3-1-2000

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Recommended Citation

Ferland, Derek R., "In Situ Treatment of Chlorinated Ethene-Contaminated Groundwater Using Horizontal Flow Treatment Wells" (2000). *Theses and Dissertations*. 4783.
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AFIT/GEE/ENV/00M-05

IN SITU TREATMENT OF CHLORINATED ETHENE-CONTAMINATED GROUNDWATER USING HORIZONTAL FLOW TREATMENT WELLS

THESIS

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AFIT/GEE/ENV/00M-05

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AFIT/GEE/ENV/00M-05

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THESIS

Presented to the Faculty of the Graduate School of Engineering and Management

Air Education and Training Command

In Partial Fulfillment of the

Requirements of the Degree of

Master of Science in Engineering and Environmental Management

Derek R. Ferland, B.S.

Captain, USAF

March 2000

AFIT/GEE/ENV/00M-05

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8 Mar 00

25 Feb 00

ACKNOWLEDGEMENTS

This thesis is dedicated in memory of my father, Norman Ferland, who passed away on 30 November 1999. Dad was an incredible husband, father, and friend. I will never forget his wisdom, sense of humor, and strength, and I hope that someday I will become half the man he was.

I owe a tremendous debt of gratitude to several people who were instrumental to the completion of this thesis. First of all, my thesis advisor, Dr. Mark Goltz, provided endless support, feedback, and helped me remain focused on the project. I am also extremely appreciative of the efforts of the other committee members, Dr. Abinash Agrawal, Dr. Dave Burris, and 1Lt John Christ. Their guidance, advice, and knowledge of relevant research greatly assisted my efforts. In particular, I would like to single out Lt Christ, whose thesis was the primary foundation for my work. His assistance during the modeling effort was invaluable and his contributions to this thesis cannot be quantified. John's high level of intuitive understanding pertaining to this research never ceased to leave me in awe.

The rigors of AFIT might have been too much to handle were it not for the support of my family. My Mom, Dad, and brother have always encouraged and supported me through good times and bad. Last, but certainly not least, I would like to thank my beautiful wife Dana. Her caring and understanding have buoyed me through the trials and tribulations of the past nine months.

Derek R. Ferland

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ABSTRACT

The limitations of conventional containment technologies for groundwater contaminated with chlorinated solvents have motivated development of innovative technologies to achieve national groundwater remediation objectives. One innovative technology that is currently under development involves metal reductants or catalysts to chemically destroy the dissolved chlorinated solvent. Models are important tools that can be used to help transition this technology to the field. Model studies can be used to gain understanding about the technology, help determine when the prospective technology might work for a given site, and design full-scale field applications.

In this study, the literature is reviewed to determine which metal reductants/catalysts might be appropriate for in-well use in a proposed Horizontal Flow Treatment Well (HFTW) system. The HFTW system involves use of two or more dual-screened wells to capture and treat chlorinated solvent contaminated groundwater without the need to pump contaminated water to the ground surface. A model is then presented which couples a chemical degradation submodel, simulating destruction of chlorinated ethenes in an in-well metal reactor, with the steady-state flow field imposed by the HFTWs. Natural and engineered parameters are varied to see how they affect HFTW system performance. Performance is quantified by simulating overall treatment efficiency (comparing contaminant concentrations downgradient and upgradient of the HFTW system) and the width of the contaminant plume captured by the system. Model results are displayed in a format that will facilitate use by designers who need to determine if this innovative technology is applicable for use at a specific contaminated site.

IN SITU TREATMENT OF CHLORINATED ETHENE-CONTAMINATED GROUNDWATER USING HORIZONTAL FLOW TREATMENT WELLS

1.0 INTRODUCTION

1.1 MOTIVATION

The harmful impact of toxic chemicals, which for years have been used in industry and subsequently released into the environment, upon human health has become evident over the past several decades. As evidence of the growing problem mounted, public attitude shifted from one of indifference to one that demanded action from the government. Action in the form of environmental cleanup legislation came in 1980 when Congress passed the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (Masters, 1997). CERCLA (also known as "Superfund") was passed to address the cleanup of abandoned hazardous waste sites and was strongly influenced by widely publicized environmental disasters such as Love Canal. The common perception was that Superfund was going to be a relatively short-lived program to clean the nation's contaminated sites.

Unfortunately, the scope of remediation efforts was vastly underestimated and the list of severely contaminated sites grew. The National Priorities List (NPL) is a running list of the most critically contaminated hazardous waste sites. The NPL is used in conjunction with Superfund to prioritize cleanup efforts. As of November 1996, the NPL contained 1,205 sites (US GAO, 1997a) and a more recent survey of the United States Environmental Protection Agency (US EPA) database by the United States General

Accounting Office (US GAO) shows that another 3,036 sites are potential candidates for the NPL (US GAO, 1998a). Unfortunately, sites on the NPL represent only a small subset of the hazardous waste sites in the nation. Real threats to human health and the environment are posed by thousands of sites that are not on the NPL. The National Research Council (NRC) has recently estimated that there are between 300,000 and 400,000 contaminated sites which could take as long as thirty years and cost up to $1 trillion to clean up (NRC, 1997).

As of 1997, 157 of the 1,205 NPL sites are owned by the federal government (Statistical Abstracts, 1998). The Department of Defense (DoD) is responsible for 120 of those 157 federal NPL sites (DERP, 1998). However, as alluded to earlier, the cleanup problem facing DoD is much greater than these 120 NPL sites. According to the 1998 Annual Report to Congress by the Defense Environmental Restoration Program (DERP), there are 23,346 sites requiring remediation at both active and Base Realignment and Closure (BRAC) installations (DERP, 1999). Cleanup of these sites is estimated to cost DoD $2 billion annually, for a total of $27 billion (US GAO, 1998b). The Air Force's portion of the DoD problem is significant. The Air Force is currently responsible for 37 of the 120 DoD NPL sites (DERP, 1998), and 6,038 of the 23,346 sites monitored by the DERP (DERP, 1999). Through the end of FY98, DoD has spent nearly $19 billion (DERP, 1999) in remediation expenditures and approximately $1.3 billion is projected to be expended in each annual budget through FY01 (DERP, 1999).

The US GAO report mentioned earlier found 3,036 sites potentially eligible for the NPL. The report also stated that an estimated 73 percent of these sites have contaminated groundwater (US GAO, 1998a). This is significant, as groundwater is an important pathway for transport of toxic chemicals to human and environmental receptors. Consequently much research has been dedicated to investigating groundwater remediation technologies. At DoD sites, chlorinated solvents such as tetrachloroethylene (PCE) and trichloroethylene (TCE) are prevalent groundwater contaminants. In fact, PCE and TCE-contaminated sites are found at over 70 percent of Air Force installations (Thiele, personal communication, 1999). PCE and TCE are probable human carcinogens (Masters, 1998) that can undergo a series of reactions in groundwater to form vinyl chloride (VC), a known human carcinogen (Vogel and McCarty, 1985). Chlorinated contaminants present a significant environmental challenge due to their widespread presence and their resistance to traditional remediation efforts.

Three strategies are currently used to contain groundwater plumes of dissolved chlorinated contaminants: pump-and-treat, funnel-and-gate systems, and natural attenuation. Pump-and-treat systems are used to remediate contaminated groundwater at 93 percent of Superfund sites. In spite of their widespread application, successful remediation of contaminated sites within regulatory standards occurs at only 10 percent of pump-and-treat applications (NRC, 1997). The limitations of pump-and-treat systems have been extensively reported (Mackay and Cherry, 1989). Among these limitations is the need to pump contaminated water to the ground surface, thereby increasing risk. Other factors that decrease pump-and-treat performance include the following:

immiscibility of contaminants with water; diffusion of contaminants into micropores and zones with limited water mobility; sorption of contaminants to subsurface materials; and heterogeneity of the subsurface (NRC, 1994; MacDonald and Kavanaugh, 1994, 1995).

Funnel-and-gate systems with metals such as zero-valent iron are emerging as an innovative technology to remediate dissolved chlorinated solvent-contaminated groundwater. Preliminary research (Starr and Cherry, 1994; Matheson and Tratnyek, 1994; Gillham and O'Hannesin, 1994; Tratnyek, 1996; Liang and others, 1997; Tratnyek and others, 1997; O'Hannesin and Gillham, 1998) has indicated that zero-valent iron can be used to destroy dissolved chlorinated contaminants. More recent research has evaluated the efficacy of palladium-based catalysts (Lowry and Reinhard, 1999; McNab, 1999). The technology consists of a permeable reactive barrier (PRB; a.k.a. the "gate") that is filled with a mixture of porous media and the reactive agent (e.g. zero-valent iron). Contaminated groundwater is directed toward the gate by strategically located sheet piles (the "funnel") (McMahon and others, 1999). Unfortunately, funnel-and-gate treatment systems are useful for only a narrow range of hydrogeologic conditions. For instance, contaminated groundwater that is relatively deep cannot be treated with the technology and variations in groundwater flow over time can allow the contaminant to bypass the treatment system (McMahon and others, 1999).

Natural attenuation is a process where physical, chemical, and biological mechanisms degrade contaminants to achieve risk objectives within a reasonable time period and without engineered approaches (Wiedemeier and others, 1998). The US EPA defines monitored natural attenuation (that is, natural attenuation that is monitored to ensure it is occurring) as (US EPA, 1997):

> …the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remedial objectives within a time frame that is reasonable… [They] include a variety of physical, chemical, or biological processes that…act without human intervention to reduce mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater.

