At the end of the investigation, acetylene was the major byproduct in all columns, and accounted for 50 to 90% of the reaction byproducts. The shift in byproducts in columns 1, 2, and 4 indicates that as the iron surfaces become increasingly passivated, less completely reduced compounds are produced.

3.4.7 Iron Corrosion Products

Throughout the investigation, measurements of dissolved iron concentrations in the effluent of all columns were below the detection limits of 0.5 or 1 \( \mu \)M. However, based on rates of halocarbon reduction, effluent iron concentrations should have been more than three orders of magnitude greater than either detection limit. This indicates that almost all of the corroding iron remains in the columns. Despite the precipitation of corrosion products, the initial and final pore volume data in Table 1 indicate that only minor changes in pore volume occurred in the three MBS columns. The greater final hydraulic conductivity values are likely due to an under measurement of the initial values due to interference by cathodically generated hydrogen gas. At the termination of the experiments, the appearance of the iron filings was similar to their appearance at the start, and no cementation of the filings was observed at either end of the columns.

The corrosion products in this investigation were similar to those previously reported (10). X-ray diffraction analyses of iron filings taken from the influent end of column 1 after more than 700 days elapsed indicated that the filings were coated with both magnetite and maghemite. Analysis of iron filings taken from the effluent end of column 1 indicated that only magnetite was present at detectable levels.
The absence of detectable corrosion products in the effluent water can be attributed in part to the low ionic strength of the feed water solutions. In low ionic strength media, the high solution resistance requires close proximity of anodic and cathodic regions on the iron surface (17). This allows the anodic reaction product ($Fe^{2+}$) to combine with the cathodic reaction product ($OH^-$) close to the iron surface to form an insoluble precipitate. However, in solutions of higher ionic strength, larger separations between anodic and cathodic regions allow the reaction products to diffuse away from the surface and precipitate in the bulk solution.

The effect of ionic strength on the adherence of iron corrosion products was tested in column 2 after termination of the experiments. Increasing the background electrolyte ionic strength from 15 mM (5 mM CaCl$_2$) to 150 mM (50 mM CaCl$_2$) increased the effluent iron concentration from less than 1 to 322 $\mu$M. However, based on the observed rate of TCE reduction, the effluent iron concentration should have been greater than 1.8 mM. This indicates that most of the corroding iron remains in the columns, even at higher ionic strengths. However, the increase in ionic strength was able to reverse the surface passivation. After six weeks elapsed, the effective half-life for TCE recovered to 559±45 min, while the PCE half-life recovered to 291±14 min. The faster reaction rate for PCE compared to TCE suggests that iron corrosion was no longer cathodically controlled. This significant increase in reaction rates shows that iron passivation was primarily controlled by the tendency of the oxide layer to adhere to the iron surfaces, and not to the overall mass of corrosion products in the column.
In addition to ionic strength, dissolved oxygen also affects the passivating tendency of iron corrosion products. Exposure of iron wire electrodes to saturated TCE solutions resulted in iron surface passivation in anaerobic solutions, but not in solutions saturated with dissolved oxygen (9 mg/L). In an anaerobic 3 mM CaSO₄ solution, the $E_{corr}$ of a fresh iron wire electrode was $-505$ mV. Purging the solution with nitrogen saturated with TCE increased the $E_{corr}$ to approximately $-390$ mV. However, after removing TCE from the solution by purging with clean nitrogen for two days, the $E_{corr}$ only partially recovered to $-400$ mV. This shows that high TCE concentrations can lead to irreversible, or slowly reversible, passivation. This effect was seen in the three MBS columns exposed to the 7.8 mM influent TCE concentration, and in the $i_{corr}$ data for the iron wire electrode in Figure 6.

Although the TCE saturated solution passivated the iron wire electrode, oxidation by dissolved oxygen was able to reverse this passivation. When the solution containing the passivated wire was purged with air for 90 minutes, the $E_{corr}$ increased from $-400$ to $-283$ mV, and the $i_{corr}$ increased by approximately 22 \( \mu \)A/cm². However, upon subsequent purging of the solution with clean nitrogen to remove the dissolved oxygen, the $E_{corr}$ recovered to $-493$ mV. This indicates that oxidation by dissolved oxygen reversed the iron surface passivation. Reversal of the passivation was accompanied by release of iron corrosion products from the electrode, and a factor of three increase in the $i_{corr}$ compared to the passivated electrode. This indicates that oxidation by TCE leads to
formation of an adherent and protective oxide layer; whereas, oxidation by dissolved oxygen leads to formation of nonadherent, and less protective corrosion products.

Results from this study indicate that TCE reaction rates are highly dependent on the condition of the iron surfaces. Surface passivation appears to be dependent on adherence of the corrosion products to the iron surfaces. Even an electrically conductive oxide, such as magnetite, may inhibit halocarbon reduction if it hinders Fe^{2+} from entering the solution. The decreasing halocarbon reduction rates with time can be attributed to anodic control of iron corrosion, and not to increasing diffusional restrictions for reactant transport through porous corrosion products.

3.5 Literature Cited


5 Schrier, C. G.; Reinhard, M. *Chemosphere* 1994 29, 1743.


4.1 Abstract

This research investigated the long-term performance of zero-valent iron aggregates for reductive dechlorination of trichloroethylene (TCE) and perchloroethylene (PCE). The effects of elapsed time, mass transfer limitation, and influent halocarbon concentration on reductive dechlorination rates were investigated using groundwater obtained from a field site contaminated with chlorinated organic compounds. Over the first 300 days of operation, reaction rates for TCE and PCE gradually increased due to increasing porosity of the iron aggregates. Although there was microbial growth within the column, biological activity did not measurably contribute to reductive dechlorination. Dechlorination rates were pseudo-first order in reactant concentration for submillimolar halocarbon concentrations. TCE concentrations near aqueous saturation resulted in passivation of the iron surfaces and deviation from first order reaction kinetics. However, this passivation was slowly reversible upon lowering the influent TCE concentration. Tafel polarization diagrams for an electrode constructed from the iron aggregates indicated that corrosion of the aggregates was anodically controlled. At all halocarbon
concentrations, aggregate oxidation by water accounted for more than 80% of the corrosion. Throughout the curse of the 3-yr column investigation, reaction rates for TCE were 2-3 times faster than those for PCE. However, current measurements with the aggregate electrode indicated that direct PCE reduction was faster than that for TCE. This disparity between amperometrically measured reaction rates and those measured in the column reactor indicated that halocarbon reduction may occur via direct electron transfer or may occur indirectly through reaction with atomic hydrogen absorbed in the iron. Comparison of the aggregate corrosion rates with those of fresh iron suggested that anodically controlled corrosion leads to predominance of the indirect reduction mechanism. The faster reaction rate for TCE under anodically controlled conditions can therefore be attributed to its faster rate of indirect reduction as compared to PCE.

4.2 Introduction

In recent years, there has been considerable interest in the use of zerovalent iron for passive remediation (1-12). Installation considerations often limit zero-valent iron barriers to the remediation of shallow contaminant plumes in sedimentary aquifers. However, a new application has recently been developed that enables zero-valent iron to be used for remediation of chlorinated organic compounds in fractured bedrock (13). This new application involves injection of zero-valent iron proppants into fractured bedrock using hydraulic fracturing techniques.

The goal of this study was to investigate the long-term effectiveness of zero-valent iron proppants for reductive dechlorination and to determine the mechanisms controlling
reaction rates on aged iron surfaces. Because the iron proppants were designed to be injected into bedrock containing pure phase halocarbons, the effectiveness of the proppants for reductive dechlorination at halocarbon concentrations near aqueous saturation were also investigated. Column experiments were conducted over a 1-yr period in order to determine the effect of elapsed time of operation, mass transfer limitations, and influent halocarbon on reaction rates of trichloroethylene (TCE) and perchloroethylene (PCE). The mechanisms responsible for the results observed during the first year of operation were then investigated by varying the column operating conditions over the next 2 years and by electrochemical investigation of halocarbon reduction and iron corrosion.

Reaction rates for one and two carbon chlorinated compounds are highly variable among different investigators (14). This variability can be attributed to differences in experimental conditions and to differences in iron type and specific surface area. Among all the rate affecting factors, the type of iron appears to be the most significant determinant of reaction rates. Even when reaction rates are normalized for the specific surface area of the iron, and are measured under the same experimental conditions, reaction rates for a particular compound have been observed to vary by up to three orders of magnitude between different types of iron (15).

Early investigations recognized that the condition of the iron surfaces also has a profound impact on reaction rates, and early batch testing was often performed on acid washed iron filings in order to achieve a repeatable initial surface condition (1). Several
investigations in batch systems have observed that reaction rates are initially first order in reactant concentration, but deviate from first order behavior with increasing elapsed time (2, 16). Declining reaction rates with time have been attributed to increasing mass transfer limitations through surface associated oxide layers (2) and to anodic control of iron corrosion (16). X-ray diffraction analyses from field and column tests indicate that the passivating layer on iron filings consists of an inner layer of magnetite (Fe$_3$O$_4$) with an outer coating of maghemite (γ-Fe$_2$O$_3$) (16, 17).

There are both direct and indirect mechanisms for halocarbon reduction by zerovalent metals. Direct reduction may occur by electron tunneling, or by formation of a chemisorption complex of the organic compound with the surface metal atoms (18). Electron tunneling may occur to halocarbons that are physically adsorbed at the zerovalent metal surface, or to halocarbons that are separated from the surface by adsorbed water or iron corrosion products (19, 20). Indirect reduction of organic compounds involves atomic hydrogen. Atomic hydrogen absorbed at the metal surface may reduce organic compounds through the formation of chemisorbed hydride complexes (18). This mechanism is fast on metals with low hydrogen overpotentials, such as platinum and palladium, but is much slower on metals with high hydrogen overpotentials, such as iron (18). Indirect evidence has also been presented that Fe$^{2+}$ may contribute to halocarbon reduction (21). However, two investigations into the effect of Fe$^{2+}$-chelating agents on halocarbon reduction rates indicated that the effect of available Fe$^{2+}$ on reaction rates is small (22, 23).
Rates of reductive dechlorination for one and two carbon compounds have been correlated with several halocarbon properties, including the equilibrium potentials for one and two electron transfer reactions (24, 25). Generally, iron mediated dechlorination rates for homologous compounds increase with increasing degree of halogenation. For example, recent review articles using data compiled from a variety of published sources have reported that PCE reaction rates are approximately five times faster than those for TCE, which in turn are 3-60 times faster than those for the three dichloroethylene isomers (14, 24). However, this trend has not been observed in all studies. For example, Burris et al. (5) reported that reaction rates for TCE and PCE were similar in short-term batch testing. This disparity from previously reported trends was attributed to possible mass transfer limitations and greater adsorption of PCE to nonreactive sites. Increasing dechlorination rates with decreasing degree of halogenation have been observed for chlorinated ethenes in bimetallic iron-palladium systems (26) and for reduction by supported palladium catalysts (27, 28).

Electrochemical Analysis. The current-voltage relationship for redox reactions involving a corroding iron electrode can be described by a form of the Butler-Volmer equation (29):

\[ i = i_{corr} \left[ e^{-\beta_c (E - E_{corr})} - e^{\beta_a (E - E_{corr})} \right] \] (1)

where \( i \) is the net current, \( i_{corr} \) is the corrosion current, \( E \) is the electrode potential, \( E_{corr} \) is the free corrosion potential, and \( \beta_c \) and \( \beta_a \) are the cathodic and anodic Tafel slopes, respectively. Under open circuit conditions where the electrode potential is equal to
$E_{corr}$, $i$ is equal to zero, and the corrosion rate of the electrode is equal to $i_{corr}$. At electrode potential sufficiently above or below $E_{corr}$, eq 1 indicates that a plot of log|$i$| versus $E$ will be linear. The linear regions of the polariation profiles have slopes equal to $\beta_a$ and $\beta_c$ and are known as the anodic and cathodic Tafel regions. The $i_{corr}$ under open circuit conditions can be determined graphically by extrapolating the anodic and cathodic Tafel slopes to their point of intersection at $E_{corr}$ (19).

Under open circuit conditions, the overall rate of iron corrosion may be limited by either the anodic or cathodic half-cell reactions. For corrosion of iron by aqueous TCE in anaerobic solutions, the anodic reaction is given by

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (2)$$

while the cathodic reactions when ethene is the product may be expressed as

$$H_2O + H^+ + 2e^- \rightarrow H_2 + OH^- \quad (3)$$

$$C_2HCl_3 + 3H^+ + 6e^- \rightarrow C_2H_4 + 3Cl^- \quad (4)$$

If the aggregate rate of the anodic reactions is slower than the potential rate of the cathodic reactions, corrosion of the iron is anodically controlled (30). Under anodically controlled conditions, the rate at which oxidants are able to accept electrons is faster than the rate at which the iron is able to release electrons. In contrast, cathodically controlled corrosion occurs when the rate at which oxidants are able to accept electrons is slower than the rate at which the iron is able to release electrons. The relative magnitude of $\beta_a$ and $\beta_c$ indicate whether the anodic or cathodic reactions are limiting the overall rate of iron corrosion. For example, when $\beta_a > \beta_c$, corrosion of the iron is anodically controlled.
The condition of the iron surfaces and the polarizing ability of potential oxidants determine whether iron corrosion is anodically or cathodically controlled.