Fuel hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX) have been shown to readily degrade in a subsurface environment (Wiedemeier and others, 1998). Chlorinated compounds, on the other hand, rely on reductive dechlorination, which means electron acceptors (the contaminant), and electron donors must be present in sufficient quantities (Wiedemeier and others, 1998). Therefore, unless site-specific conditions are conducive to this process, natural attenuation may not be appropriate. The US EPA has published a technical protocol that includes indicator parameters to help determine when microbial degradation of chlorinated compounds will most likely occur (Murray and others, 1999). Some disadvantages of natural attenuation include a longer time period to achieve remediation goals, complex and costly site characterization, production of toxic daughter compounds, extensive education and communication in order to gain public trust (Wiedemeier and others, 1998). For these reasons, natural attenuation as a strategy to deal with chlorinated compounds is not yet generally accepted.

Clearly, new remediation technologies are needed to treat dissolved plumes of chlorinated contaminants. Recent budget cutbacks have intensified the need to develop lower-cost remediation technologies. In April 1995, legislation was enacted that cut the

Defense Environmental Restoration Account (DERA) by $300 million. This reduction was in addition to an earlier DERA budget cut of nearly $400 million (West, 1995). In spite of these massive budgetary constraints, environmental remediation projects are expected to progress.

New, innovative technologies are needed to help clean up sites with contaminated groundwater more quickly, with greater efficiency, and at lower cost. Recent analysis of US EPA data has shown that innovative technologies are implemented at only six percent of the Superfund groundwater restoration sites (NRC, 1997). A Congressional push to develop new technologies was partially embodied in the 1986 Superfund Amendments and Reauthorization Act (SARA) (Sullivan, 1997). SARA highlighted the need for innovative technologies to help combat the hazardous waste site problem. Science, research, and innovation are needed to help overcome the inadequacies of available remediation technology.

As noted above, one particular innovative technology that is being used to remediate dissolved chlorinated solvent- contaminated groundwater employs a funnel-and-gate system using metals such as zero-valent iron. *In situ* destruction of the contaminant in the metal treatment media is a major advantage of this technology. Unfortunately, the funnel-and-gate treatment systems are only useful under specific hydrogeologic conditions.

One approach for dealing with the narrow range of application of a funnel-and-gate system is through the use of horizontal flow treatment well (HFTW) systems with an in-well reactor (McNab and others, 1999). Figure 1.1 shows the concept of how an HFTW system can be installed to contain a contaminant plume. As shown in the figure, certain wells will pump in an upflow mode and others will pump in a downflow mode so that contaminated water will circulate between the wells. The chlorinated contaminant is treated with each pass through the in-well reactor. Due to the circulation between the wells, the contaminant is treated multiple times, so that contaminant removal efficiencies (comparing contaminant concentration upgradient versus downgradient of the treatment wells) can be greatly increased versus removal efficiencies that would be obtained employing a single-pass reactor system. An HFTW system provides greater flexibility and hydraulic control than funnel-and-gate systems allowing for contaminant capture at significant depths and under fluctuating flow conditions. In-well reactors containing reactive metals would degrade chlorinated contaminants using the same chemical reaction pathways as seen in current funnel-and-gate systems. Potential metals could include zero-valent iron, palladium, palladized iron, or a combination of these enhanced by ultrasound.

A technology that combines metallic dehalogenation with an HFTW system offers several advantages over currently available technologies. Using an HFTW system with in-well reactors will destroy contaminants *in situ*. This technology will (1) reduce risk and minimize operating costs by eliminating the need to pump contaminants to the surface, (2) use well-understood chemical reactions rather than more complicated bioremediation techniques, and (3) decrease concerns about harmful daughter products or residuals to dispose of because the chemical process completely dechlorinates the contaminants (Tratnyek, 1996). The HFTW system combines the best features of pump-and-treat and funnel-and-gate technologies because it actively controls the contaminant plume, and by using in-well reactors, *in situ* degradation is achieved. To apply this technology, it is envisioned that a line of treatment wells equipped with *in situ* reactors will be located downgradient of a contaminant plume. These wells will actively contain the contaminated groundwater plume. The primary goal of this technology is to ensure that contaminant concentrations downgradient of the HFTW system are within regulatory limits. A hydraulic model of the HFTW system has been developed (Christ, 1997) which simulates groundwater flow due to multiple wells.

The goal of this thesis is to model a technology that incorporates the dehalogenation of chlorinated organic contaminants in an active, rather than passive, system. This model will combine Christ's (1997) HFTW flow model with kinetic models of various metallic reaction pathways that have the potential for in-well applications. This model will then be used to analyze how the system may be applied for contaminant plume containment.

Specific questions will focus on which types of metals can be used in an in-well system, the dechlorination rates associated with each type of reactive metal and long-term performance of each metal. Long-term performance is expected to vary based on groundwater geochemistry and whether or not the geochemistry causes precipitation or inactivation of the metals.

Development and application of a model will enhance understanding of how in-well metallic reactors can be utilized in an HFTW system to remediate groundwater contaminated with chlorinated solvents. The model will also be invaluable in helping to design and implement full-scale systems.

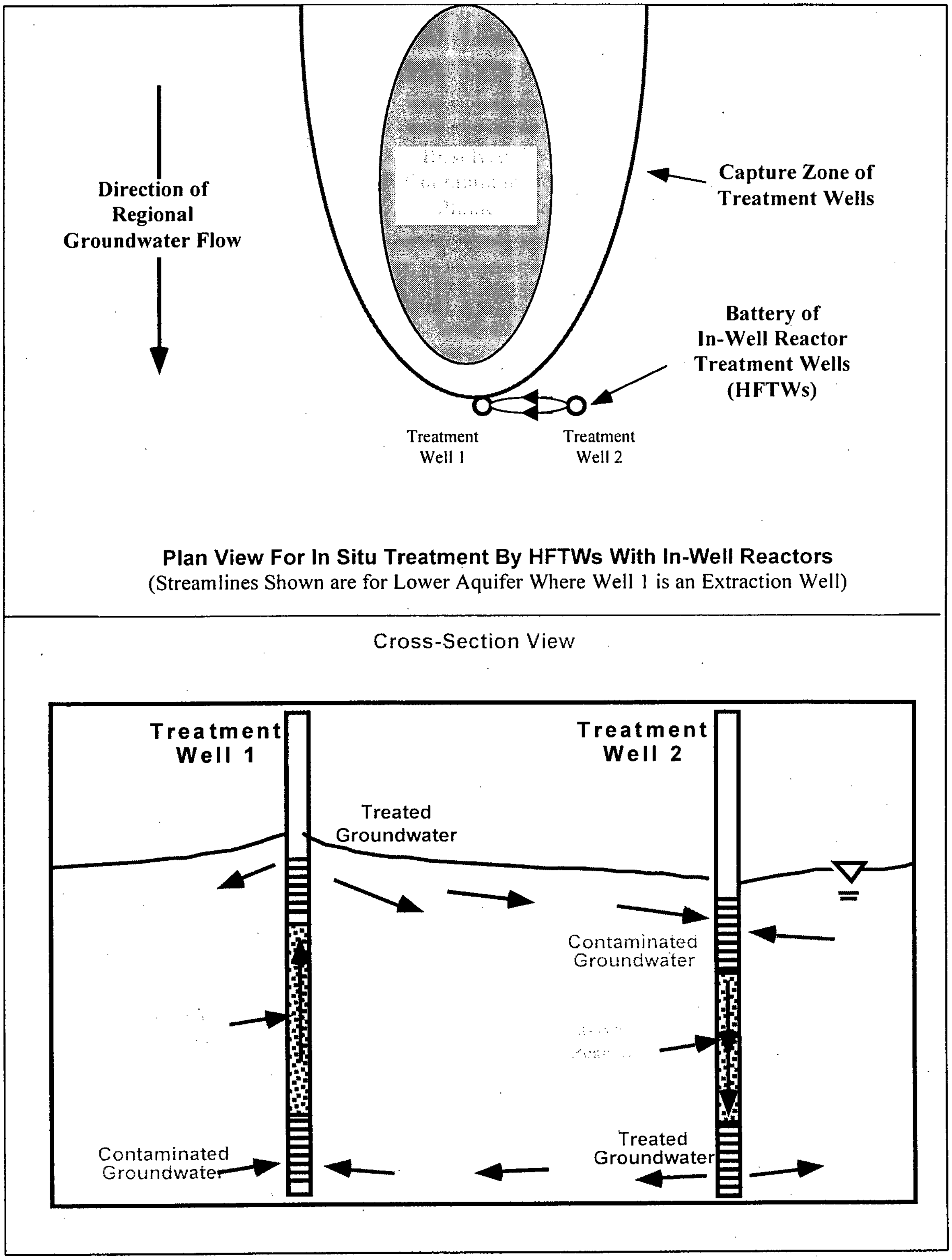


Figure 1.1: Schematic of Horizontal Flow Treatment Well (HTFW) System With In-Well Reactors

1.2 RESEARCH OBJECTIVES

1. Develop a model that combines Christ's (1997) hydraulic model of the HFTW system with first-order dechlorination kinetics of various metals to be used as in-well reactors.
2. Determine which metals can be used in an in-well system, what dechlorination rates can be expected, how long metals can be expected to last, and how groundwater geochemistry will affect system performance.
3. Using the model, determine expected performance for an *in situ* treatment system under typical conditions at a contaminated site.
4. Using the model, explore how an *in situ* catalytic treatment system can be applied under varying hydrogeochemical conditions.

1.3 DEFINITION OF TERMS

The following terminology will be used in the thesis:

Abiotic: Referring to processes that occur in the absence of living organisms.

Chlorinated Ethenes: The family of chlorinated organic contaminants including tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC).

Horizontal Flow Treatment Well (HFTW) System: A series of two or more dual-screened wells used to capture and treat contaminated groundwater.

Hydrogenolysis: See also: Reductive Dehalogenation.

<u>*In situ* Treatment System</u>: *In situ* is Latin for “in its original place. *In situ* treatment systems degrade contaminants without bringing them to the surface (Christ, 1997).

<u>Interflow</u>: The amount of water recirculated between injection and extraction wells in an HFTW system (Christ, 1997).

<u>Overall Treatment Efficiency</u>: Amount of contaminant removed by a series of treatment wells, comparing contaminant concentration upgradient and downgradient of an HFTW system.

<u>Pseudo-First-Order Kinetics</u>: Contaminant degradation that depends on both contaminant concentration and the amount of metallic reductant but can be modeled using first-order kinetics (Johnson and others, 1996).

<u>Reductive Beta-elimination</u>: Removal of two chloride ions from a chlorinated compound in a single step (Roberts and others, 1996).

<u>Reductive Dehalogenation</u>: Removal of a single chloride ion from a chlorinated compound (Matheson and Tratnyek, 1994).

<u>Single-Pass Treatment Efficiency</u>: Amount of contaminant removed by a catalytic/reductant treatment well, comparing the contaminant concentration before and after the well.

<u>Sonication</u>: Use of ultrasound to degrade halogenated hydrocarbons (Suslick, 1990).

2.0 LITERATURE REVIEW

2.1 OVERVIEW

This chapter reviews literature relevant to the formulation of a model combining horizontal flow treatment wells and in-well treatment technologies in order to degrade dissolved chlorinated contaminant-containing groundwater. The first section of the chapter reviews the different in-well treatment technologies and the second section provides a description of the groundwater flow model that is used in this thesis effort.

2.2 ZERO-VALENT IRON

The concept of using zero-valent iron to degrade chlorinated pesticides was patented in 1972 (Gillham and O'Hannesin, 1994; Wilson, 1995). However, the potential for zero-valent iron to degrade chlorinated organic (aliphatic) compounds dissolved in groundwater did not become apparent until the mid-1980's, when researchers discovered the process almost by accident (Wilson, 1995). Since that time, much research has been devoted to developing remediation technologies that use zero-valent iron (in the commonly available form of industrial scrap iron filings) that will degrade chlorinated compounds *in situ* (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Agrawal and Tratnyek, 1996; Orth and Gillham, 1996; Roberts and others, 1996). Research on this technology has focused on the reaction mechanism and kinetics for various contaminants, and the effect of biogeochemistry. Increased understanding of these factors will serve to enhance the efficacy of zero-valent iron technologies to remediate chlorinated aliphatic compounds.

2.2.1 Zero-Valent Iron Reaction Mechanisms

Matheson and Tratnyek (1994) suggested three primary reaction mechanisms for reductive dehalogenation of chlorinated methane compounds by zero-valent iron. They are zero-valent iron corrosion, ferrous iron oxidation, and reduction caused by hydrogen produced by corrosion with water (Matheson and Tratnyek, 1994). The investigators concluded that reductive dehalogenation by zero-valent iron corrosion (i.e. hydrogenolysis) was the predominant pathway for chlorinated methane degradation (Matheson and Tratnyek, 1994). Based on their findings, it was largely assumed that chlorinated ethene degradation using zero-valent iron was also due to hydrogenolysis. Hydrogenolysis by zero-valent iron is shown in the following equation.

$$Fe^0 + RX + H^+ \rightarrow Fe^{2+} + RH + X^- \qquad (1)$$

RX = alkyl halide
RH = hydrodehalogenated product
X^- = halide ion

The hydrogen ions in equation (1) are produced by the dissociation of water. For a chlorinated methane compound such as carbon tetrachloride, a single chloride ion is stripped away at each step. Eventually, hydrogenolysis removes all of the chlorines as chloride ions until methane, a harmless compound, is ultimately produced.

However, Roberts and others (1996) have suggested that although hydrogenolysis degrades chlorinated methanes, it is not the dominant reaction mechanism for chlorinated ethenes. They found that reductive β-elimination is just as energetically favorable as hydrogenolysis for chlorinated ethenes. The mechanism of reductive β-elimination is differentiated from hydrogenolysis because two halide ions are released in a single step instead of one (Roberts and others, 1996). Figure 2.1 shows the potential pathways and intermediates of the hydrogenolysis and reductive β-elimination pathways (Arnold and Roberts, 2000).

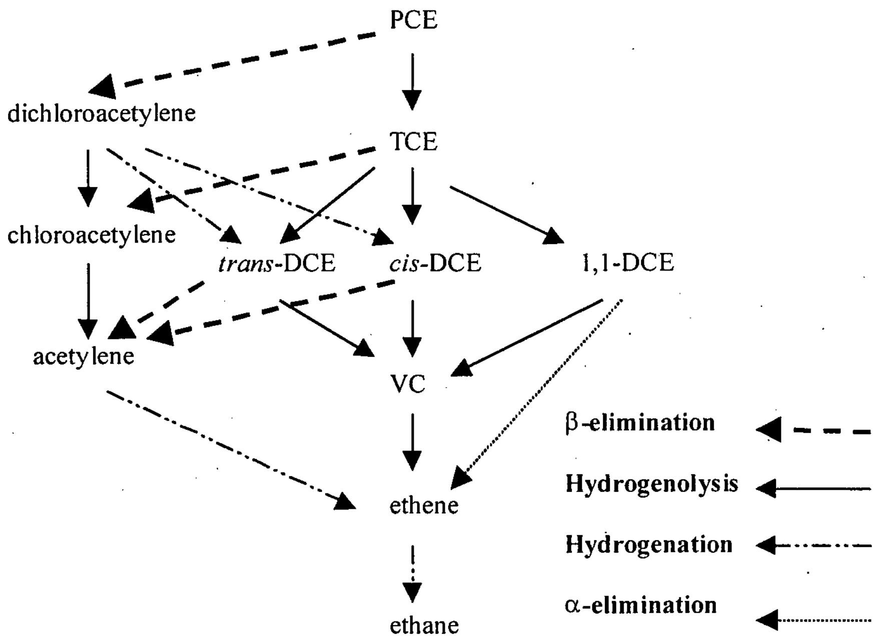


Figure 2.1: Hydrogenolysis and Reductive β-Elimination Pathways

Hydrogenolysis and reductive β-elimination operate by transferring electrons from the surface of the iron directly to the chlorinated compound (Matheson and Tratnyek, 1994; Roberts and others, 1996). For this to occur it is required that (1) chlorinated compounds sorb to reactive sites on the iron particles, and (2) the chlorinated compounds are soluble in water and can be transported to the reaction sites (Weber, 1996). Burris and others (1995) investigated sorption of PCE and TCE to zero-valent iron. They concluded that the majority of sorption by PCE and TCE was to non-reactive sites on the zero-valent iron. The PCE and TCE molecules that did sorb to reactive sites experienced first-order degradation (Burris and others, 1995). Transport to these sites may be modeled as a five-step process. The steps are: (1) mass transport of contaminant from bulk solution to the iron surface, (2) adsorption onto the iron surface, (3) chemical reaction at the site, (4) desorption from the reaction site, and (5) mass transport of the reaction products to the bulk solution (Matheson and Tratnyek, 1994)

2.2.2 Zero-Valent Iron Reaction Kinetics

The degradation of chlorinated compounds by zero-valent iron may be modeled as a pseudo first-order reaction (Johnson and others, 1996; Orth and Gillham, 1996). New research has suggested that at TCE concentrations greater than 2.6 mg/L, a pseudo zero-order rate expression may be appropriate (Wüst and others, 1999). In this work, we will assume pseudo first-order kinetics. A pseudo first-order reaction is defined by the following mathematical expression (Clark, 1996):

$$\frac{dC}{dt} = -k'C \qquad \text{where } k' = k[\text{concentration of iron}] \tag{2}$$

and the concentration of iron is assumed constant.

Integration of equation (2) yields

$$\frac{C(t)}{C_0} = e^{-k't} \tag{3}$$

The pseudo first-order rate constant, k′, is dependent on the concentration of iron (as shown in equation (2)). For simplicity, k′ will be referred to as k from this point onward. Rate constants have been found to increase with increasing surface area of the iron (O'Hannesin and Gillham, 1998). In order to allow meaningful comparisons, most k values are normalized to the surface area of iron. Degradation pathways are also crucial when considering reaction kinetics because each step in the pathway contributes to the overall rate constant. The primary degradation pathway for chlorinated ethenes via zero-valent iron is reductive β-elimination (Roberts and others, 1996; Campbell and others, 1997). In fact, new research has shown that for the chlorinated ethenes, the percentage following the reductive β-elimination pathway is 87% for PCE, 97% for TCE, 94% for *cis*-DCE, and 99% for *trans*-DCE (Arnold and Roberts, 2000). Therefore, only a small percentage of chlorinated ethenes experience sequential dehalogenation strictly via hydrogenolysis (Matheson and Tratnyek, 1994). Figure 2.2 depicts the reaction mechanisms for degradation of chlorinated ethenes by zero-valent iron (Arnold and Roberts, 2000).