4.3 Materials and Methods

4.3.1 Iron Column Experiments

Pseudo-steady state column experiments were used to measure reaction rates and determine reaction byproducts of TCE and PCE transformation. The iron reactants used in this investigation consisted of 300-1000 μm diameter, spherical iron aggregates obtained from Cercona of America (Dayton, Ohio). The iron aggregates are a commercially available material produced for use as reactive proppants for in-situ remediation of halocarbons in fractured bedrock. The iron aggregates were composed of smaller (<100 μm diameter) iron particles cemented together with an aluminosilicate binder which comprised 2% of the particle mass. The specific surface area and internal porosity of the iron aggregates were measured before and after the investigation by Micromeritics (Norcross, GA) using nitrogen BET analysis (31) and mercury porosimetry.

The iron reactants were packed in a 60 cm long by 4.8 cm internal diameter, glass chromatography column (Kontes, Vineland, NJ). The column was adapted by installing three intracolumn sampling ports sealed with silicone rubber septa at 15, 30 and 45 cm from the column inlet. After 250 days elapsed, port 3 (at 45 cm) became damaged and could no longer be sampled. The column void volume and axial dispersivity (α) were
determined using a potassium bromide tracer solution. Properties of the column and the zerovalent iron reactants are listed in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Column and Iron Properties</th>
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<tr>
<td>empty bed volume (mL)</td>
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<td>mass of iron aggregates (g)</td>
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<td>initial aggregate specific surface area (m²/g)</td>
</tr>
<tr>
<td>final aggregate specific surface area (m²/g)</td>
</tr>
<tr>
<td>initial aggregate internal pore vol (mL/g)</td>
</tr>
<tr>
<td>final aggregate internal pore vol (mL/g)</td>
</tr>
<tr>
<td>initial packed bed pore vol (mL)</td>
</tr>
<tr>
<td>final packed bed pore vol (mL)</td>
</tr>
<tr>
<td>initial axial dispersivity (cm)</td>
</tr>
<tr>
<td>final axial dispersivity (cm)</td>
</tr>
</tbody>
</table>

For the first 426 days of the investigation, the column was operated using ground water obtained from a leach field associated with a former aerospace facility in southern California. The ground water obtained from the leach field was contaminated with a variety of chlorinated hydrocarbons at concentrations up to 180 mg/L (13). The site ground water also contained a variety of inorganic contaminants, including nitrate at concentrations up to 45 mg/L. Carbonate was added to the water at a level of 3 mM, and dissolved oxygen was removed by purging the feedwater reservoir with a mixture of nitrogen and carbon dioxide.

The influent halocarbon and carbonate concentrations were controlled using a water-gas contacting vessel. The water-gas contactor consisted of 1 m of 0.25 cm o.d. silicone rubber tubing contained inside a 1 liter sealed, glass vessel fitted with stainless steel pipe fittings. The feed water was pumped through the silicone rubber tubing, while a carbon dioxide and nitrogen gas mixture containing the halocarbon reactants was purged through
the glass vessel. Constant carbonate (3 mM) and organic compound concentrations were maintained via diffusion of the gas phase compounds through the silicone rubber tubing. Between the water-gas contacting vessel and the column inlet, stainless steel tubing was used to prevent compound losses and oxygen contamination.

Reactant concentration profiles were measured by withdrawing 100 μl samples from the inlet, outlet and three intracolumn sampling ports. The 100 μl aqueous samples were injected into 1 g of pentane, and analyzed by injection into a Hewlett Packard 5890 gas chromatograph (GC) equipped with an electron capture detector and autosampler. Analyses of nonchlorinated reaction byproducts were performed using a molecular sieve chromatography column (Alltech, Deerfield, IL) and a flame ionization detector connected to a SRI Instruments GC (Torrance, CA). Chlorinated reaction byproducts below the detection limit of the normal sampling procedures were determined by purge and trap analysis of 4.7 ml samples of the column effluent. A 6-port sampling valve was used to inject the samples into a Tekmar (Cincinnati, OH) purge and trap apparatus. Analysis was then performed using a SRI GC equipped with a Hall electrolytic conductivity detector. Trace reaction byproducts were identified using a Finnigan (San Jose, CA) gas chromatograph/mass spectrometer. Anion and dissolved iron concentrations were determined by the Soil, Water, and Plant Analysis Laboratory (SWPAL) at the University of Arizona.

Over the course of the 3-yr investigation, the column was operated over a flow rate range of 0.04 to 5 ml/min. For the first 30 days, the column was operated with only TCE
in the feed stream at an influent concentration of 0.3 mM. After 30 days elapsed, the feed stream was supplemented with PCE at a concentration of 0.3 mM. Between 309 and 427 days elapsed, the TCE concentration was increased to 7.8 mM and the PCE was removed from the feed stream. After 427 days elapsed, the site ground water was replaced with ultrapure deionized (DI) water (18 MΩ cm resistivity) in order to eliminate potential nutrients for microbiological activity. Between 427 and 507 days, 0.40 M lithium chloride was added to the feed water to inhibit microbiological activity (32). Hexachloroethane (HCA) was added to the feed stream for a short period in order to investigate mass transfer limitations associated with adsorption-retarded aqueous diffusion through porous iron corrosion products. A summary of the operating conditions is listed in Table 2.

**Table 2 Column Operating Conditions.**

<table>
<thead>
<tr>
<th>Days Elapsed</th>
<th>0-30</th>
<th>30-309</th>
<th>309-427</th>
<th>427-507</th>
<th>507-1063</th>
<th>1063-1111</th>
</tr>
</thead>
<tbody>
<tr>
<td>water type</td>
<td>site</td>
<td>site</td>
<td>site</td>
<td>DI + LiCl</td>
<td>DI</td>
<td>DI</td>
</tr>
<tr>
<td>TCE conc. (mM)</td>
<td>0.3</td>
<td>0.3</td>
<td>7.8</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>PCE conc. (mM)</td>
<td>0.3</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.01</td>
</tr>
<tr>
<td>HCA conc. (mM)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.01</td>
</tr>
</tbody>
</table>

4.3.2 Amperometric Experiments

The effect of halocarbon concentration on iron corrosion rates and surface passivation was investigated by measuring the corrosion current and free corrosion potential for an electrode constructed from 0.75 g of the iron aggregates cemented together with a conducting epoxy. These experiments were performed by placing the aggregate electrode in anaerobic 10 mM CaSO₄ solutions of varying TCE or PCE concentration. The
corrosion currents and free corrosion potentials were measured by analysis of Taefel diagrams produced by polarizing the electrode ±50 mV with respect to its open circuit potential (30). The polarization experiments were performed using an EG&G (Oak Ridge, TN) model 273A scanning potentiostat and EG&G M270 software. For comparative purposes, corrosion currents were also determined for iron wire electrodes in 10 mM CaSO₄ solutions of varying TCE or PCE concentration. The iron wire electrodes were obtained from Aesar (Ward Hill, MA) and consisted of 2.8 cm long and 1.2 mm diameter iron wire of 99.9% purity.

Chronoamperometric experiments were performed with the aggregate and iron wire electrodes in a custom glass cell with a nitrogen-purged headspace. The test solutions were purged with nitrogen gas containing TCE or PCE at 50% of vapor phase saturation. Once the solutions were equilibrated with the halocarbon vapors, the solution purge was terminated and the electrode potential was stepped to -50 mV with respect to the open circuit potential. The resulting current was recorded using the potentiostat and associated software.

4.3.3 Adsorption Experiments

Adsorption of TCE, PCE and HCA onto simulated iron corrosion products was measured in order to evaluate adsorption retarded diffusion through a porous layer of iron corrosion products. The simulated iron corrosion products were produced by oxidizing a sample of the iron aggregates at 650 °C under an air atmosphere for five days. Halocarbon adsorption to the oxidized aggregates was then measured using a previously described
batch testing procedure (33). Adsorbed/aqueous phase distribution coefficients ($K_d$) for each compound were determined from the slope of the adsorption isotherms.

4.4 Results and Discussion

4.4.1 Reaction Kinetics

Upon commencement of operation, 90 days was required to establish reactant concentration profiles that conformed to a first-order reaction rate model. Once first-order conditions were established, the reactant concentrations ($C$) along the length of the column could be described by

$$\frac{C}{C_o} = \exp \left[ x \frac{u - \sqrt{u^2 + 4Dk_i}}{2D} \right]$$

(5)

where $C_o$ is the influent reactant concentration, $x$ is the coordinate of position, $u$ is the interstitial fluid velocity, $D$ is the dispersion coefficient, and $k_i$ is the first order reaction rate constant. For a reaction that is first order in reactant concentration, dispersion will decrease the extent of reactant as compared to that in a plug flow reactor (34). However, at all flow rates tested, the reaction rate constants determined using a plug flow model and those incorporating the effects of dispersion differed by less than 2%, indicating that dispersion effects on reactant conversion were negligible (34). Under these conditions, the dechlorination rate may be characterized by a single parameter, such as the disappearance half-life ($t_{1/2}$), as determined by $t_{1/2}=0.693/k_i$. However, before 90 days elapsed, the observed reaction rate constant decreased with distance into the column. Therefore, in these cases (i.e.; where the regression coefficient for the first-order model
was less than 0.80), the reported $t_{1/2}$ values have been calculated from only the influent and effluent ($C_e$) reactant concentrations, according to $t_{1/2} = 0.693 \theta \ln(C_o / C_e)$, where $\theta$ is the hydraulic residence time. These $t_{1/2}$ values are representative of the integrated reaction rates along the length of the column and will hereafter be referred to as effective half-lives. For all flow rates tested between 0.04 and 2.0 mL/min, the first-order reaction rate constants for TCE and PCE were independent of the fluid velocity. This indicates that hydrodynamic boundary layer mass transfer limitations had a negligible effect on the reported half-life values.

Dissolved and colloidal iron concentrations in the column effluent were below the detection limit of 1 $\mu$M. However, in the absence of iron precipitation, effluent iron concentrations should have been more than 3 orders of magnitude greater, based on rates of halocarbon reduction. This indicates that almost all of the corroding iron remained in the column. Despite precipitation of the corrosion products, the initial and final pore volume data in Table 1 show only a 14% loss in column pore volume over the course of the investigation. For consistency in calculating the $t_{1/2}$ values, all $\theta$ values were based on the initial pore volume of the column.

Over the first 309 days, reaction rates for both TCE and PCE gradually increased, as shown by the data in figure 1. The increasing reaction rate with elapsed time cannot be attributed to pH effects since the pH in the column was approximately constant after 30 days, as illustrated by the data in Figure 2. The increase in reaction rates can be attributed to an increase in reactant-accessible iron surface area. Because the iron
reactants were aggregates cemented together with a nonreactive binder, oxidation of the iron resulted in increased intraparticle porosity, as shown by the initial and final intraparticle pore volume data in Table 1. The increase in particle porosity resulted in an increase in accessible surface area over the course of the investigation, as shown in Table 1 by the initial and final specific surface area measurements.

![Graph](image)

Figure 1. $t_{1/2}$ values with 95% confidence intervals for TCE and PCE as a function of elapsed time of operation. At 280 days, the flow rate was increased from 0.075 to 0.15 mL/min. The increased $t_{1/2}$ for PCE at 302 days indicates that more than 7 pore vol was required to resume pseudo-steady-state operation after the increase in flow rate. The faster equilibration of TCE as compared to PCE can be attributed to its faster reaction rate and smaller adsorption coefficient ($K_d$).

Ethene was the major reaction product and accounted for more than 80% of the TCE and PCE that were transformed. Ethane and acetylene were the next most abundant byproducts, and the sum of all chlorinated products accounted for less than 4% of the total TCE and PCE disappearance. These reaction products suggest that the $\beta$-elimination
pathway proposed by Roberts et al. (35, 36) was the primary dechlorination pathway. Trace amounts of vinyl chloride and the three dichloroethylene isomers suggest that dechlorination also occurred via the sequential hydrogenolysis pathway (35, 36).

![Figure 2. Column pH profiles at different elapsed times of operation.](image)

The data in Figure 1 show that reaction rates for TCE were 2-3 times faster than those for PCE. This is surprising given that data from several batch and column studies indicate that PCE transformation rates are typically 5 times faster than those for TCE (11, 14). In a recent paper summarizing results from a number of laboratory investigations, Tratnyek et al. (14) reported representative half-life values for TCE and PCE of 110 and 20 min, respectively, for systems with 1 m² of iron surface area/mL of solution volume. Using the initially measured iron-specific surface area of 3.7 m²/g, the reaction rates observed at 309 days correspond to half-life values of >10,000 and >22,000 min, respectively, for TCE and PCE when normalized to a 1 m²/mL surface area to solution
volume ratio. Although some of the measured surface area may be due to the nonreactive binder, the normalized reaction rates observed in this study are more than 2 orders of magnitude slower than most previously reported values.

4.4.2 Iron Surface Passivation

Because the iron aggregates were intended for use in fractured bedrock containing bulk phase halocarbons, it was important to determine if reaction rates would remain first order at TCE concentrations near aqueous saturation. To answer this question, the TCE concentration was increased from 0.3 to 7.8 mM (~92% of aqueous saturation) between 309 and 427 days elapsed. As shown by the nonlinear concentration profiles for TCE in Figure 3 at 408 and 426 days, reaction rates were no longer first order in TCE concentration. This type of deviation from first-order reaction kinetics is often attributed to saturation of reactive sites and has been described using a combined zero- and first-order kinetic model (11, 37). The combined model is given by (37)

\[
\frac{dC}{dt} = \frac{k_0 C}{k_0 / k_1 + C}
\]

where \(k_0\) is the zero-order rate constant, and \(k_1\) is the previously defined first-order rate constant. This model was fit to the data at 408 and 426 days using the Solver function in Excel (38) to optimize the value for \(k_0\) by minimizing the sum of the squared errors between the model and the data. Comparison of the model to the data in Figure 3 indicates that the combined model adequately describes the TCE concentration profiles for an influent TCE concentration of 7.8 mM. However, as described below, this model
does not mechanistically describe halocarbon reduction kinetics and, therefore, is not useful for extrapolation to other conditions. For example, the combined model predicts an effluent TCE concentration of $5.4 \times 10^{-3}$ M at 507 days, whereas the actual concentration was 2.8 M.