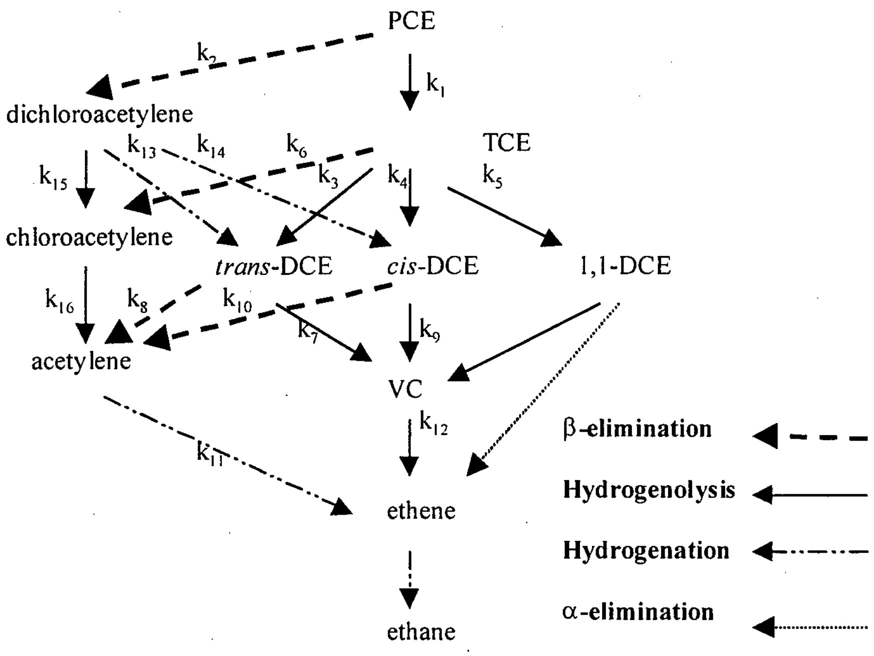


Figure 2.2: Hydrogenolysis and Reductive β-Elimination Pathway with Rate Constants

Other data concerning degradation kinetics for chlorinated ethenes by zero-valent iron have been published. These data assume hydrogenolysis is the primary mechanism of dehalogenation (Matheson and Tratnyek, 1994; Johnson and others, 1996; Tratnyek and others, 1997; O'Hannesin and Gillham, 1998). However, these data simply report the rate of contaminant disappearance, and do not measure daughter product formation. Therefore, one cannot determine if the contaminant is degraded or merely sorbed to an inactive iron site. Table 2.1 summarizes normalized half-lives determined in several recent studies. Table 2.1 shows that half-lives from field experiments are usually at least an order of magnitude longer than half-lives determined in the laboratory. Laboratory experiments are conducted under carefully controlled conditions that allow for complete mixing of the contaminants and the zero-valent iron. Field experiments are susceptible to variations in site hydrology that can inhibit mixing, and naturally occurring compounds in the groundwater can interfere with the dehalogenation reaction. These interactions result in longer observed half-lives for field experiments.

New research being reported in the literature is beginning to question the importance of sorption to non-reactive sites. Wüst and others (1999) recently found that sorption to non-reactive sites was not important in their experiments. This contradicts the findings of Burris and others (1995) and is an on-going subject of study. The uncertainty as to the importance of sorption to non-reactive sites should be considered when applying the half-lives in Table 2.1 to model dehalogenation kinetics.

Compound	Laboratory vs. Field Disappearance Half-Lives (hr) Normalized to 1 m^2/mL iron surface area
PCE	.33[1] vs. 193[2]
TCE	1.78[1] and 7.79 – 18.7[3] vs. 109[2]
1,1-DCE	10.8[1] vs. 103[2]
cis-DCE	16.9[1] vs. 80[2]
trans-DCE	5.78[1] vs. 170[2]
VC	13.9[1] (No Field Data)

[1] Johnson and others, 1996; Tratnyek and others, 1997

[2] O'Hannesin and Gillham, 1998

[3] Wüst and others, 1999

Table 2.1 Disappearance Half-Lives for Chlorinated Ethenes by Zero-Valent Iron

The recent debate about whether sorption occurs to reactive or non-reactive sites on the zero-valent iron does not diminish the important role sorption plays in the degradation process. This is because contaminants generally remain sorbed to the iron particles until the reaction is complete for both hydrogenolysis (Orth and Gillham, 1996) and reductive β-elimination (Campbell, 1997). Complete degradation of chlorinated ethenes to a harmless product (i.e. ethene) is important because the intermediate products of PCE produced during hydrogenolysis increase in toxicity (Masters, 1997) and persistence (Domenico and Schwartz, 1998). The intermediate products formed from the reductive β-elimination pathway are chloroacetylenes, which are known to be toxic (Campbell, 1997). Fortunately, the chloroacetylenes continue to degrade to acetylene, ethene, and ethane. Toxic intermediate production ranges from 2 percent of the original PCE/TCE concentration (1999; Farrel and others, 2000) to 3.5 percent (Orth and Gillham, 1996).

2.2.3 Biogeochemical Considerations

Some studies showed that zero-valent iron remediation technologies generally exhibit declining performance over time (McMahon and others, 1999; Liang and others, 1997a). However, other results from long-term field testing shows that zero-valent iron remediation technologies can last for an extended period time without experiencing significant reductions in performance (O'Hannesin and Gillham, 1998; Reeter and others, 1998). It appears the long-term effectiveness of zero-valent iron varies due to different biogeochemical properties within each contaminated aquifer. Three main problems that may result from biogeochemistry include (1) excessive mineral precipitation caused by increasing pH, (2) decreased hydraulic conductivity resulting from precipitation and/or growth of microbial populations, and (3) gradual consumption of iron due to excessive corrosion (McMahon and others, 1999; O'Hannesin and Gillham, 1998).

Laboratory column studies have been conducted in an attempt to predict biogeochemical interactions for zero-valent iron treatment systems. Early laboratory work focused on investigating the zero-valent iron dehalogenation mechanism and reaction kinetics (Matheson and Tratnyek, 1994; Gillham and O'Hannesin, 1994; Roberts and others, 1996; Orth and Gillham, 1996; Weber, 1996; Campbell and others, 1997). The only biogeochemical influence considered in early research was pH (Matheson and Tratnyek, 1994). Low pH would greatly increase corrosion rates (thereby consuming the iron) and high pH would cause mineral precipitation (resulting in clogged pore spaces) (Matheson and Tratnyek, 1994). Subsequent field studies have shown that pH generally increases in the reactive zone and then decreases to normal levels. Sass and others reported a near-neutral pH upgradient and downgradient of the treatment system, and a pH ranging from 10 to 11 within the reactive zone of the treatment system (Sass and others, 1998). Another laboratory column study reported pore clogging due to cementation of the zero-valent iron media (Liang and others, 1997a). The consumption of zero-valent iron over time due to precipitation reduced TCE degradation efficiency and created hydraulic conductivity heterogeneities within the columns (Liang and others, 1997a). A new study by Farrell and others (2000) reported declining performance of TCE degradation by zero-valent iron columns over a two-year period. However, they did not observe any cementation of the reactive media and did not experience problems with hydraulic conductivity within the columns (Farrell and others, 2000).

The focus of recent laboratory studies has been to determine which *in situ* biogeochemical interactions are detrimental to potential groundwater remediation systems. This is because mineral precipitation and microbial fouling have plagued some projects; while other field tests have operated without any problems (Gu and others, 1999). A laboratory study by Gu and others (1999) indicated significant mineral precipitation was likely in water with elevated levels of bicarbonate (i.e. alkalinity) and sulfate. Another likely development in water with high bicarbonate levels was enhanced hydrogen gas production due to carbonate-induced corrosion of the iron metal. Excessive hydrogen gas can lead to the growth of substantial sulfate-reducing microbial populations (Gu and others, 1999), which have the potential to foul treatment systems. The laboratory study concluded that total porosity of an iron treatment system could be reduced by approximately 16 percent due to high concentrations of bicarbonate and sulfate (Gu and others, 1999). The study by Farrell and others (2000) included several columns to simulate groundwater containing nitrate, chloride, and sulfate. The TCE degradation half-life for the chloride- and sulfate-containing waters increased from 400 minutes (after 10 days) to 2500 minutes (after 667 days) (Farrell and others, 2000). Nitrate was found to have a more pronounced effect on TCE degradation because the half-life increased from 1500 minutes (after 10 days) to 3500 minutes (after 667 days) (Farrell and others, 2000).

Long-term field studies of zero-valent iron remediation technologies provide valuable data that cannot be accurately recreated within a laboratory environment. Because contaminated aquifers have biogeochemical properties specific to their location, multiple field tests are needed to demonstrate when the technology will work and when it will not work. Fortunately, there are several published articles on long-term funnel-and-gate treatment systems that use zero-valent iron gates (McMahon and others, 1999; O'Hannesin and Gillham, 1998; Reeter and others, 1998). As mentioned earlier in this section, a wide range of long-term effectiveness was found in these studies. The relationship between biogeochemistry and zero-valent iron treatment efficiency has not been thoroughly explored. Therefore, it is difficult to predict when groundwater biogeochemistry will have a negative impact on treatment system performance. Table 2.2 summarizes some of the inorganic parameters of concern from two different field applications of a zero-valent iron wall, along with a laboratory study. The field sites did not experience any observable decline in performance due to inorganic precipitation; whereas significant precipitation was observed during the laboratory study. In the laboratory study, iron oxyhydroxide, carbonates, and sulfides precipitated (Gu and others, 1999).