![Graph showing concentration profiles for TCE](image)

**Figure 3.** Concentration profiles for TCE at an influent concentration of 0.3 mM and a flow rate of 0.075 mL/min (276 and 280 days) as compared with profiles at a flow rate of 0.15 mL/min (302 and 309 days). Also shown are profiles for an influent TCE concentration of 7.8 mM and flow rates of 0.060 mL/min (408 days) and 0.068 mL/min (426 days). For TCE $C_0 = 0.3$ mM, the data were fit to a first-order model (eq 5, $k_I = 0.0014$ min$^{-1}$); for $C_0 = 7.8$ mM, the data were fit to the combined model (eq 6, $k_0 = 0.0016$ mM/min).

The combined model in eq 6 assumes that the number and reactivity of cathodic sites on the surface of the iron is fixed (37). However, the number of reactive sites for TCE reduction may actually decrease with increasing concentration. This can be attributed to
the effect of $E_{corr}$ on the rate of halocarbon reduction and to passivation of the iron surfaces. According to the Butler-Volmer equation, the rate constant for TCE reduction by corroding iron should be dependent on $E_{corr}$ according to (19, 29)

$$k_1 = \hat{k} e^{-\tilde{\alpha} F (\varepsilon_{corr} - \varepsilon^\circ)} e^{-\tilde{\alpha} F (\varepsilon_{corr} - \varepsilon^\circ)}$$

(7)

where $\hat{k}$ is the standard rate constant, which is dependent on only chemical factors; $F$ is the Faraday constant; $R$ is the gas constant; $T$ is the temperature; $E^0'$ is the formal potential for the redox reaction; and $\tilde{\alpha}$ and $\tilde{\alpha}$ are the transfer coefficients for the reduction and oxidation reactions, respectively. The transfer coefficients depend on the number of electrons transferred before and after the rate-determining step and whether the rate-determining step is limited by chemical- or potential-dependent factors (19). Under the conditions of this study, the $E^0'$ for TCE reduction to chloroacetylene is $\sim 420$ mV (SHE) (35). Therefore, the second bracketed term in eq 7, which represents the rate of the reverse oxidation reaction, will be negligibly small as compared to the first term. Therefore, the effect of $E_{corr}$ on the TCE reduction rate constant can be described by

$$k_1 = \hat{k} e^{-\tilde{\alpha} F (\varepsilon_{corr} - \varepsilon^\circ)}$$

(8)

As shown in Figure 4, the $E_{corr}$ of the iron increases with increasing TCE concentration. Therefore, if the rate of TCE reduction is limited by the rate of electron transfer (i.e., $\tilde{\alpha} \neq 0$), the rate constant for TCE reduction should decrease with increasing concentration. This effect may explain part of the deviation from first-order reaction kinetics observed at 408 and 426 days and may also explain the decrease in $k_0$ values with increasing TCE concentration in a previously reported study (37).
Figure 4. Corrosion currents for the iron aggregate electrode in 10 mM CaSO₄ electrolyte solutions containing TCE. Also shown are the free corrosion potentials of the iron aggregate electrode with respect to the standard hydrogen electrode (SHE).

Passivation of the iron surfaces also contributed to the deviation from first-order reaction kinetics at 408 and 426 days. Two lines of evidence confirm that the iron surfaces became passivated by exposure to the 7.8 mM TCE concentration. Upon lowering the influent TCE concentration back to 0.3 mM, the $t_{1/2}$ for TCE did not recover to its previous value at 309 days, as indicated in Table 3. This indicates that the reactivity of the iron surfaces declined as a result of exposure to the 7.8 mM TCE concentration. However, this passivation was slowly reversible, and both the TCE and
PCE reaction rates gradually recovered to their values before passivation, as indicated by $t_{1/2}$ data in Table 3 at 592 days.

Table 3. Summary of $t_{1/2}$ values and 95% confidence intervals for different operating conditions and elapsed times.

<table>
<thead>
<tr>
<th>Days Elapsed</th>
<th>Operating Conditions</th>
<th>TCE Half-life (min)</th>
<th>PCE Half-life (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>309</td>
<td>before passivation / TCE conc. = 0.3 mM</td>
<td>481 ± 36</td>
<td>1076 ± 93</td>
</tr>
<tr>
<td>426</td>
<td>TCE conc. = 7.8 mM</td>
<td>2528 ± 1817</td>
<td>-</td>
</tr>
<tr>
<td>507</td>
<td>post passivation / TCE conc. = 0.3 mM</td>
<td>1528 ± 255</td>
<td>4537 ± 549</td>
</tr>
<tr>
<td>565</td>
<td>partially recovered from passivation</td>
<td>949 ± 274</td>
<td>1935 ± 534</td>
</tr>
<tr>
<td>592</td>
<td>fully recovered from passivation</td>
<td>443 ± 70</td>
<td>1031 ± 163</td>
</tr>
<tr>
<td>886</td>
<td>pre-autoclaving</td>
<td>478 ± 22</td>
<td>685 ± 58</td>
</tr>
<tr>
<td>933</td>
<td>post-autoclaving</td>
<td>273 ± 24</td>
<td>514 ± 70</td>
</tr>
<tr>
<td>954</td>
<td>post-methanol disinfection</td>
<td>278 ± 14</td>
<td>500 ± 22</td>
</tr>
</tbody>
</table>

Corrosion current measurements for an electrode constructed from the iron aggregates also indicated that the iron surfaces became passivated by exposure to high TCE concentrations. As shown in Figure 4, the corrosion rate of the electrode was measured as a function of the aqueous TCE concentration in a 10 mM CaSO$_4$ electrolyte solution. Up to a concentration of 6 mM, the iron corrosion rate increases in an approximately linear fashion with TCE concentration. However, TCE concentrations greater than 6 mM increase the corrosion current above the passivation threshold and lead to a decreased rate of iron corrosion. In fact, the iron corrosion rate in the 8 mM solution was less than that in the blank electrolyte solution. This indicates that the number of reactive sites for dechlorination actually declines for TCE concentrations above 6 mM.
The data in Figure 4 also show that the $E_{corr}$ of the iron is not a good indicator of the degree of passivation, since it increases monotonically with TCE concentration, despite the decrease in corrosion current.

![Tafel polarization profiles for iron aggregate electrode in 10 mM CaSO$_4$ electrolyte solutions containing TCE or PCE present at 50% of aqueous saturation.](image)

**Figure 5.** Tafel polarization profiles for the iron aggregate electrode in 10 mM CaSO$_4$ electrolyte solutions containing TCE or PCE present at 50% of aqueous saturation.

The corrosion current data indicate that oxidation by TCE contributes only minimally to the overall rate of iron aggregate corrosion. The small effect of TCE on the corrosion rate may be attributed to the fact that corrosion of the iron aggregates was anodically controlled. Tafel polarization diagrams for the iron aggregate electrode in solutions with TCE and PCE each at 50% of aqueous saturation are shown in Figure 5. The anodic Tafel slopes ($\beta_a$) of 0.016 decade/mV as compared to cathodic slopes ($\beta_c$) of 0.032 decade/mV indicate that corrosion of the aggregates is anodically controlled (30). Polarization experiments in blank 10 mM CaSO$_4$ solutions without added halocarbons
indicate that corrosion of the aggregates by water alone is also anodically controlled. Anodic control of iron corrosion can be attributed to adherent corrosion products on the surfaces of the iron. These corrosion products reduce the rate at which Fe$^{2+}$ produced at anodic sites on the iron surface may enter the solution. This results in concentration polarization at anodic sites and reduces the thermodynamic favorability for further iron oxidation (30).

4.4.3 Microbiological Effects

The increasing reaction rate over the first 309 days could potentially be attributed to an increasing contribution over time of microbiological reductive dechlorination. The presence of microbial growth in the column was confirmed by cell counts of influent and effluent water samples. The site groundwater had cell counts of approximately $10^6$/mL, while cell counts in the column effluent were approximately 2 orders of magnitude greater. However, despite the presence of microbial growth, subsequent testing described below indicated that there was no significant biological reductive dechlorination of either TCE or PCE.

Several changes were made to the column operating conditions to investigate the contribution of biological reductive dechlorination. To eliminate nutrients for microbial activity, the feed water was changed from the site ground water to deionized water after 427 days elapsed. Also, LiCl was added as a microbial inhibitor between 427 and 507 days elapsed. As shown by the half-life data in Table 3, the effect of adding the LiCl to
the column was inconclusive since the effective $t_{1/2}$ for TCE decreased at the same rate during periods when LiCl was present (between 427 and 507 days elapsed) and when LiCl was not present (between 507 and 592 days).

To determine whether the recovery in reaction rates between 427 and 592 days elapsed was due to gradual recovery of a biological reduction mechanism, the column was removed from operation and autoclaved for 60 minutes at 121 °C and 2 bar after 921 days elapsed. As indicated by the $t_{1/2}$ data in Table 3 at 886 and 933 days, the TCE and PCE $t_{1/2}$ values after the autoclaving procedure were faster than those before autoclaving. This indicates that biological reductive dechlorination did not significantly contribute to the observed rates of halocarbon reduction in the column. This increase in reaction rates can be attributed to loss of corrosion products from the iron surfaces due to exposure to oxygen. A previous investigation has shown that exposure of passivated iron surfaces to air leads to exfoliation of corrosion products from the iron surfaces and a concomitant reversal of passivation (16). This same phenomenon occurred in this investigation, and visible rust was observed in the effluent water upon resaturating the column after the autoclaving procedure. However, prior to this time, iron concentrations in the column effluent were always below the detection limit of 1 μM.

After 937 days, one additional test was performed to validate the absence of biological reductive dechlorination. Between 937 and 940 days, the column was flushed with pure methanol in order to eliminate any microbial activity. As shown by the $t_{1/2}$ data in Table 3, the TCE and PCE reaction rates were statistically identical before and
after the methanol treatment. This confirmed that biological reductive dechlorination did not significantly contribute to TCE and PCE transformation.

### 4.4.4 Mass Transfer and Adsorption Effects

The faster TCE versus PCE transformation observed in this investigation could potentially be due to greater mass transfer limitations for PCE. The independence of the $t_{1/2}$ values with flow rate indicates that diffusion through the hydrodynamic film boundary layer at the exterior surface of the iron aggregates was fast as compared to the rate of reaction. However, because the iron aggregates were covered with a porous oxide layer, reaction rates at the iron surface may have been limited by adsorption retarded diffusion through iron corrosion products. Although the aqueous diffusion coefficient for PCE is only 10% smaller than that for TCE (39), greater adsorption of PCE on the oxide pore surfaces could contribute to a greater difference in intraoxide diffusion rates. To investigate this possibility, the adsorbed/aqueous phase distribution coefficients ($K_d$) for TCE and PCE adsorption onto the oven oxidized aggregates were determined. The $K_d$ of 0.18 mL/g for PCE confirmed that PCE adsorbed more strongly than TCE, which had a $K_d$ of 0.15 mL/g. This indicates that adsorption retarded diffusion through a porous oxide layer would be slower for PCE as compared to TCE.

To investigate possible mass transfer limitations associated with the oxide film, HCA was added to the feed stream after 1063 days elapsed. The hypothesis behind adding HCA was that if adsorption retarded diffusion through a porous oxide layer was
limiting reaction rates, the reaction rate for HCA should be slower than that for TCE, since HCA adsorbs more strongly than TCE, as indicated by its $K_d$ of 1.0 ml/g. However, the short half-life measured for HCA of less than 23 minutes compared to a TCE half-life of approximately 250 minutes indicates that intraoxide diffusional limitations are not responsible for the difference in TCE and PCE reaction rates.

4.4.5 Direct and Indirect Reduction

Although the faster reaction rate of TCE versus PCE is not consistent with most other investigations of halocarbon reduction by zero-valent iron, it is consistent with previously published data for halocarbon reduction by palladium catalysts and by an iron-palladium bimetallic system (26-28). Since hydrocarbon reduction by palladium catalysts is believed to occur via reaction with atomic hydrogen, the faster reduction of TCE observed in this investigation suggests that the predominant reaction mechanism may involve indirect reduction by atomic hydrogen. A recent investigation of halocarbon reduction by iron cathodes has reported that the predominant mechanism for TCE reduction is indirect and involves atomic hydrogen (40).

For reduction by zero-valent iron, comparisons of amperometrically measured reaction rates with those measured analytically can be used to assess the relative rates of direct and indirect reduction. Chronoamperometry (CA) and corrosion current measurements can be used to measure rates of direct halocarbon reduction but cannot detect indirect reduction by atomic hydrogen. For example, by comparing the current in a blank electrolyte solution to that measured in a solution containing TCE or PCE, the rate
of direct halocarbon reduction can be determined. CA experiments performed with the iron aggregate electrode show that there was greater current going toward direct PCE reduction as compared to that for TCE. Figure 6 compares CA profiles for the aggregate electrode in a blank electrolyte solution and in electrolyte solutions containing TCE or PCE, each present at 50% of aqueous saturation. At early elapsed time before the electrode currents became mass transfer limited, the current in the PCE containing solution was greater than that in the TCE solution. This indicates that direct reduction of PCE is faster than direct TCE reduction. There is greater current in the PCE solution despite the fact that the PCE concentration of 0.45 mM is ~9 times lower than the TCE concentration of 4 mM.

![Figure 6. Chronoamperometric profiles for the iron aggregate electrode in 10 mM CaSO₄ electrolyte solutions without added halocarbons and with TCE or PCE present at 50% of aqueous saturation. The profiles were generated by polarizing the electrode to -453 mV (SHE).](image)
Corrosion current measurements for the proppant electrode also indicate that direct PCE reduction is faster than that for TCE. For example, the presence of PCE at a concentration of 0.91 mM increased the corrosion rate of the aggregate electrode by 4.0 μA as compared to the blank electrolyte. However, as shown in Figure 4, this same concentration of TCE increased the corrosion rate of the electrode by only 0.44 μA. Assuming a six-electron transfer for TCE and an eight-electron transfer for PCE, this suggests that the rate constant for direct PCE reduction was 6.8 times greater than that for TCE. Thus, the CA and corrosion current measurements indicate that direct PCE reduction by the iron aggregates is faster than direct TCE reduction. However, as shown in the column experiments, the analytically measured rate constant for TCE is approximately twice as fast as that for PCE. This disparity between the current measurements and analytically measured reaction rates suggests that halocarbon reduction may also occur indirectly via reaction with atomic hydrogen adsorbed to the iron.

The Tafel diagrams for the iron proppant electrode in Figure 5 indicate that corrosion of the iron was anodically controlled. Under this condition, the rate of direct halocarbon reduction was limited by the rate at which the iron was able to release additional electrons. In contrast to the anodically controlled shortage of electrons available for direct halocarbon reduction, there may be an excess of atomic hydrogen for indirect reduction since more than 80% of the aggregate corrosion was due to reduction of water at submillimolar halocarbon concentrations. Under this scenario, the faster
reaction rate of TCE can be attributed to its faster rate of indirect reduction compared to that for PCE. Faster rates of TCE versus PCE reduction by atomic hydrogen in catalytic systems (26-28) is consistent with this hypothesis.

Figure 7. (a) Corrosion currents for the iron wire electrode in 10 mM CaSO4 electrolyte solutions containing TCE or PCE; (b) anodic and cathodic Tafel slopes for the iron wire electrode in 10 mM CaSO4 electrolyte solutions containing TCE.
The fact that most other investigators have observed faster PCE versus TCE reaction rates may be attributed to the fact that iron corrosion rates were not anodically controlled in those investigations. In the absence of dissolved oxygen, iron corrosion by water is normally cathodically controlled (30). Even in solutions containing high concentrations of TCE, corrosion of fresh iron was cathodically controlled, as indicated by the data in Figure 7a,b for corrosion of a fresh iron wire in solutions containing TCE. At each aqueous TCE concentration, the cathodic Tafel slope for the iron wire was smaller than the anodic Tafel slope, as shown in Figure 7b. Under these conditions, iron corrosion rates were limited by the rate at which oxidants were able to accept electrons. Thus, the faster PCE versus TCE reaction rates observed in other studies can likely be attributed to cathodically controlled corrosion leading to faster rates of direct PCE reduction.

For the fresh iron wire, direct reduction of PCE is faster than that for TCE. For example, the data in Figure 7a show that, at equivalent aqueous concentrations, the corrosion current from the iron wire going toward PCE reduction was greater than that going toward reduction of TCE. Assuming a six-electron transfer for TCE and an eight-electron transfer for PCE, the corrosion currents in Figure 7a at concentrations of 0.91 mM indicate that the rate constant for direct PCE reduction was a factor of 4.3 times greater than that for TCE. However, the chloride balance from the experiment in Figure 7a indicates that the total rate constant for PCE reduction by the iron wire was only a factor of 2.8 times greater than that for TCE. This indicates that there is also faster
indirect reduction of TCE by the iron wire. These results suggest that the relative rates of TCE and PCE reduction by zero-valent iron depend on the relative contributions of the direct and indirect reduction pathways.

Data from this study does show that zero-valent iron systems are capable of maintaining their reactivity over a long period of operation. However, high halocarbon concentrations may contribute to iron surface passivation. At submillimolar concentrations, corrosion current measurements for both 99.9% pure iron and the iron aggregates indicate that oxidation by TCE contributes only minimally to the overall rate of corrosion. Therefore, the iron consumption rate in reactive barrier remedial systems may be only weakly dependent on the influent halocarbon concentration.

The finding of anodically controlled corrosion of aged iron surfaces is not unique to the iron aggregates used in this investigation. In a previously reported study, corrosion of Masters Builders' Supply iron and 99.9% pure iron coated with magnetite was also anodically controlled (16). The faster reduction of TCE as compared to PCE in anodically controlled systems is consistent with results from a long-term field test of a zero-valent reactive barrier (41). In that study, reaction rates for TCE were approximately 2 times faster than those for PCE after 5 years. This suggests that after a long period of operation reaction rates become anodically controlled, even at low halocarbon concentrations. Therefore, reaction rates measured with fresh iron particles may not yield realistic long-term rates of halocarbon reduction.
4.5 References


CHAPTER 5
REDUCTIVE DECHLORINATION OF TRICHLOROETHENE AND CARBON TETRACHLORIDE USING IRON AND PALLADIZED IRON CATHODES

5.1 Abstract

This research investigated the effectiveness of electrochemical reduction for removing trichloroethylene (TCE) and carbon tetrachloride (CT) from dilute aqueous solutions. The kinetics, reaction mechanisms, and current efficiencies for TCE and CT reduction were investigated using flow-through, iron electrode reactors, and with amperometric measurements of reduction rates. The electrode reactors were operated over a range of flow rates, pH, ionic strength, dissolved oxygen concentration, and working electrode potentials. Typical reduction half-lives for TCE and CT in the iron reactor were 9.4 and 3.7 minutes, respectively. The addition of palladium as an electrocatalyst at a level of 1 mg-Pd per square meter of electrode surface area increased the reaction rates by a factor of three. When operated continuously, reaction rates in the palladized iron reactor were stable over a nine month period of operation, indicating that there was no loss of palladium from the electrode. In both the iron and Pd-iron reactors, TCE was reduced primarily to ethane and ethene, while CT was reduced almost exclusively to methane. Under all operating conditions, chlorinated compounds accounted for less than 2% of the total reaction byproducts. Comparisons of amperometrically measured current efficiencies with those measured in the flow-through reactors, and the weak effect of electrode potential on TCE reaction rates, indicated that
the primary pathway for TCE reduction by iron and palladized iron electrodes is indirect, and involves atomic hydrogen as the reducing agent. Direct reduction of TCE appeared to be inhibited by the preferential reduction of water. The finding that electrodes coated with a hydrophobic polymer to inhibit water reduction showed current efficiencies greater than 90% for direct TCE reduction supports this hypothesis. For CT, similar amperometric and analytically measured current efficiencies indicated that the primary mechanism for CT reduction is direct electron transfer. Carbon dioxide and bisulfide, which have been found to foul palladium in other catalytic systems, did not deactivate the catalyst. The fast reaction kinetics and electrode stability indicate that electrochemical reduction may be feasible for treating waters contaminated with chlorinated organic compounds.

5.2 Introduction

In recent years there has been considerable interest in developing destructive treatment methods for removing chlorinated organic compounds from contaminated waters (1-11). Most of these treatment techniques have focused on reductive dechlorination methods that transform chlorinated organic compounds to their nonchlorinated analogs and chloride ions. Reductive dechlorination promoted by zerovalent metals has been a very active research area since Gillham and O’Hannesin (1) proposed that metallic iron filings could be utilized for in situ passive ground water remediation (2-6).

In addition to in situ treatment using zerovalent iron, several investigations have reported on reductive dechlorination methods that are fast enough to be employed in above ground canister treatment systems (7-19). Most of these methods use palladium as
an electrocatalyst and hydrogen as the reducing agent. The first use of palladium for reductive dechlorination was reported by Muftikian et al. (7) who showed that palladium plated on the surface of zerovalent iron yielded rapid dechlorination rates for trichloroethylene (TCE). However, the effectiveness of the catalyst declines over time due to the buildup of an iron (hydr)oxide film which obstructs reactant access to the catalytic sites (19).

To avoid the problem of catalyst fouling by iron oxide precipitates, some investigators have used palladium supported on porous alumina or zeolites for reduction of chlorinated and nonchlorinated hydrocarbons (12-15,18). In one of the earliest studies, Schreier and Reinhard (13) showed that supported palladium catalysts and dissolved hydrogen gas could rapidly dechlorinate aqueous phase TCE. Other investigators have shown that similar methods were also effective for reductive dechlorination of vapor phase halocarbons (14).

Although hydrogen gas and supported palladium catalysts rapidly dechlorinate a wide range of halocarbons, the catalysts are readily deactivated by reduced sulfur compounds, carbonate, or carbon dioxide gas (13-15). Deactivation of palladium by carbon dioxide has been attributed to chemisorption of carbon monoxide produced from carbonate reduction (20). Chemisorption of carbon monoxide with the catalyst renders the palladium electron deficient, and hinders the dissociative adsorption of molecular hydrogen at the catalyst surface. The mechanisms for sulfur poisoning of palladium catalysts are also well understood, and include: competitive adsorption of hydrogen
sulfide with the reactant species, modification of the electronic properties of the
palladium in the vicinity of sulfur atoms, and formation of Pd-S compounds (21-24).

Other investigators have attempted electrochemical reduction of chlorinated
aliphatic and aromatic compounds using palladium supported on carbon and graphite
cathodes (9,10,16,17). Although rapid dechlorination rates have been achieved with
palladium coated cathodes, the effectiveness of the catalyst is short-lived. Several
investigators have reported declining reaction rates over time due to loss of palladium
from the electrode (16,17). The use of solid palladium cathodes eliminates the problem
of palladium flaking off the electrode surface. However, a recent investigation reported
that a palladium gauze electrode was ineffective for chlorophenol reduction, despite rapid
reaction rates by palladium supported on carbon and graphite (10). This result suggests
that the mechanisms involved in reductive dechlorination are not well understood.

Halocarbon reduction at cathode surfaces may occur through both direct and
indirect mechanisms. Direct reduction may occur by electron tunneling, or by formation
of a chemisorption complex of the organic compound with the cathode material (25). Electron tunneling may occur to hydrocarbons that are physically adsorbed at the cathode
surface, or to compounds that are separated from the cathode surface by adsorbed water
or a metal oxide film. Because the probability of electron tunneling to compounds that
are not physically adsorbed decreases exponentially with distance from the electrode
surface, this mechanism is expected to be insignificant over distances greater than 10 Å
(26). Indirect reduction of organic compounds may occur via reaction with atomic
hydrogen. Atomic hydrogen adsorbed on the cathode may reduce organic compounds
through formation of chemisorbed hydride complexes (25). Reduction by this mechanism is fast on cathodes with low hydrogen overpotentials, such as platinum and palladium, but is much slower on metals with high hydrogen overpotentials, such as iron (25).

The purpose of this research was to investigate the effectiveness of cathodic protection for maintaining the performance of iron and palladium treated iron for reductive dechlorination of aqueous phase halocarbons, and to determine the mechanisms responsible for halocarbon reduction. Reaction rates and byproducts of TCE and carbon tetrachloride (CT) reduction were measured in flow-through, porous iron electrode reactors, with and without the addition of palladium as an electrocatalyst. The effects of elapsed time, pH, ionic strength, dissolved oxygen, electrode potential, and the catalyst poisons, bicarbonate and bisulfide, on TCE and CT dechlorination rates were determined. The mechanisms responsible for TCE and CT reduction were investigated by comparing reaction rates and current efficiencies in the flow-through reactors with amperometric measurements of direct reduction rates.

5.3 Materials and Methods

5.3.1 Flow-Through Electrode Experiments.

Two flow-through reactors containing porous iron cathodes 2 cm in diameter and 3 cm long were used in the investigation. The electrodes were supplied by Cercona of America (Dayton, OH), and contained 5% by weight aluminosilicate binder and 95% iron. The iron electrodes had a B.E.T. (27) measured surface area of approximately 4.5 m$^2$, and an internal pore volume of approximately 2 ml. A schematic diagram of the
electrode reactors and experimental setup is shown in Figure 1. The anodes consisted of platinum wire screens that were wrapped around the iron cathodes. An ESC-7000 cation exchange membrane (Electrosynthesis Co., Lancaster, NY) was used to separate the anodes and cathodes, and water passed through only the cathode compartment of each reactor. The electrodes were contained within a 2.5 cm o.d. glass tube fitted with stainless steel pipe fittings at each end. The working electrode potentials were set using a potentiostat and saturated calomel electrode. The reactors were operated at cathodic potentials ranging from -755 to -1200 mV with respect to the standard hydrogen electrode (SHE). All potentials are reported with respect to the SHE.

Figure 1. Schematic diagram of the electrode reactor and experimental setup.
Except where indicated, the reactors were operated using a 3 mM CaSO₄ background electrolyte solution which was deoxygenated by purging with nitrogen gas. The effect of ionic strength on reaction rates was investigated by adding 100 mM NaCl to the background electrolyte solution. The effects of dissolved oxygen and carbonate on reaction rates were investigated by purging the feed water with 15 ml/min of air or carbon dioxide. Potential catalyst deactivation by reduced sulfur compounds was investigated by adding 1 mM Na₂S to the feed water. The palladized iron electrodes were prepared by passing a tetra-amminepalladium(II) chloride solution through the reactor to achieve a palladium loading of 1.0 mg/m².