Biogeochemical Parameter	Moffett Field[1]	Borden, Ontario[2]	Laboratory[3]
Alkalinity (HCO_3^-)	131-191	158-170	1037-2013
Calcium	134-177	55-278	0
Magnesium	64-73	3-4	0
Sulfate	264-362	609	672-1920

NOTE: Values given in mg/L

[1] Sass and others, 1998; Reeter and others, 1998, Reeter and others, 1999

[2] O'Hannesin and Gillham, 1998

[3] Gu and others, 1999

Table 2.2 Common Biogeochemical Parameters Found in Chlorinated Ethene-Contaminated Aquifers

Additional studies have focused on potential microbial and inorganic precipitation within the reactive zones of funnel-and-gate systems (Vogan and others, 1998; Sass and others, 1998). The study performed by Vogan and others concluded that problems caused by mineral precipitation were minimal and that the systems would operate effectively for years before requiring maintenance (Vogan and others, 1998). Their total carbonate solids concentration obtained from core samples was only 5.6% $CaCO_3$ (Vogan and others, 1998). The results of the study performed by Sass and others also showed little or no effect on system performance due to mineral precipitation (Sass and others, 1998). Both studies did not find significant microbial growth within the reactive zones. It was surmised that microbial growth was inhibited by the elevated pH resulting from reductive dehalogenation (Vogan and others, 1998; Sass and others, 1998).

Based on the literature cited previously, it appears likely that funnel-and-gate treatment systems will operate effectively for years with little or no maintenance. The primary potential problems of mineral precipitation and microbial fouling have not been shown to be significant (O'Hannesin and Gillham, 1998; Reeter and others, 1998, Sass and others, 1998, Vogan and others, 1998). However, there are occasions when bicarbonate and sulfate levels in laboratory test samples can lead to increased mineral precipitation (Gu and others, 1999). If these biogeochemical conditions persist, hydraulic conductivity within the treatment system will be reduced which will also reduce system efficiency. Based on the range of values in Table 2.2, finding the precise point at which biogeochemistry will become a problem is an interest item for future research.

2.2.4 Zero-Valent Iron Limitations

Based on the prior discussion in this section, it is likely that zero-valent iron would not be an appropriate material for use in an HFTW system as described in Chapter 1. The in-well reactors shown in Figure 1.1 require a diameter less than the well in which they are placed. Therefore, contaminated water that is pumped through the in-well reactors has a residence time of less than an hour (depending on the pump rate and reactor volume) compared to a funnel-and-gate treatment system consisting of a wide trench that has a residence time of several days. Another complicating factor is the possibility that columns containing zero-valent iron are prone to clogging as reported by Liang and others (1997a). The normalized field half-lives reported for zero-valent iron (from Table 2.1) are too long for application in an HFTW system. There are claims that with newer commercially available zero-valent iron, normalized half-lives for field applications ranging from 1.1-4.6 hours for TCE and 2.1-10.8 hours for PCE are possible (O'Hannesin and Gillham, 1998). However, even iron capable of achieving these more optimistic values is not adequate for application in an in-well reactor whose residence time is less than an hour. The half-lives reported by O'Hannesin and Gillham in Table 2.1 have been corroborated by other studies, most recently by Arnold and Roberts (2000), thus reaffirming our supposition that zero-valent iron is an unsuitable material for an HFTW system. Materials other than zero-valent iron that have faster degradation kinetics will be required for use in an in-well reactor.

The life expectancy of the zero-valent iron is another uncertainty in a funnel-and-gate system. As discussed above, various biogeochemical parameters such as pH and inorganic minerals in the contaminated aquifer can either accelerate corrosion and consume the iron prematurely (Matheson and Tratnyek, 1994) or cause mineral precipitation and clog pore spaces (Liang and others, 1997a; Gu and others, 1999). These problems for funnel-and-gate treatment systems will be exacerbated in an HFTW treatment system due to the restricted size of the in-well reactors.

2.3 PALLADIUM

Although zero-valent iron-based groundwater remediation treatment systems have shown considerable promise for passive treatment in walls and funnel-and-gate systems, their application in an HFTW treatment system appears not to be feasible due to the relatively slow reaction rates. Therefore, additional research has focused on finding other materials that will achieve substantial dechlorination in a short amount of time. The investigation of palladium-based catalysts as a tool to degrade chlorinated compounds is attracting considerable attention in the research community (Schreier and Reinhard, 1995; McNab and Ruiz, 1998; Lowry and others, 1998; Lowry and Reinhard, 1999; Lowry and Reinhard, 2000). Much like the case of zero-valent iron, research on this technology has focused on the reaction mechanism and kinetics for various contaminants, and the effect of biogeochemistry.

2.3.1 Reaction Mechanism with Palladium

Section 2.2.1 discussed Matheson and Tratnyek's conclusion that hydrogenolysis (Figure 2.1) was the dominant reaction mechanism for zero-valent iron degradation of chlorinated methanes. One of the reaction mechanisms they discarded as insignificant relative to hydrogenolysis utilizes the hydrogen produced by the anaerobic corrosion of iron by water and is shown in equation (4) (Matheson and Tratnyek, 1994).

$$H_2 + RX \rightarrow RH + H^+ + X^- \qquad (4)$$

Hydrogen itself is not an effective reductant, but in the presence of certain catalysts, equation (4) can achieve substantial dehalogenation of chlorinated compounds. Zero-valent iron is not an effective catalyst for this type of reaction mechanism; however, palladium is extremely effective. A key difference between zero-valent iron and palladium is that corrosion of zero-valent iron produces the hydrogen gas required in equation (4). In a palladium-catalyst system, no hydrogen is produced by corrosion so the hydrogen gas must be introduced separately. McNab and others (2000) have summarized the reaction mechanism for the palladium catalyst system:

$$\mathrm{TCE} + 4\mathrm{H_2} \xrightarrow{(\mathrm{Pd})} \text{ethane} + 3\mathrm{HCl} \tag{5}$$

Research has shown that TCE is completely dechlorinated to ethane at the surface of the catalyst (Lowry and Reinhard, 1999). This is significant, because it does not allow for the formation and accumulation of toxic intermediate products. Lowry and Reinhard (1999) also concluded that palladium supported on alumina was more effective than pure palladium powder. The palladium-alumina combination has also been shown to achieve significant rates of dechlorination in other research (Schreier and Reinhard, 1995; McNab and Ruiz, 1998).

2.3.2 Palladium Reaction Kinetics

The reaction for degradation of chlorinated compounds by palladium-alumina catalysts is reported as pseudo-first order (Schreier and Reinhard, 1995; McNab and Ruiz, 1998; Lowry and Reinhard, 1999). Degradation rate constants do not appear to be dependent on available metal surface area (as in zero-valent iron systems); however, they do depend on catalyst concentration (Lowry and Reinhard, 1999). The concentration of hydrogen gas and its impact on reaction rate has not been fully investigated, but it appears not to affect the reaction rate (Lowry and Reinhard, 1999). However, the reaction will not occur without any hydrogen present. On alumina-supported media, the weight of palladium relative to the alumina support used in laboratory experiments has been .5% (Schreier and Reinhard, 1995) or 1% (McNab and Ruiz, 1998; Lowry and Reinhard, 1999; McNab and others, 2000). The degradation pathway depicted in Figure 2.3 (Lowry and Reinhard, 1999) shows the direct transformation of the chlorinated-ethene compounds to ethane.

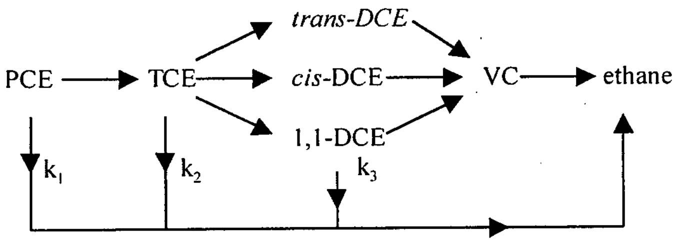


Figure 2.3: Palladium-Based Catalytic Degradation Pathways for Chlorinated Ethenes

Pseudo-first order reaction constants obtained from the published literature are tabulated in Table 2.3. Note that the laboratory column degradation rates are faster than the laboratory batch degradation rates. This is likely due to the fact that higher concentrations of catalyst were available in the column study than in the batch study, though, unfortunately, catalyst concentrations for the laboratory column study were not reported (McNab and Ruiz, 1998). The laboratory versus field half-life data (comparing a laboratory column with a field test column) in Table 2.3 show that a carefully controlled laboratory environment (McNab and Ruiz, 1998) yields results that are comparable to field results (McNab and others, 2000). This is not surprising, as the field application involves use of a reactor similar to a laboratory column.

Step	Laboratory k values (min^{-1}) (batch vs. column)	Laboratory vs. Field half-lives (min) (column vs. column)
k_1	.1175[1] to ≥ 1.2[2]	.578[2] vs. .414[3]
k_2	.1414[1] to 1.26 ± .005[2]	.550[2] vs. .510[3]
k_3	.154 -.1824[1] to 1.14 ± .002[2]	.608[2] vs. .581[3]

[1] Lowry and Reinhard, 1999 (using .22 grams Pd/L)
[2] McNab and Ruiz, 1998 (catalyst concentration not available)
[3] McNab and others, 2000 (using 300 grams Pd/19 L)

Table 2.3 Pseudo-First Order Reaction Constants and Half-Lives for Dehalogenation of Chlorinated Ethenes Using Palladium-Alumina Catalyst

Although a degradation rate for vinyl chloride using a palladium-alumina catalyst has not been measured quantitatively, the degradation has been reported to be significant (Schrier and Reinhard, 1995; McNab and others, 2000). Comparing the half-lives for palladium-alumina catalysts, which are on the order of fractions of a minute (Table 2.3), versus zero-valent iron which are on the order of tens of hours (Table 2.1), reveals great promise for the application of palladium-based catalyst groundwater remediation systems.