Influent and effluent concentrations of TCE and CT were measured by extracting 50 µL aqueous samples into 1 g of pentane. Analytes in the pentane were then quantified by injection into a Hewlett-Packard 5890 gas chromatograph equipped with an electron capture detector and an autosampler. Nonchlorinated reaction byproducts were measured by injecting 50 µL aqueous samples into a counter-current stripping apparatus purged with nitrogen gas. The analytes stripped into the purge gas were then quantified using a molecular sieve column mounted in a SRI Instruments gas chromatograph equipped with a flame ionization detector (FID). Trace reaction byproducts such as chloroform, methylene chloride and dichloroethylene isomers were identified using a Finnigan ITD 700 gas chromatograph/mass spectrometer. Dissolved iron and palladium concentrations were determined by the Soil, Water and Plant Analysis Laboratory at the University of Arizona, using inductively coupled plasma mass spectroscopy. X-ray diffraction
analyses of the electrodes were performed by the Geosciences X-ray Diffraction Laboratory at the University of Arizona.

5.3.2 Amperometric Analyses.
Amperometric analyses using chronoamperometry were performed in a custom three electrode cell using an EG&G (Oak Ridge, TN) Model 273A potentiostat and M270 software. All experiments utilized a Ag/AgCl reference electrode and a platinum wire counter electrode. An iron disk (Metal Samples Company, Munford, AL), and iron, platinum and palladium wires (Aesar, Ward Hill, MA) were used as working electrodes. Supporting electrolyte solutions were deoxygenated prior to use by purging with argon. An EG&G model 616 rotating disk electrode was used to amperometrically measure CT reduction rates and current efficiencies over a range of CT concentrations and electrode potentials. Electrode currents were independent of the rotation rate for speeds greater than 1000 rpm. Current efficiencies and reaction rates were determined by comparing electrode currents in blank electrolyte solutions and those containing CT.

5.4 Results and Discussion
5.4.1 Degradation Kinetics
Zerovalent iron is thermodynamically unstable in water and must be cathodically protected in order to prevent anodic dissolution of the iron. The potential ($E_H$) required to prevent anodic dissolution depends on the ferrous iron activity [$Fe^{2+}$] as given by the Nernst equation at 25 °C (28):
Although cathodic protection can minimize anodic dissolution of the iron, cathodic polarization cannot prevent the formation of an oxide coating on the electrode surface. Since the feed solutions used in this study contained no dissolved iron, anodic dissolution of the electrodes occurred until a visible oxide formed on the electrode surfaces. During the first day of operation, formation of the oxide was evident by a change in electrode color from metallic silver to black. Subsequent X-ray diffraction analysis of the surface oxide from one electrode indicated that it was composed of magnetite. To eliminate the effects of changing electrode surface chemistry on halocarbon reaction rates, all measurements were taken after equilibrating the electrodes with the solutions for at least one day.

The reactors were operated at cathode potentials ranging from -755 mV to -1200 mV. Although this potential range is below the stability domain of water, visible amounts of hydrogen gas were observed only at potentials below -900 mV. The low rate of hydrogen production can be attributed to the high overpotential of the hydrogen evolution reaction on iron and iron oxide surfaces (26). Over the range of potentials investigated, the degree of cathodic protection was sufficient to maintain constant reaction rates in both the palladized and untreated iron reactors over a nine month period of continuous operation. Dissolved iron concentrations in the reactor effluent were below the detection limit of 60 μg/L. Within the limits of experimental precision, effluent pH values were the same as influent values.
Both mass transfer and reaction rate limitations may affect the degree of reactant conversion in flow-through reactors. Under all operating conditions, the performance of the electrode reactors was well described by a plug flow, packed bed reactor model with a first order reaction rate\(^{(29)}\). For all the kinetic data reported in this investigation, the reactors were operated at flow rates where mass transfer limitations and dispersion effects on reactant conversion were negligible. At low flow rates, where the hydraulic residence time was greater than 4 minutes, preliminary testing indicated that reaction rates increased with increasing flow rate in quantitative accord with boundary layer mass transfer theory for packed bed reactors\(^{(29)}\). However, at hydraulic residence times shorter than 2 minutes, the effect of mass transfer limitations on reaction rates was negligible.

Over the concentration range investigated (0.1 to 1.2 mM), reaction rates were first order in reactant concentration. Therefore, the reaction rates can be characterized in terms of a single parameter, such as a first order rate constant \(k\), or the reaction half-life\(^{(29)}\). Table 1 compares reaction rates for TCE and CT in the untreated and palladized iron reactors at hydraulic residence times of 1 to 2 min and a cathode potential of \(-755\) mV. In the iron reactor, the half-lives for TCE and CT were \(9.4\pm1.5\) and \(3.7\pm0.2\) minutes, respectively. Palladium treatment at a level of 1 mg/m\(^2\) reduced the TCE half-life to \(2.7\pm0.2\) minutes, and the CT half-life to \(1.3\pm0.1\) minutes. These reaction rates can be compared to rates in other systems by normalizing the observed \(k\) by the surface area to solution volume in the reactor, as in \(k_{sa} = k(V/\sigma)\); where, \(V\) is the pore volume of the reactor, and \(\sigma\) is the reactive surface area of the electrode. In Table 1, the surface area...
normalized rate constants \((k_{sa})\) for the iron reactor are compared to those previously reported \((3)\) for CT and TCE reduction by zerovalent iron filings. For both CT and TCE, the electrode \(k_{sa}\) values are within the range of those reported for reduction by zerovalent iron. This suggests that there is not a substantial increase in reaction rates due to cathodic protection of the iron. However, reaction rates in the electrode reactors did not show the declining performance over time that has been observed with zerovalent iron filings \((6,30)\).

Small performance differences were observed between different electrodes due to variations in electrode surface area and pore volume. Therefore, comparisons of reaction rates under different operating conditions can only be made for reactors using the same electrode. Removal of the palladized iron electrodes from the reactor resulted in a partial loss of catalytic activity upon subsequent use. This loss in catalytic activity was due to the buildup of iron oxides on top of the palladium, similar to that observed for palladized iron filings \((19)\).

Table 1. Half-lives with 95% confidence intervals for CT and TCE reduction at a cathode potential of -755 mV, neutral pH, and influent concentrations of 0.12 and 0.28 mM, respectively *

<table>
<thead>
<tr>
<th>Compound</th>
<th>Iron Reactor</th>
<th>Pd-Iron Reactor</th>
<th>Iron Reactor</th>
<th>Iron Filings (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Half-life (min)</td>
<td>Half-life (min)</td>
<td>(k_{sa} , \text{L/(m}^3\text{hr)})</td>
<td>(k_{sa} , \text{L/(m}^3\text{hr)})</td>
</tr>
<tr>
<td>CT</td>
<td>3.7 ± 0.2</td>
<td>1.3 ± 0.1</td>
<td>5.6 \times 10^{-3}</td>
<td>5 \times 10^{-3} to 0.5</td>
</tr>
<tr>
<td>TCE</td>
<td>9.4 ± 1.5</td>
<td>2.7 ± 0.2</td>
<td>2.2 \times 10^{-3}</td>
<td>6 \times 10^{-3} to 0.03</td>
</tr>
</tbody>
</table>

*Also listed are normalized first order reaction rate constants for CT and TCE reduction in the iron electrode reactor and literature values for CT and TCE reduction by zero-valent iron filings.
5.4.2 Reaction Byproducts and Pathways

The reaction byproducts for TCE reduction by cathodically protected iron and palladized iron are similar to those reported for reduction by zerovalent iron (4). In both the iron and palladized iron reactors, ethane and ethene accounted for more than 95% of the TCE reaction byproducts, with acetylene accounting for up to 5%. Carbon mass balances of more than 90% were obtained, and trace amounts of the three dichloroethene isomers, vinyl chloride, 1-butene and 2-butene were also detected. Under all experimental conditions, the sum of all chlorinated byproducts accounted for less than 1% of the TCE that was reduced. The exact ratio of the two major byproducts varied by ±20% depending on the flow rate, with lower flow rates favoring greater ethane production.

The observed distribution of reaction byproducts suggests that the β-elimination mechanism proposed by Roberts et al. (5) is the primary reaction pathway. The β-elimination pathway involves a two-electron transfer to produce chloroacetylene from TCE. The resulting chloroacetylene then undergoes hydrogenolysis to form acetylene, or undergoes another two electron transfer to form ethene. Although no chloroacetylene was detected in any experiments, the absence of this intermediate product has been explained by its rapid reaction rate (6).

Methane was the major reaction product of CT reduction in both the iron and palladized iron reactors, and accounted for more than 95% of the CT that was transformed. The chlorinated byproducts, chloroform and methylene chloride, together accounted for less than 2% of the transformed CT. The low yield of chlorinated
byproducts from CT reduction contrasts with reports of near stoichiometric production of chloroform for CT reduction by zerovalent iron (4).

Previous investigators have reported that cathodic reduction of CT initiates with a one electron transfer to form a trichloromethyl radical as given by (31):

\[ \text{CCl}_4 + e^- \rightarrow ^*\text{CCl}_3 + \text{Cl}^- \]  \hspace{1cm} (2)

For reduction by zerovalent iron, the trichloromethyl radical is normally reduced to chloroform as in (4):

\[ ^*\text{CCl}_3 + e^- + H^+ \rightarrow \text{HCCl}_3 \]  \hspace{1cm} (3)

However, a second pathway exists in which the trichloromethyl radical is reduced to dichlorocarbene and a chloride ion as given by (32):

\[ ^*\text{CCl}_3 + e^- \rightarrow \text{CCl}_2 + \text{Cl}^- \]  \hspace{1cm} (4)

The dichlorocarbene is then hydrolyzed to give CO and HCl. Thus, the second pathway illustrated by eqn. 4 does not produce chlorinated daughter products from CT reduction. The high yield of methane suggests that CO is rapidly reduced in the reactors.

Previous investigators have reported that the reaction 4 pathway becomes more favored the lower the potential of the reducer (33). The near absence of chlorinated products supports this reaction pathway. Because of the small degree of reactant conversion (~50%), if CT reduction produced chloroform followed by methylene chloride, these products should have been present at significant yields, due to their slower reaction rates compared to CT. In independent tests with each halocarbon, the rate constants for chloroform and methylene chloride were smaller than the rate constant for CT by factors of 3.5 and 26, respectively.
5.4.3 Current Efficiency

Comparisons of amperometrically measured current efficiencies, defined as the fraction of the total cell current going toward halocarbon reduction, with current efficiencies in the electrode reactor can be used to determine the relative contributions of direct and indirect reduction. Dehalogenation of compounds for which the reduction mechanism is direct can be measured amperometrically by comparing currents in blank electrolyte solutions to those with added halocarbons. In contrast, indirect reduction by atomic hydrogen cannot be detected amperometrically, but can be determined from the extent of halocarbon reduction in the electrode reactors. Amperometrically measured current efficiencies for CT reduction by a rotating disk electrode are shown in Figure 2 as a function of the CT concentration and electrode potential. The current efficiency for CT reduction increases with increasing CT concentration, and decreases with decreasing electrode potential. The high current efficiencies for direct CT reduction at an aqueous concentration of 3 mM indicate that CT reduction is more favorable than water reduction. This conclusion is also supported by high current efficiencies measured for CT reduction by iron wire electrodes in solutions saturated with CT. At an electrode potential of -680 mV, a current efficiency of 94% was measured for CT reduction using potential step chronoamperometry. The high current efficiency was obtained despite a low adsorbed phase concentration of CT. Anson analysis (34) of the early time chronoamperometry profile indicated that the fraction of the electrode surface covered with CT was only 18%, based on the nominal geometric surface area of the electrode. However, due to molecular
scale roughness, the actual electrode surface area is greater than its geometric surface area, and therefore, the actual adsorbed surface coverage by CT is even smaller than 18%.

Figure 2. Amperometrically determined current efficiencies for CT reduction by an iron rotating disk electrode as a function of electrode potential and CT concentration.

The current efficiencies for CT reduction in the iron electrode reactor were close to those measured amperometrically using the rotating disk electrode. Agreement of the amperometric and analytically determined current efficiencies indicates that the predominant mechanism for CT reduction involves direct electron transfer from the electrode.

The current efficiencies for TCE reduction at an electrode potential of -755 mV in the iron and palladized iron reactors are shown in Figure 3. The data in Figure 3 show that the current efficiency for TCE reduction by the iron electrode is greater than 90% at
a TCE concentration of 1 mM. At this same concentration and electrode potential of -755 mV, the data in Figure 2 show that the current efficiency for CT reduction is only 38%. The high current efficiency for TCE is surprising given that TCE reduction cannot be measured amperometrically using the rotating disk electrode, or by potential step chronoamperometry. Iron and platinum wire electrodes polarized to -780 mV in solutions saturated with TCE give the same currents as those polarized in blank electrolyte solutions. This indicates that TCE reduction is indirect, and occurs via reaction with atomic hydrogen stored in the electrode.

![Graph](image)

**Figure 3.** Current efficiency for TCE reduction in the iron and palladized iron reactors at an electrode potential of -755 mV and a hydraulic residence time of 1.4 min.

Potential step amperometric analysis of TCE reduction by a palladium wire electrode indicates that TCE reduction by palladized iron is also indirect. Figure 4 shows chronoamperometry profiles for TCE and CT reduction by a palladium wire electrode
immersed in 3 mM CaSO₄ solutions, with and without added halocarbons. In the TCE saturated electrolyte solution, the steady state current was 25% smaller than the current in the blank electrolyte solution. This indicates that adsorption of TCE blocks reduction of water. In contrast, adding CT to the electrolyte solution resulted in an order of magnitude increase in the initial current before mass transfer limitations became a factor. This indicates that CT can be directly reduced by the palladium wire. Experiments analytically measuring TCE reduction by the palladium wire electrode found that the kₘₐₚ of $1.3 \times 10^3$ Lm⁻²hr⁻¹ was a factor of two smaller than the kₘₐₚ for TCE reduction in the iron electrode reactor, and more than 600 times smaller than the kₘₐₚ for CT reduction by the palladium wire. The slow reduction rate of TCE by the palladium wire electrode suggests that the reaction rate enhancement by palladium supported on iron is due to its strong adsorption of TCE, which then allows indirect reduction by atomic hydrogen.

**Figure 4.** Chronoamperometric profiles at a potential of -780 mV for a palladium wire electrode in a blank 10 mM CaSO₄ solution, and in 10 mM CaSO₄ solutions saturated with TCE or CT.
The absence of significant direct TCE reduction by iron, platinum and palladium wire electrodes can most likely be attributed to preferential reduction of water at the electrode surface. If this is the case, then coating the electrode with a hydrophobic material should decrease water reduction and allow amperometric measurement of direct TCE reduction. This hypothesis was tested by coating an iron disk electrode with silicone vacuum grease and measuring chronoamperometry profiles in 100 mM K₂SO₄ solutions, with and without TCE. As shown in Figure 5, coating the electrode with a hydrophobic polymer reduced the steady state current associated with water reduction from 60 μA to 0.43 μA. However, after adding TCE to the solution, the steady state current increased from 0.43 μA to 5.1 μA. This corresponds to a current efficiency of 92% for TCE reduction, and indicates that inhibition of water reduction can lead to direct reduction of TCE.

![Figure 5](image-url)

*Figure 5. Chronoamperometric profiles for an iron disk electrode, with and without a hydrophobic silicone surface coating, at a potential of -780 mV in 100 mM K₂SO₄ solutions.*
5.4.4 Effect of Electrode Potential

The effect of electrode potential on TCE reaction rates in the flow through reactors can be used to assess the contribution of direct electron transfer to the overall rate of TCE reduction. In the absence of mass transfer limitations, the potential dependence of electrochemical reaction rates can be described by the Butler-Volmer equation (26):

\[
i = i_0 \left[ e^{-\frac{\alpha F (E - E_{eq})}{RT}} - e^{\frac{\alpha F (E - E_{eq})}{RT}} \right]
\]

(5)

where \(i\) is net current associated with the reaction, \(i_0\) is the exchange current, \(F\) is the Faraday constant, \(R\) is the gas constant, \(T\) is the temperature, \(E\) is the potential of the electrode, \(E_{eq}\) is the equilibrium potential for the redox reaction, and \(\alpha\) and \(\tilde{\alpha}\) are the transfer coefficients for the reduction and oxidation reactions, respectively. The first term in brackets gives the rate of the forward reduction reaction, while the second term gives the rate of the reverse oxidation reaction. The transfer coefficients depend on the number of electrons transferred before and after the rate determining step, and whether the rate determining step is limited by chemical or potential dependent factors (26). Since reductive dechlorination reactions are not reversible, the \(E_{eq}\) for a particular reaction cannot be measured directly, but can be estimated from thermodynamic data for reactant and product species (5). At neutral pH, and a chloride activity of \(10^{-3}\) M, the equilibrium potential for a two electron reduction of TCE to chloroacetylene has been estimated to be 599 mV (5). Therefore, the potentials used for TCE reduction in this investigation were sufficiently below the \(E_{eq}\) that the term representing the rate of the reverse reaction in equation 5 is negligible compared with the term accounting for the
forward reduction reaction. Therefore, the effect of electrode potential on the TCE reduction rate constant \( k_r \) should be described by:

\[
k_r = k_0 e^{-\frac{\Delta F(E - E_a)}{RT}}
\]  

(6)

where \( k_0 \) is the standard rate constant, which is dependent on only chemical factors. Thus, according to equation 6, the ratio of reaction rate constants at two electrode potentials, \( E_1 \) and \( E_2 \), is then given by:

\[
k_{r_1}/k_{r_2} = e^{-\frac{\Delta F(E_1 - E_2)}{RT}}
\]  

(7)

The effect of electrode potential on TCE reaction rates in the iron and palladized iron reactors is shown in Figure 6. In the iron reactor, decreasing the electrode potential resulted in small increases in the TCE reaction rate. However, the increases in reaction rate were less than expected based on the behavior predicted by equation 7. In order to evaluate equation 7, the transfer coefficient must be known. For a multistep, multiple electron transfer reaction in which the rate determining step is potential dependent, the minimum value of the transfer coefficient is close to 0.5 (26). Taking the reaction rate constant at \(-782 \text{ mV} \) as \( k_{r_1} \), and, the rate constant, \( k_{r_2} \), at \(-0.882 \text{ mV} \) should be a factor of 49 times greater than that at \(-782 \text{ mV} \), if the reaction rate limiting step involves electron transfer. However, the measured reaction rate constant for TCE increased by only 23% between \(-0.782 \text{ mV} \) and \(-0.882 \text{ mV} \). The small potential dependence of the TCE reaction rate indicates that the rate limiting step for TCE reduction does not involve electron transfer, or that the primary TCE reduction pathway is indirect. A similar conclusion can be made for TCE reduction in the palladized iron reactor.
Figure 6. The effect of electrode potential on the half-life of TCE in the iron and palladized iron reactors at a hydraulic residence time of 1.4 min and influent concentration of 0.28 mM.

5.4.5 Water chemistry effects

The effect of pH on reaction rates was investigated by comparing TCE and CT reduction rates in solutions with pH values of 4, 7 and 10. As shown by the data in Table 2 for the iron reactor, the reduction half-life for TCE increased by a factor of three between pH 4 and 10. Smaller pH effects were observed for TCE reduction in the palladized iron reactor. The greater pH effect in the untreated iron reactor supports the conclusion that molecular hydrogen is involved in TCE reduction by the iron electrode. Although the higher pH values contribute to decreased cathodic production of hydrogen in both the untreated and palladized iron reactors, the palladium serves to concentrate the available hydrogen, thereby reducing the influence of pH on reaction rates. The effects of pH on CT reduction in the palladized iron reactor were small, and there was no
consistent trend in the iron electrode reactor. The small pH effects are consistent with a reaction mechanism involving direct CT reduction.

Table 2. Effect of pH of the reduction half-lives of CT and TCE at an electrode potential of -755 mV, and influent concentrations of 0.26 and 0.24 mM, respectively.

<table>
<thead>
<tr>
<th>pH</th>
<th>TCE Half-life (min)</th>
<th>CT Half-life (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iron</td>
<td>Pd Iron</td>
</tr>
<tr>
<td>4</td>
<td>5.5 ± 0.3</td>
<td>3.8 ± 0.2</td>
</tr>
<tr>
<td>7</td>
<td>6.2 ± 0.4</td>
<td>4.5 ± 0.2</td>
</tr>
<tr>
<td>10</td>
<td>16.8 ± 3.0</td>
<td>6.0 ± 0.4</td>
</tr>
</tbody>
</table>

Because oxygen is more facilely reduced than either CT or TCE, oxygen reduction may compete with reduction of the target compounds. To investigate this possibility, TCE and CT reaction rates in the palladized iron reactor were measured in solutions with dissolved oxygen concentrations of 0 and 9 mg/L. At an electrode potential of -755 mV, adding oxygen to the feed water resulted in an increase in the cell current from 11 to 18 mA, but did not affect the rates of TCE or CT reduction. This indicates that there were no competitive effects with dissolved oxygen for reactive sites on the electrode surface. Tests comparing reaction rates in 3 mM CaSO₄ and 100 mM NaCl solutions indicated that reaction rates were also independent of the background electrolyte solution.

The effect of carbonate species on palladium deactivation was investigated by comparing TCE reaction rates in feed waters with and without dissolved carbon dioxide. Purging the feed water with carbon dioxide gas resulted in an H₂CO₃(aq) concentration of 31.6 mM at a pH of 4.3. Bicarbonate and carbonate levels were 0.32 mM and 3.2 x 10⁻⁴ μM, respectively. After four days of operation with carbon dioxide in the feed stream at
an electrode potential of -755 mV and a hydraulic residence time of 1 min, the reaction rate for TCE was the same as that before addition of carbon dioxide. This indicates that dissolved carbon dioxide does not deactivate the palladium catalyst. The addition of carbon dioxide did increase the cell current from 11 to 16 mA, mostly due to increased hydrogen evolution resulting from the lower pH value of the influent solution. However, some of the increase in current was due to reduction of carbon dioxide itself. The reaction products of carbon dioxide reduction were determined after removing TCE from the feed stream. Carbon dioxide reduction produced methane, ethane and ethylene. These are similar to the reaction products previously reported for reduction of carbon dioxide by zerovalent iron (35).

Complete reduction of carbon dioxide to hydrocarbons may explain the absence of poisoning effects by carbon monoxide. In this experiment, polarization of the electrode maintained the palladium at sufficiently negative potentials to reduce carbon monoxide completely to hydrocarbons. However, in catalytic systems where dissolved hydrogen is the electron donor, the low aqueous solubility of hydrogen gas may not produce sufficiently negative cathodic potentials to completely reduce carbon monoxide.

To test the effect of reduced sulfur compounds on catalyst poisoning, the palladized iron reactor was operated at a potential of -780 mV for four days with a feed water containing 0.44 mM HS\(^-\) and 0.56 mM H\(_2\)S. Addition of the sulfide increased the TCE half-life in the palladized iron reactor from 3.8±0.2 to 5.2±0.3 min. However, upon removing sulfide from the feed stream, the TCE half-life recovered 3.6±0.2 min, indicating that that sulfide did not permanently deactivate the palladium catalyst.
slower reaction rate in the presence of sulfide can likely be attributed to competitive adsorption of H₂S on the palladium (21-23).

The fast reaction rates and electrode stability observed in this investigation indicate that cathodic reduction may be a practical process for treating waters contaminated with chlorinated organic compounds. Although iron is a base metal that forms an oxide coating even under cathodic polarization, it may be a practical electrode material due to its low cost and high overpotential for hydrogen evolution. At the electrode potentials used in this investigation, noble metal cathodes, such as platinum and palladium, would produce more than two orders of magnitude more hydrogen per unit surface area of electrode (36). Furthermore, noble metal cathodes are highly susceptible to deactivation by deposition of metallic impurities, whereas oxide coated electrodes are much less susceptible to deactivation (37). Although the performance enhancement of the palladium catalyst may have been limited by mass transfer effects associated with reactant diffusion through a surface oxide layer, the fast reaction rates in the untreated iron reactor indicate that precious metal catalysts may not be necessary to achieve practically feasible halocarbon reduction rates.

5.5 Literature Cited


30. Schrier, C. G.; Reinhard, M. *Chemosphere* 1994, 29 (8), 1743.


CHAPTER 6
ELECTROCHEMICAL INVESTIGATION OF THE RATE LIMITING MECHANISMS FOR TRICHLOROETHYLENE AND CARBON TETRACHLORIDE REDUCTION AT IRON SURFACES

6.1 Abstract

The mechanisms involved in reductive dechlorination of carbon tetrachloride (CT) and trichloroethylene (TCE) at iron surfaces were studied to determine if their reaction rates were limited by rates of electron transfer. Chronoamperometry (CA) and chronopotentiometry (CP) analyses were used to determine the kinetics of CT and TCE reduction by a rotating disk electrode in solutions of constant halocarbon concentration. Rate constants for CT and TCE dechlorination were measured as a function of the electrode potential over a temperature range from 2 to 42°C. Changes in dechlorination rate constants with electrode potential were used to determine the apparent electron transfer coefficients at each temperature. The transfer coefficient for CT dechlorination was 0.22±0.02, and was independent of temperature. The temperature independence of the CT transfer coefficient is consistent with a rate limiting mechanism involving an outer sphere electron transfer step. Conversely, the transfer coefficient for TCE was temperature dependent, and ranged from 0.06 ± 0.01 at 2°C to 0.21 ± 0.02 at 42°C. The temperature dependent TCE transfer coefficient indicated that its reduction rate was limited by chemical dependent factors, and not exclusively by the rate of electron transfer. In accord with a rate limiting mechanism involving an electron transfer step, the
apparent activation energy ($E_a$) for CT reduction decreased with decreasing electrode potential, and ranged from $33.0 \pm 1.6$ to $47.8 \pm 2.0$ kJ/mole. In contrast, the $E_a$ for TCE reduction did not decline with decreasing electrode potential, and ranged from $29.4 \pm 3.4$ to $40.3 \pm 3.9$. The absence of a potential dependence for the TCE $E_a$ supports the conclusion that its reaction rate was not limited by an electron transfer step. The small potential dependence of TCE reaction rates can be explained by a reaction mechanism in which TCE reacts with atomic hydrogen produced from reduction of water.

6.2 Introduction
Permeable reactive barriers containing zerovalent iron are becoming increasingly popular for in situ remediation of groundwater contaminated with chlorinated organic compounds (1-7). In zerovalent iron remedial systems, the iron serves as an electron donor that transforms chlorinated organic compounds to their nonchlorinated analogs and chloride ions. Redox active metals, water, and other groundwater constituents, such as nitrate and carbonate, may also be reduced by reactions with the zerovalent iron (8, 9).