2.3.3 Biogeochemical Considerations

While the relatively rapid pseudo-first order rate constants for palladium-based catalysts show the potential of these systems, additional research is needed prior to their application in full-scale remediation. One area that must be fully investigated is the potentially detrimental impact of biogeochemistry on catalyst reactivity. Many compounds and ions commonly found in groundwater environments can poison the catalyst which effectively halts the dechlorination process unless the catalyst is regenerated. Schreier and Reinhard (1995) found that 2mM sodium bisulfide added to 100mM bicarbonate solution with .055 μmoles palladium completely poisoned the palladium catalyst, while 11 μmoles of nitrite, nitrate, and sulfate reduced the degradation rate of PCE. McNab and Ruiz (1998) also reported catalyst deactivation and noted that it appeared to be related to high concentrations of bicarbonate. They were able to regenerate the catalyst by shutting off the hydrogen source periodically. Munakata and others (1998) investigated the catalyst deactivation caused by nitrate, phosphate, carbonate, and carbon dioxide. Nitrate, carbonate, and carbon dioxide produced significant deactivation, and although phosphate produced decreased degradation rates initially, the negative effect of phosphate stabilized after two days, and the reduced dechlorination reaction continued at the decreased rates without an additional decline in performance (Munakata and others, 1998). Lowry and Reinhard (2000) examined palladium catalyst performance in the presence of several inorganic species. Carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), carbonate (CO_3^-), sulfate (SO_4^{-2}), and chloride (Cl^-) did not poison the catalyst material (Lowry and Reinhard, 2000). These findings seem to contradict earlier findings reported by McNab and Ruiz (1998) and Munakata and others (1998) that the presence of carbonate species leads to catalyst deactivation. Lowry and Reinhard also found that 87 mg/L sulfite (SO_3^{-2}) or .4 mg/L hydrogen sulfide (HS^-) rapidly reduced catalyst performance (Lowry and Reinhard, 2000). The presence of dissolved oxygen also reduces the reaction rate slightly (Schreier and Reinhard, 1995; McNab and Ruiz, 1998; McNab and others, 2000).

The deactivation phenomenon is not yet fully understood and is currently being studied. Long-term field studies of palladium catalyst remediation systems are not available as they are for zero-valent iron systems. Therefore, it is too early to tell if the compounds and ionic species mentioned previously that are commonly found in groundwater will critically affect a palladium catalyst remediation system. Lowry and Reinhard (2000) monitored catalyst degradation performance over 60 days using groundwater samples from Moffett Field. They found that HS^- production continuously poisoned the catalyst and hampered system performance; however, systematic pulsing of sodium hypochlorite completely regenerated catalyst activity and overcame the deleterious effects of HS^-. Additional research is needed to determine if this technique is effective at maintaining catalyst activity for the entire suite of biogeochemical parameters found in natural aquifer systems.

2.4 PALLADIZED IRON

Palladized iron is another material that has been studied in the laboratory and has demonstrated chlorinated ethene degradation rates that may be fast enough for in-well use (Muftikian and others, 1995; Liang and others, 1997a; Liang and others, 1997b).

2.4.1 Reaction Mechanism with Palladized Iron

Palladized iron-based degradation of chlorinated ethenes is a hybrid of the zero-valent iron and palladium mechanisms previously discussed in this chapter. In section 2.3.1, it was mentioned that hydrogen in a palladium catalyst-based system must be introduced separately. For palladized iron, this is not necessary because the iron that is coated with palladium is corroded by water and the corrosion process produces hydrogen ions (Muftikian and others, 1995). The free hydrogen ions bond to form hydrogen gas, and the palladized iron system operates according to equation (4) in section 2.3.1.

2.4.2 Palladized Iron Reaction Kinetics

Degradation rate constants are dependent on the surface area of the palladium that is coated on the iron as well as the iron (Muftikian and others, 1995). This dependency is similar to the zero-valent iron system, which was also heavily dependent on surface area. Early laboratory batch experimentation showed that palladized iron (.05% palladium on iron metal) degraded TCE significantly faster than zero-valent iron alone (Muftikian and others, 1995). Their studies did not explore the mechanism or quanitfy the kinetics, but it did compare TCE degradation due to palladized iron versus zero-valent iron. Additional research quantified the kinetics and substantiated the early conclusions that palladized iron degraded TCE faster than iron alone. Liang and others (1997b) published a half-life for TCE degradation by zero-valent iron of 7.41 hours, but the half-life for a palladized iron system under similar conditions was only .59 hours (Liang and others, 1997b). No DCE isomers were detected in the palladized iron system and the long-term concentration of vinyl chloride was an order of magnitude lower than the zero-valent iron system (Liang and others, 1997b).

2.4.3 Biogeochemical Considerations

Palladized iron has not received as much attention as either zero-valent iron or palladium catalyst-based remediation systems. Therefore, there has been very little information provided regarding potential biogeochemical interference or long-term performance data. Because the palladized iron reaction mechanism is a combination of the zero-valent iron and palladium catalyst systems, it can be surmised that palladized iron systems could be subject to similar performance detractors. Sulfide and bicarbonate were discussed in section 2.3.3 as primary species that can poison a palladium catalyst system so they might be detrimental to palladized iron as well. Liang and others (1997a) reported long-term performance of palladized iron filings in their column study deteriorated due to sulfide poisoning caused by sulfate-reducing bacteria. Other than the Liang and others (1997a) study, very little established in the literature.

Long-term performance has yet to be verified by field studies. The Liang and others (1997a) bench-scale column test was conducted for 23 days. As mentioned earlier, their palladized iron column's performance deteriorated due to sulfide poisoning of the palladium (Liang and others, 1997a). This was attributed to the high levels of sulfate in the groundwater, which spawned a population of sulfate-reducing bacteria (Liang and others, 1997a). The bacteria did not clog the pore spaces, but they did reduce the sulfate to sulfide. As a result, the rapid dechlorination rates observed in the short-term (which were much faster than zero-valent iron rates) declined over time and the palladized iron was not as effective over the long-term (Liang and others, 1997a).

2.5 OTHER METALLIC REDUCTANTS

Other metals besides zero-valent iron, palladium, and palladized iron have been studied for their potential to degrade chlorinated ethenes. Zero-valent zinc (Arnold and Roberts, 1998), zero-valent tin (Su and Puls, 1999), a combination of zero-valent iron and zero-valent tin (Su and Puls, 1999), copper-plated iron (Fennelly and Roberts, 1998), and nickel-plated iron (Fennelly and Roberts, 1998; Appleton, 1996) have all been studied.

The reaction mechanisms for these other materials are similar to the parallel β-elimination/hydrogenolysis mechanisms discussed in section 2.2.2. Some of these materials offer faster degradation kinetics of chlorinated contaminants than zero-valent iron, but they are usually still much slower than the degradation kinetics of palladium catalysts. Table 2.4 summarizes kinetic data for degradation of 1,1,1-TCA by various metallic reductants (Fennelly and Roberts, 1998).

Material	Laboratory Half-Lives (hr) Normalized to $1 mL/m^2$ iron surface area
Fe(0)	1.51
Zn(0)	.0693
Nickel-iron	.392
Copper-iron	.537
[1] Fennelly and Roberts, 1998	

Table 2.4 Disappearance Half-Lives for 1,1,1-TCA by Zero-Valent Metals and Bimetallic Reductants

Arnold and Roberts (1998) have investigated chlorinated ethene degradation by zero-valent zinc. The reaction mechanisms follow Figure 2.2, and the normalized half-life data for zero-valent zinc are shown in Table 2.5 (Arnold and Roberts, 1998).

Step	Half-Lives (hr)[1] Normalized to 1mL/m^2 zinc surface area
k_1	2.31
k_2	15.4
k_3	462
k_4	1155
k_5	10,191
k_6	737
k_7	1,082,813
k_8	53,308
k_9	1,332,692
k_{10}	231,000
k_{11}	1386
k_{12}	6930
k_{13}	.0336
k_{14}	Not reported
k_{15}	.158
k_{16}	.107

[1] Parameter values PCE 5g Zn (0)/125 mL buffer solution; other chlorinated ethenes, acetylene, and ethene used 25 g Zn(0)/125 mL buffer solution; and chlorinated acetylenes used .5 g Zn(0)/125 mL buffer solution

Table 2.5 Half-Lives for Dehalogenation of Chlorinated Ethenes by Zero-Valent Zinc (Arnold and Roberts, 1998)

Reductive β-elimination accounts for 15% of PCE degradation, 30% of the TCE, 85% of the *cis*-DCE, and 95% of the *trans*-DCE degradation (Arnold and Roberts, 1998).

Zero-valent iron plated with nickel has been reported to be ten times faster than zero-valent iron systems (Appleton, 1996). Initial laboratory testing of nickel-iron degradation kinetics of the chlorinated ethene family has revealed half-lives of about 5-10 minutes (O'Hannesin, 1999). These half-lives would seem to rival palladium catalyst systems in terms of kinetic performance; however, they have yet to be substantiated in the literature.

Degradation of TCE by zero-valent iron, zero-valent tin, and a combination of both was investigated by Su and Puls (1999). The reaction mechanisms are the same as the zero-valent iron mechanism presented in Figure 2.2. The normalized half-life data for this study are presented in Table 2.6 (Su and Puls, 1999).