Dechlorination rates and byproducts for most environmentally relevant halocarbons have been determined under a wide range of experimental conditions (1-7, 10, 11). In most instances, rates of dechlorination within a homologous series of compounds increases with the degree of chlorination (3). This observation has led investigators to develop linear free energy relationships (LFERs) between reaction rates and halocarbon physicochemical properties (11-13).

LFERs with high correlation coefficients have been found between rates of halocarbon dechlorination and physical parameters such as the energy of the lowest
unoccupied molecular orbital (E-LUMO), two-electron reduction potential (E2), one-electron reduction potential (E1), and carbon-halogen bond dissociation energies (11-13). These correlations between reaction rates and potential dependent parameters, such as E-LUMO, E1 and E2, have led investigators to conclude that rates of electron transfer control dechlorination rates. However, the correlation between many physical properties makes LFERs unsuitable for determining whether halocarbon reaction rates are limited by rates of electron transfer. For example, parameters such as E1 and E2 correlate with the degree of chlorination within a homologous series. Therefore, these parameters also correlate with halocarbon hydrophobicity, and the extent of adsorption to reactive sites. Thus, faster dechlorination rates for more highly chlorinated homologues may arise from greater adsorption to reactive sites, and not from a greater thermodynamic driving force for reduction, as indicated by E-LUMO, E1 and E2.

Although most investigators have reported faster dechlorination rates with increasing degree of halogenation, not all studies are consistent with this trend. For example, Arnold and Roberts (11) reported that dechlorination rates for a series of chlorinated ethenes decreased with increasing degree of chlorination, and Farrell et al. (14) reported faster reaction rates for trichloroethylene (TCE) than for perchloroethylene. Other investigators have found that the relative rates of TCE and dichloroethylene reduction varied along the length of column reactors, and also varied between batch and column systems (7). These observations suggest that there may be multiple mechanisms for chlorinated ethene reduction on iron surfaces.
These multiple mechanisms may include direct and indirect electron transfer reactions. Direct reduction may occur by electron tunneling, or by formation of a chemisorption complex of the organic compound with the iron surface (15). Electron tunneling may occur to halocarbons that are physically adsorbed at the iron surface, or to halocarbons that are separated from the iron surface by one or more layers of adsorbed water. Halocarbons may also be reduced indirectly via reaction with atomic hydrogen produced from water reduction (16). These reactions may involve formation of hydrocarbon-hydride complexes on the iron surface (15).

Electrochemical Kinetics

In the absence of mass transfer limitations, the potential dependence of electrochemical reaction rates can be described by the Butler-Volmer equation (17):

\[ i = i_0 [e^{-\alpha F (E - E_{eq}) / RT} - e^{-\alpha F (E - E_{eq}) / RT}] \]

where \( i \) is net reaction current, \( i_0 \) is the exchange current, \( F \) is the Faraday constant, \( R \) is the gas constant, \( T \) is the temperature, \( E \) is the electrode potential, \( E_{eq} \) is the equilibrium potential for the redox reaction, and \( \alpha \) and \( \alpha \) are the transfer coefficients for the reduction and oxidation reactions, respectively. The first term in brackets represents the rate of the forward reduction reaction, while the second term gives the rate of the reverse oxidation reaction. The transfer coefficients depend on the number of electrons transferred before (\( \gamma \)) and after (\( \gamma \)) the rate determining step, the number of times the rate determining step must occur, and the symmetry factor (\( \beta \)) for the reaction (18). For overall reactions involving only a single CT or TCE molecule, the transfer coefficients may be expressed as:
\[ \tilde{a} = \tilde{r} + r\beta \]  \hspace{1cm} (2) \\
\[ \tilde{a} = \tilde{r} + r(1 - \beta) \]  \hspace{1cm} (3)

where \( r = 0 \) if the rate determining step does not involve electron transfer, otherwise \( r = 1 \). The \( \beta \) parameter is dependent on the symmetry of the potential energy surface between the transition state and the reactant and product species \((18)\). For a single step electron transfer reaction, \( \beta \) represents the fraction of the applied overpotential which goes towards overcoming the activation energy of the cathodic reaction, while \((1 - \beta)\) represents the fraction of the overpotential which goes towards increasing the activation energy for the reverse, anodic reaction \((18)\).

Transfer coefficients for a range of halocarbons on iron electrodes have been measured by other investigators \((13, 19)\). However, no attempts were made to determine whether dechlorination rates were actually limited by the rate of electron transfer. In multistep electrodic reactions, the overall reaction rate may be limited by rates of reactant chemisorption, rates of bond breaking, or rates of molecular rearrangement. These are chemical, rather than potential, dependent factors. If the overall reaction rate is limited by chemical dependent factors, the measured transfer coefficient may be only a fitting parameter, or an apparent transfer coefficient.

The goal of this study was to determine if the rate limiting mechanisms for iron mediated reductive dechlorination of CT and TCE involve electron transfer. Reaction rate constants and apparent transfer coefficients were measured at different temperatures and electrode potentials. The effect of temperature on the electron transfer coefficients, and the effect of potential on the activation energies of the reactions, were used to
determine whether dechlorination rates were limited by chemical or potential dependent factors.

6.3 Materials and Methods

6.3.1 Rotating Disk Electrode (RDE) Reactor

![Diagram of rotating disk electrode reactor.

All kinetic experiments were performed with an EG&G (Oak Ridge, TN) model 616 rotating disk electrode in a custom glass reaction cell, as depicted in Figure 1. The cylindrical glass reactor was contained within a water-jacket and had an inner diameter of 2.2 cm and a length of 11 cm. The temperature in the reaction cell was controlled to within ± 0.2 °C with a circulating water bath. An iron disk (Metal Samples Co., Mumford, AL) with a geometric surface area of 1 cm² was used as the working electrode. A Hg/Hg₂SO₄ electrode (Perkin Elmer, Oak Ridge, TN) was used as the reference electrode, and a 0.3 mm diameter by 4 cm long platinum wire (Aesar, Ward Hill, MA) was used as the counter electrode. The counter electrode was encased within a Nafion®
(Dupont) proton permeable membrane in order to prevent oxidation of chloride ions or the target organic compounds.

6.3.2 Voltammetric Experiments.

All experiments were performed in 25 mL of a 10 mM CaSO₄ background electrolyte solution. The solutions were continuously purged with ~100 mL/min of nitrogen gas in order to maintain anaerobic conditions, and to remove reaction byproducts from the solution. Halocarbon concentrations in the reaction cell were controlled by adding TCE or CT to the nitrogen purge stream. Experiments to determine the transfer coefficients were conducted at a constant CT concentration of 2 mM, or a constant TCE concentration of 3 mM. Before each experiment, the iron disk was chemically and mechanically polished with an EG&G electrode polishing kit. The iron disk was then conditioned at -785 mV prior to each experiment in order to reduce any remaining surface oxides. The disk electrode was rotated at speeds of 100 or 1000 rpm to eliminate the effect of mass transfer on rates of TCE or CT dechlorination.

Chronoamperometry (CA) analyses (17) were performed in background electrolyte solutions, and in solutions containing TCE or CT at potentials ranging from -600 mV to -1200 mV. Chronopotentiometry (CP) analyses (17) were also performed in electrolyte solutions with or without CT by applying currents ranging from 0.1 to 400 µA to the disk electrode. Electrode potentials or electrode currents were controlled and recorded with an EG&G model 273A potentiostat and M270 software. All potentials are reported relative to the standard hydrogen electrode (SHE), and cathodic currents are reported as positive.
6.3.3 Analyses.

TCE and CT concentrations in the reactor were determined by analysis of 100 μL aqueous samples. The 100 μL samples were injected into 1 g of pentane and analyzed by injection into a Hewlett-Packard 5890 Series II gas chromatograph (GC) equipped with an electron capture detector (ECD) and autosampler. Chloride ion concentrations were determined by analysis of 5 mL samples using a DX 500 ion chromatograph (Dionex, Sunnyvale, CA). An Orion pH probe was used to determine the initial and final pH values of the electrolyte solutions.

Because operation of the RDE required that the solution be exposed to the atmosphere through the electrode shaft opening, reaction byproducts were determined in separate experiments in a 25 mL sealed, glass cell. After a short period of electrolysis at each potential, the solutions were sampled and analyzed for chloride ions and hydrocarbon concentrations.

6.4 Results and Discussion

6.4.1 CT Results

Initiation of CT reduction may proceed via a stepwise mechanism in which the first step involves only outer sphere electron transfer, according to (20):

\[
\text{CCl}_4 + e^- \overset{\text{step 1}}{\leftrightarrow} \text{CCl}_4^- \overset{\text{step 2}}{\leftrightarrow} \text{CCl}_3^+ + C\Gamma
\]  

(4)

or it may proceed via a concerted electron transfer and bond breaking step, according to (20, 21):

\[
\text{CCl}_4 + e^- \leftrightarrow \text{CCl}_3^+ + C\Gamma
\]  

(5)
The electrode potential, electrode material, and the solvent determine which of these initiation steps predominates (20, 21). Over the potential range investigated in this study, reaction 4 or 5 is followed by a second electron transfer, in which the trichloromethyl radical reacts according to (21, 22):

\[ CCl_3^* + e^- + H^+ \rightarrow CHCl_3 \]  

The reaction byproducts observed in this study are consistent with these reactions. GC-ECD analyses indicated that CF accounted for >90% of the CT disappearance, while chloride analyses indicated that the CF yield was ~95%. The disparity between these two measurements can likely be attributed to an adsorptive loss of CF to Teflon fittings in the sealed, glass cell.

The initial pH of the electrolyte solutions was ~6.5, and there was a decline of less than 2 pH units over the course of each experiment. In most cases the decline in pH was less than 1 pH unit. The effect of pH on CT reduction rates was determined at potential of -785 mV at pH values of 4.1, 5.3 and 7.2. In these experiments, there was less than a 10% increase in the CT reaction rate for a solution pH decrease from 7.2 to 4.1. Therefore, the decrease of less than 2 pH units over the course of each experiment had a very small impact on the measured rates of CT dechlorination.

The stronger pH dependency of reaction rates observed with corroding iron media (23, 24) can be attributed to the effect of pH on the condition of the iron surfaces, and on the corrosion rate, which affects the iron's free corrosion potential. Lower pH values lead to cleaner iron surfaces and faster corrosion rates. Since the iron in this investigation was
cathodically protected and at a fixed potential, there were minimal oxides on the iron surface, and pH did not affect the iron potential.

Figure 2: CA profiles of iron disk electrode in a 10mM CaSO₄ electrolyte with and without 2 mM CT, at a rotating speed of 1000 rpm and an applied potential of −785mV.

Chronoamperometry (CA) experiments were performed at 22 °C to determine the reaction rate constants for CT as a function of electrode potential. A profile from a typical CA experiment is illustrated in Figure 2. At the start of each experiment, the electrode potential was stepped cathodically from its open circuit potential in the blank electrolyte solution to the desired potential. This generated a constant current for water reduction, as indicated by the blank current in Figure 2. After 30 minutes of electrolyzing the blank solution, CT was added to the nitrogen purge gas. Once the solution concentration had reached its steady state value of 2 mM, the applied potential was momentarily terminated, and the potential was again stepped from the open circuit potential to the desired potential. As shown in Figure 2, this potential step resulted in a
surge in current due to charging of the electrical double layer at the electrode surface, and
to reduction of CT adsorbed to the electrode under open circuit conditions. Throughout
each experiment, there was a slight decline in the cell current between 3 and 30 minutes
elapsed, as illustrated in Figure 2. This can be attributed primarily to the buildup of iron
oxides and atomic and molecular hydrogen on the electrode surface.

Under steady state conditions, the rate of CT reduction (r_{CT}) equals the rate of CT
mass transfer to the electrode surface. This rate can be expressed as (25):

\[ r_{CT} = k_{CT} C_S = \frac{D}{\delta}(C_B - C_S) \]  

(7)

where \( k_{CT} \) is the reduction rate constant, \( C_S \) is the surface CT concentration, \( C_B \) is the bulk
solution concentration, \( \delta \) is the diffusion layer thickness, and \( D \) is the CT aqueous
diffusion coefficient. The diffusion layer thickness can be determined from the Levich
equation and the electrode rotation speed (17). Under the conditions of these
experiments, \( D/\delta \) was more than 2 orders of magnitude greater than \( k_{CT} \). Therefore, at all
electrode potentials, \( C_S \) was greater than 0.99 \( C_B \), and thus all experiments were
performed at essentially the same \( C_S \), despite difference in \( k_{CT} \).

The \( k_{CT} \) values for CT reduction were determined both amperometrically and
analytically at each potential. According to the reaction stoichiometry in equations 4-6,
each CT molecule dechlorinated to CF requires 2 electrons. Average amperometric rate
constants for each 30 minute electrolysis period were determined from the difference in
integrated currents between the blank and 2 mM CT solutions. Figure 3 shows the
average amperometrically determined rate constants as a function of electrode potential at
22 °C. Analytic rate constants for CT reduction were determined from a chloride balance on each solution, and are also shown in Figure 3. The nearly identical analytic and amperometric rate constants indicate that CT reduction occurred via direct electron transfer, and that reduction of CT did not measurably impact water reduction.