Material	Laboratory Half-Lives (hr)[1] Normalized to 1mL/m^2 iron surface area
Fe(0)	.64
Sn(0)	5.67
Fe(0) and Sn(0)	2.25
[1] For Fisher Fe(0) and Sn(0) (15 g/50 mL) at 25 degrees C	

Table 2.6 Disappearance Half-Lives for TCE by Zero-Valent Iron, Tin, and a 1:1 Combination of Iron and Tin

2.6 SONICATION

The use of ultrasound to degrade halogenated hydrocarbons is a relatively new area of research (Suslick, 1990; Hua and Hoffman, 1996). The chemistry of ultrasound, sonochemistry, deals with the transfer of sound energy through a process called acoustic cavitation (Suslick, 1990). Acoustic cavitation has three stages: formation, growth, and collapse of bubbles (Suslick, 1990). These bubbles are created from sound waves, and the energy generated when they collapse can be harnessed to dehalogenate certain chlorinated compounds. Sonication can also be used in heterogeneous solutions (i.e. containing both liquids and solids) to degrade chlorinated contaminants because of its impact on the solid surface. Sonication of powdered zinc and nickel catalysts has been shown to increase catalyst activity by a factor of 10^5 for nickel (Suslick and Casadonte, 1987) and by a factor of 50 for zinc (Suslick and Doktycz, 1989). The catalysts (which are the solid in the liquid-solid heterogeneous solution) increase in activity because acoustic cavitation (due to collapsing bubbles) creates localized erosion (resulting in increased reactivity) (Suslick and Casadonte, 1987). Sonication is also beneficial because it improves contaminant mass transport to the catalyst surface and removes oxide layers from the catalyst surface (Suslick and Casadonte, 1987; Suslick and Doktycz, 1989).

Experimental studies have shown that sonochemistry by itself can effectively destroy different types of chlorinated compounds (Cheung and others, 1991; Bhatnagar and Cheung, 1994). The degradation rate constant was reported as first-order, and the half-lives for PCE and TCE destruction are reported below (Bhatnagar and Cheung, 1994):

Contaminant	Laboratory half-life values (hr)
PCE	.44
TCE	.55

Table 2.7 Half-Lives for Dehalogenation of PCE and TCE by Sonication

The mechanism for the first-order degradation by sonication alone is due to acoustic cavitation as explained previously (Bhatnagar and Cheung, 1994).

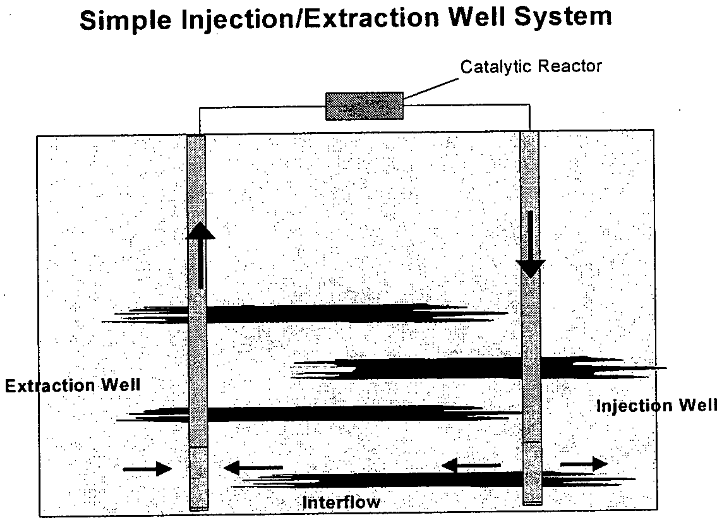
Sonication in conjunction with zero-valent iron has been shown to enhance the degradation of chlorinated compounds in four ways. First, acoustic cavitation acts directly on the compounds (such as PCE and TCE as shown in Table 2.7); and second, the shockwaves produced by acoustic cavitation cleanse the surface of the zero-valent iron and prolong its reactivity (Hung and Hoffman, 1998; Ruiz and others, 1998). This cleansing action is similar to the effect shown on nickel and zinc catalysts as reported by Suslick and Casadonte (1987) and Suslick and Doktycz (1989), respectively. Third, Hung and Hoffman found that sonication improved contaminant mass transport to the iron surface which also corroborates the findings of Suslick and Casadonte (1987) and Suslick and Doktycz (1989) (Hung and Hoffman, 1998). Fourth, sonication of zero-valent iron has been shown to increase the fraction of non-chlorinated degradation products (Ruiz and others, 1998). Zero-valent iron treatment systems coupled with ultrasound increased the first-order degradation rate of carbon tetrachloride by a factor of 40 versus a zero-valent iron system (Hung and Hoffman, 1998) and TCE degradation for a similar system was observed to increase by a factor ranging from 2.17 (Ruiz and others, 1998) to 3 (Reinhart and others, 1996).

2.7 GROUNDWATER FLOW MODELING

The purpose of this study is to model degradation of chlorinated ethene-contaminated groundwater using in-well reactors. To this point, we have investigated the literature dealing with the abiotic degradation mechanisms and kinetics associated with various materials that can be used in in-well reactors. However, a critical factor affecting the efficacy of an *in situ* groundwater plume containment system is transport of the contaminated groundwater itself through the treatment system. In this study, we will look at plume control by a horizontal flow treatment well (HFTW) system. Christ (1997) developed an analytical model of an HFTW system. In this section we will describe the system and how it is modeled. This will be accomplished first by describing a simple injection-extraction well system to introduce the flow modeling terminology, and then moving on to the more complex HFTW system.

2.7.1 Injection-Extraction Well System

Overall contaminant removal using an HFTW system with in-well reactors depends on two factors: (1) destruction of the contaminant during each pass of contaminated groundwater through the in-well reactors, and (2) the fraction of contaminated groundwater that is recirculated between the treatment wells (which results in multiple passes of groundwater through the in-well reactors (Christ and others, 1999). Christ and others (1999) developed a fast and simple technique to determine recirculation in an HFTW system. In order to introduce this technique, we will first look at an injection/extraction well system (Figure 2.4) that is somewhat simpler than an HFTW system. The concepts and formulae used for this simple system will be used later in the more complex HFTW system. The analytical method developed by Christ (1997) is based on the following simplifying assumptions: (1) regional groundwater flow is steady, horizontal, and uniform at Darcy velocity U in a homogenous confined aquifer of constant thickness B, (2) well injection/extraction rates, Q, are constant, and (3) well locations are co-linear (Christ, 1997).


Simple Injection/Extraction Well System

Adapted from ESTCP proposal

Figure 2.4: Single-Screened Injection/Extraction Well Pair with Aboveground Catalytic Treatment Reactor

Christ's mathematical approach followed Javendal and Tsang (1986) and employed complex potential theory (Christ and others, 1999). Christ's approach involves using complex potential theory to locate the flow field's stagnation points (Christ, 1997; Christ and others, 1999). The stagnation points are locations where groundwater is not moving, and may be found where the derivatives of the complex potential with respect to location are zero (Shan, 1999). Interflow (the amount of groundwater that is recirculated between the wells associated with the stagnation points) may be determined by calculating the difference in the value of the stream function at the stagnation points (DaCosta and Bennett, 1960). Figure 2.5 illustrates a four-well system (two injection/extraction well pairs), with stagnation points associated with each of the four wells, and interflow between the well pairs. Notice that the stagnation point locations and interflow are functions of aquifer properties, well locations, and pumping rate. In particular, the interflow is a function of a parameter we will call α: α is defined as the angle between the direction of regional flow and the axis formed by the injection and extraction wells (see Figure 2.5, after Christ, 1997). The details of locating stagnation points and calculating interflow are beyond the scope of this study. The interested reader can refer to Christ (1997), Christ and others (1999), DaCosta and Bennett (1960), and Haitjema (1995) for further information. For the purposes of this study, we only need to understand that complex potential theory can be used to calculate total interflow (I_T) of an N-well system, where total interflow is defined as the ratio of flow through all extraction wells that originated in injection wells and the flow through a single extraction well (Q).

Having used complex potential theory to calculate total interflow of an N-well system, the capture zone width (CZW) for the system can be determined by equating flow into the system from upgradient with the portion of flow being pumped through the extraction wells that comes from upgradient.

$$CZW * U * B = Q * \frac{N}{2} - Q * I_T \tag{6}$$

$$CZW = \frac{Q}{UB}\left[\frac{N}{2} - I_T\right] \tag{7}$$

Christ (1997) also defined an average interflow, I_{AVG}, as the fraction of flow through all extraction wells that originated in injection wells. By this definition,

$$I_{AVG} = \frac{I_T}{\left[\frac{N}{2}\right]} \tag{8}$$

If we further define overall contaminant removal efficiency of the treatment system (η) as

$$\eta = 1 - C_{down}/C_{up} \tag{9}$$

where

C_{down} = contaminant concentration downgradient of the treatment system

C_{up} = contaminant concentration upgradient of the treatment system

and the single-pass removal efficiency (η_{sp}) as the contaminant removal obtained when contaminated water passes through the catalytic reactor, through mass balance we derive the following relationship (Christ, 1997; Christ and others, 1999):

$$\eta = \frac{\eta_{sp}}{1 - I_{AVG}(1 - \eta_{sp})} \tag{10}$$

This equation is very important because it relates the parameters that are the focus of the modeling effort in this study. Equation (10) demonstrates that increasing recirculation between the wells (I_{AVG}) increases overall contaminant removal efficiency (η) for a given single-pass removal treatment efficiency (η_{sp}).