![Figure 3: CT reduction currents in RDE reactor at different electrode potentials. The $i_{CT}$ values were determined from the chloride generated during the second CA run at each potential.](image)

Combining equation 1 with the Nernst equation for reaction 5, shows that the current going towards CT reduction should depend on electrode potential, and the surface activity of reactants ($\{CCl_4\}$) and products ($\{CCl_3^+\} \& \{Cl^-\}$) according to (17):

$$i = FA \left[ k_f^0 \{CCl_4\} e^{-\Delta G^{\circ} / RT} - k_b^0 \{CCl_3^+\} \{Cl^-\} e^{\Delta G^{\circ} / RT} \right]$$  \text{(8)}

where $A$ is the electrode area, and $k_f^0$ and $k_b^0$ are the forward and backward reaction rate constants, respectively, at the standard reduction potential ($E^{\circ}$). Since the electrode
potentials were significantly below the $E^o$ for reaction 5 (26), the rate of the reverse anodic reaction was more than 2 orders of magnitude smaller than the rate of the forward reaction. Therefore, the second term in equation 8 can be neglected, and the $	ilde{\alpha}$ for CT reduction can be determined from the reaction rate constant, $k_{CT}$, according to:

$$\tilde{\alpha} = \frac{2.3RT}{F} \left( \frac{d \log k_{CT}}{dE} \right)$$

(9)

Calculation of the transfer coefficient from the $k_{CT}$ values at 22 °C is illustrated in Figure 3.

Since the CT current efficiencies, defined as the fraction of the total cell current going towards CT reduction, were greater than 90%, CP analysis was used to determine the transfer coefficient for CT at other temperatures. The advantage of the CP technique is that all experiments may be performed in the same solution, since blank current values at each potential are not needed. This eliminates some variability in the condition of the electrode surface, since the electrode need not be removed from the solution between experiments. In accord with equation 1, the transfer coefficients were determined from measurements of the overpotential $(E-E_{eq})$ at each imposed current, as illustrated in Figure 4. Only absolute overpotential values greater than 100 mV were used to calculate the slope in Figure 4 because the relationship between overpotential and $\log(i)$ approaches linearity only at overpotentials where the second term in equation 1 becomes negligible compared to the first term. Average electron transfer coefficients with 95% confidence intervals measured with CP analysis for CT are shown in Figure 5. Note that
the transfer coefficient of $0.20 \pm 0.02$ determined at $22 \, ^\circ C$ using CP analysis was close to the $\alpha$ of $0.24 \pm 0.02$ measured using CA analysis at this temperature.

![Graph](image1)

**Figure 4:** Overpotentials at different imposed cathodic currents from CP analysis of iron disk electrode in 10 mM CaSO$_4$ electrolyte with 2 mM of CT in solution. Transfer coefficients were calculated with eq 1 using overpotential values $> 50$ mV.

![Graph](image2)

**Figure 5:** The effect of temperature on the apparent transfer coefficients for reduction of water, CT, and TCE. Error bars represent 95% confidence intervals.
6.4.2 Trichloroethylene Results

In contrast to CT that reacts primarily via sequential dechlorination (19, 22), the dominant pathway for TCE reactions with iron involves a β-elimination mechanism (11, 26). In this mechanism, the first detectable product of TCE reduction is chloroacetylene, which is produced according to:

\[ \text{C}_2\text{HCl}_3 + 2e^- \rightarrow \text{C}_2\text{HCl} + 2\text{Cl}^- \]  \hspace{1cm} (10)

The chloroacetylene is then rapidly reduced to acetylene and ethylene (11, 26, 27). The TCE reaction products observed in this study are consistent with this pathway. GC analyses and chloride balances indicated complete TCE dechlorination, and no chlorinated products were detected. The initial pH of the solutions was ~6.5, and there was a decline of less than 1 pH unit over the course of each 30 minute experiment.

CA experiments similar to those described for CT were performed with TCE. In contrast to CT, reaction rates for TCE could not be determined amperometrically, since TCE interfered with water reduction. Figure 6 shows that at a potential of -685 mV, the presence of TCE in the solution resulted in an increase in current compared to the blank electrolyte. The current increase indicates that TCE may undergo reduction via direct electron transfer. However, at lower potentials, currents in the TCE solutions were less than those in the blank electrolyte, as illustrated in Figure 6 for a potential of -1085 mV. This shows that there was measurable competition between water and TCE for reaction sites on the iron surface. Therefore, rate constants \(k_{TCE}\) for TCE dechlorination were determined from the chloride generated during CA runs at each potential. Average apparent transfer coefficients for TCE reduction were determined using equation 9, and
are shown in Figure 5. Note that the transfer coefficient measured at 22 °C of 0.14 is close to the value of 0.15 measured by other investigators (13).

Figure 6: CA profiles of iron disk electrode in 10mM CaSO₄ electrolyte with and without 3 mM TCE, at a rotation speed of 100 rpm and applied potentials of −685 and −1085mV.

6.4.3 Transfer Coefficient Analysis and Activation Energy Analysis

The temperature dependencies of the transfer coefficients can be used to assess whether the rate limiting step for TCE or CT reduction involves outer sphere electron transfer. Since cathodic transfer coefficients depend only on the number of electrons transferred before the rate limiting step (\( \gamma \)) and the symmetry factor (\( \beta \)), the transfer coefficient should show the same, or weaker, temperature dependence as \( \beta \). At room temperatures and above, the shape of the potential energy surface between the products and reactants is normally considered to be independent of temperature (28). Therefore, \( \beta \) and the electron transfer coefficient should also be independent of temperature (29). If the measured transfer coefficient is temperature dependent, this indicates that the rate
limiting mechanism is not an outer sphere electron transfer step. In this case, the reaction rate may be limited by an inner sphere electron transfer step that involves bond breaking or molecular rearrangement (20, 21, 29).

A multiple partial f-test (30) was performed to determine if the transfer coefficients for CT, TCE and water were functions of temperature. The statistical analysis found that the transfer coefficient for CT was independent of temperature at the 99.9% confidence level. This indicates that the rate of CT reduction was limited by the rate of outer sphere electron transfer, as illustrated by step 1 in equation 4. In contrast, the statistical analysis found that $\bar{\alpha}$ values for TCE were temperature dependent at the 99.9% confidence level. This indicates that the TCE reaction rates were limited by chemical dependent factors, and not by rates of electron transfer alone. Analysis of the transfer coefficients for water indicate that the $\bar{\alpha}$ values in Figure 5 were independent of temperature at the 99.9% confidence level. This suggests that the rate limiting step for water reduction was an outer sphere electron transfer step.

The apparent activation energies ($E_a$) for CT, TCE and water reduction at different electrode potentials are shown in Figure 7. A regression analysis (30) found that the apparent $E_a$ for CT reduction decreased with increasingly negative electrode potentials. This is consistent with a rate limiting step that involves electron transfer. In electron transfer reactions, a fraction of the polarization energy goes towards changing the chemical activation energy, and the apparent $E_a$ depends on the electrode potential according to (18):

$$E_a = E_a^{\infty} + \bar{\alpha}F(E - E_{eq})$$  \hspace{1cm} (11)
where \( E^o_a \) is the activation energy at the equilibrium potential. For CT reduction, cathodic polarizations resulted in negative overpotentials \( (E-E_{eq}) \), and therefore resulted in decreasing \( E_a \) values with increasingly negative electrode potentials. The trend in \( E_a \) values for water reduction is also consistent with a rate limiting step that involves electron transfer. In contrast to the data for CT and water, statistical analysis at the 99.9% confidence level indicates that the \( E_a \) values for TCE did not decline with decreasing electrode potential, as required by equation 11 for electron transfer reactions. This clearly indicates that the rate limiting step for TCE dechlorination did not involve electron transfer.

According to equation 2, the \( \tilde{\alpha} \) for a multistep reaction in which the rate limiting step does not involve electron transfer \( (i.e., r=0) \) should be equal to \( \tilde{\gamma} \). However, since \( \tilde{\gamma} \) must be an integer, the observed transfer coefficients for TCE in Figure 5 indicate that there were no electrons transferred before the rate limiting step. Therefore, according to equation 2, an \( \tilde{\alpha} \) value of zero should have been observed for TCE. However, the \( \tilde{\alpha} \) value for TCE was not zero, indicating that its rate of reaction was dependent on the electrode potential. This apparent paradox can be explained by a TCE reaction mechanism that involves atomic hydrogen produced from water reduction.

There are several simultaneous reactions that occur on the iron electrode in TCE solutions. As illustrated in equations 12 through 15, these reactions include the formation of adsorbed atomic hydrogen by electrolysis of water (Volmer reaction), molecular hydrogen evolution resulting from electrochemical desorption (Heyrovsky reaction), hydrogen evolution resulting from the chemical recombination of atomic hydrogen (Tafel
recombination), and the reaction between adsorbed atomic hydrogen and the halocarbon molecule (hydrodechlorination) (31).

\[
Fe + H_2O + e^- \leftrightarrow Fe - H + OH^- \quad \text{(Volmer discharge)} \quad (12)
\]
\[
Fe - H + H_2O + e^- \leftrightarrow Fe + H_2 + OH^- \quad \text{(Heyrovsky reaction)} \quad (13)
\]
\[
2Fe - H \leftrightarrow 2Fe + H_2 \quad \text{(Tafel recombination)} \quad (14)
\]
\[
Fe - RX + Fe - H \rightarrow RH + Fe + X^- \quad \text{(hydrodechlorination)} \quad (15)
\]

The rate of the hydrodechlorination reaction \( r_{TCE} \) for TCE can be expressed as (31):

\[
r_{TCE} = k_{TCE} \Theta_H^n \Theta_{TCE} \quad (16)
\]

where \( \Theta_H \) and \( \Theta_{TCE} \) are the surface coverages of adsorbed hydrogen and adsorbed TCE, respectively, and \( n \) is the reaction order of hydrogen in the hydrodechlorination reaction. Equation 16 shows that the rate of TCE reduction is a function of both the \( \Theta_H \) and \( \Theta_{TCE} \). The hydrogen coverage depends on the relative rates of the Volmer, Heyrovsky, and Tafel reactions.Reaction 12 has been reported as rate limiting reaction for hydrogen evolution at iron surfaces at circumneutral pH values (32). With this rate limiting reaction, \( \Theta_H \) increases with decreasing electrode potential (31-33). Therefore, the increase in TCE reaction rates with decreasing potential may be attributed to the effect of potential on \( \Theta_H \).

Results from this study show that at potentials relevant to dechlorination by iron media in aqueous systems, rates of CT reduction are limited by the rate of outer sphere electron transfer, while rates of TCE reduction are not limited by rates of electron transfer. At more negative electrode potentials, CT dechlorination may also become limited by chemical dependent factors, since rates of electron transfer, but not chemical
dependent steps, increase with decreasing potential. The different reaction mechanisms for CT and TCE may explain why rates of chloroethene reduction do not follow LFER trends established for chloroalkanes (11-13).

Reduction via an outer sphere mechanism, such as electron tunneling, requires only physical adsorption of CT on or near the electrode surface. Since physical adsorption interactions are of short temporal duration, and electrons are transferred one at a time briefly, interactions with the electrode surface may explain why chloroalkanes undergo primarily stepwise dechlorination, and produce chlorinated byproducts. For TCE, rates of chemisorption likely control its overall rate of dechlorination. TCE chemisorption has been postulated to involve di-sigma bond formation between the carbon atoms of TCE and the iron surface (11). This chemisorption step may then be followed by direct electron transfer through the chemical bonds. The potential dependence of TCE reaction rates suggests that TCE may also be indirectly reduced via reaction with atomic hydrogen. Evidence for this mechanism has been reported in previous investigations (14,16). This indirect mechanism for reduction likely involves formation of hydrocarbon-hydride complexes with atomic hydrogen adsorbed on the iron surface (15). Both proposed TCE reaction mechanisms require chemisorption, and thus involve longer TCE interactions with the iron surface than mere physical adsorption. This may explain why the primary pathway for TCE reduction produces completely dechlorinated byproducts.
Figure 7: The effect of electrode potential on the apparent activation energies for reduction of (a) CT, (b) TCE, and (c) water. Error bars represent 95% confidence intervals.
6.5 Literature Cited


CHAPTER 7
CONCLUSIONS

This work showed that reaction rates decline with time when halocarbons are present at milli-molar concentrations. The declining reaction rates are due to passivating films that make iron corrosion anodically controlled. Nitrate in groundwater would also contribute to increased iron surface passivation and decreased rates of iron corrosion. There are also multiple reaction pathways for chloroethylene reduction at iron surfaces. Halocarbon reduction may occur via direct electron transfer or may occur indirectly through reaction with atomic hydrogen absorbed in the iron. Indirect reduction mechanism becomes more important under anodically controlled corrosion conditions. The faster reaction rate for TCE under anodically controlled conditions can therefore be attributed to its faster rate of indirect reduction as compared to PCE.

Rapid degradation rates with half-lives of several minutes were obtained for TCE and CT in flow through iron electrode reactors. Reaction rates were also increased by the addition of palladium as an electrocatalyst to iron surface. Hydrocarbons ethane and ethene were the primary product of TCE reduction while methane was the major product of CT reduction. The primary mechanism for CT reduction by iron and palladized iron electrodes is direct electron transfer. The primary pathway for TCE reduction is indirect, and involves atomic hydrogen as the reducing agent. The direct reduction of TCE appeared to be inhibited by the preferential reduction of water. Coating of iron electrodes
with a hydrophobic polymer to inhibit water reduction increased the current efficiencies for direct TCE reduction.

This work also studied the temperature dependence of transfer coefficient and the potential dependence of apparent activation energies ($E_a$) for TCE and CT reduction. The results indicated that CT reduction was limited by the rate of electron transfer, whereas TCE reduction was limited by chemical dependent factors, and not by the rate of electron transfer. An electrocatalytic hydrodechlorination mechanism in which chemisorbed TCE reacts with atomic hydrogen adsorbed at the iron surface was used to explain the small potential dependence of TCE reaction rates, and the increasing $E_a$ with decreasing potential.