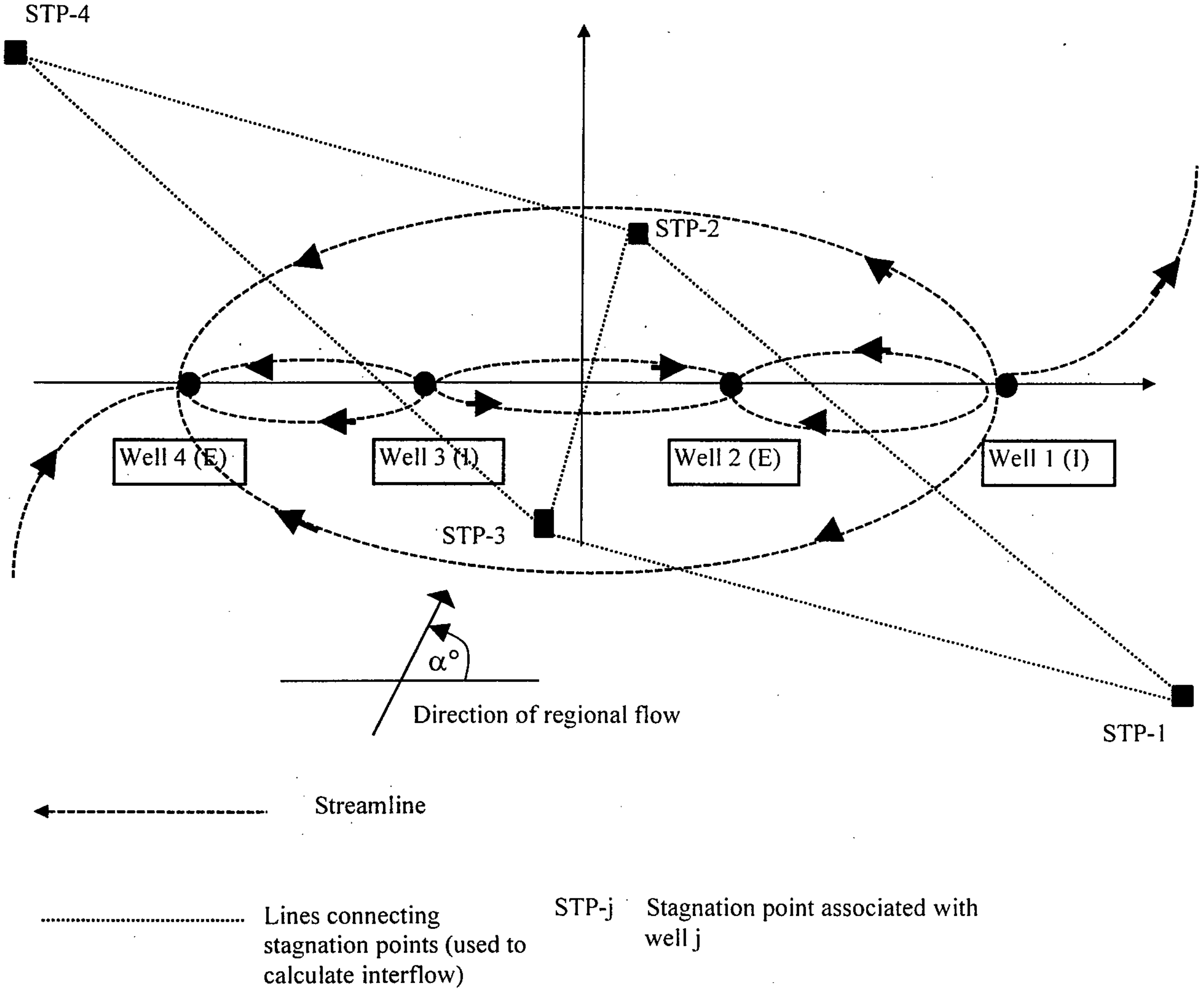


Figure 2.5: Flow Field for Four-Well System Depicting Stagnation Points (after Christ, 1997)

Note, however, that as recirculation increases for given well pumping rates (Q), less contaminated groundwater is introduced into the system from upgradient, effectively reducing the CZW of the treatment system.

2.7.2 Horizontal Flow Treatment Well (HFTW) Systems

The HFTW system is slightly more complex than the system of injection and extraction wells described in section 2.7.1. The HFTW system employs two or more dual screened wells (Figure 1.1) with water moving in the wells in either an upflow mode or downflow mode. The HFTW system we model in this study will be assumed to operate in either a two aquifer system (Figure 2.6) or in an anisotropic aquifer where vertical flow is minimal so that the HFTW system operating in a single anisotropic aquifer may be modeled as if there were two separate aquifers (Figure 2.7). Aquifers are quite commonly anisotropic, so this assumption is not very restrictive (Domenico and Schwartz, 1998).

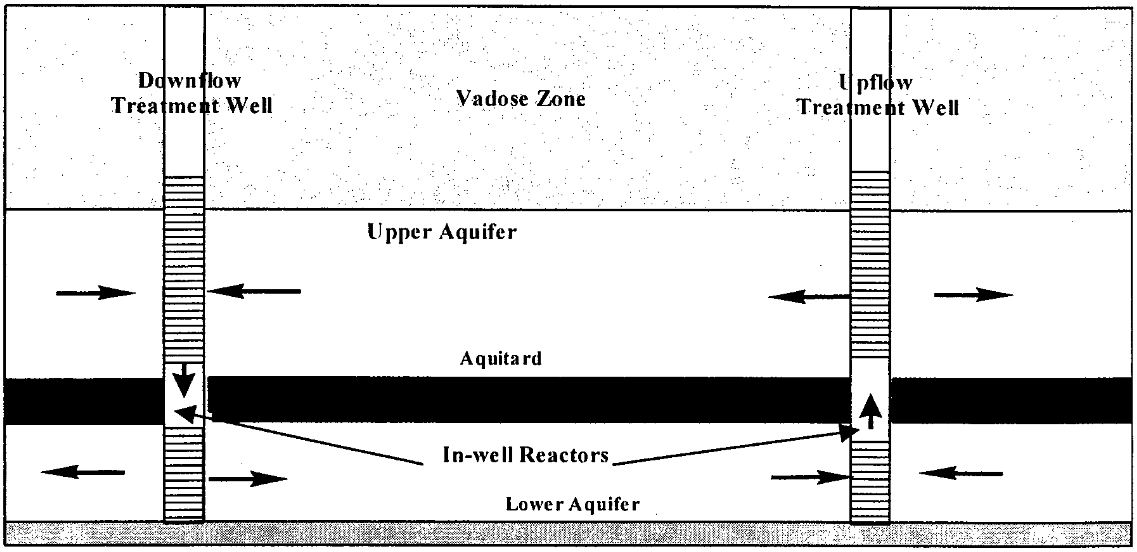


Figure 2.6: HFTW System Operating in Two Aquifers

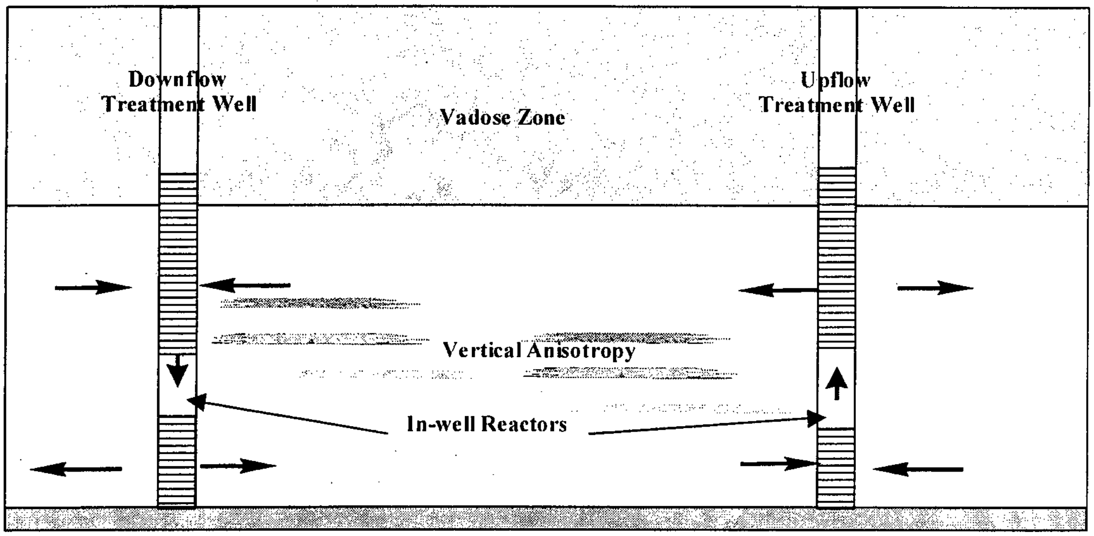


Figure 2.7: HFTW System Operating in Single Aquifer with Vertical Anisotropy

With these assumptions, the HFTW system may be modeled as a system of injection and extraction wells in two aquifers with upflow wells injecting and downflow wells extracting water from the upper aquifer, while upflow wells extract and downflow wells inject water into the lower aquifer. Thus, by mass balance and applying equation (10) to the upper and lower aquifer, we find (Christ, 1997):

$$C_{outU} = C_{in}\left[\frac{(1-I_L)(1-\eta_{spU}) + I_L(1-I_U)(1-\eta_{spL})(1-\eta_{spU})}{1-I_U I_L(1-\eta_{spL})(1-\eta_{spU})}\right] \tag{11a}$$

$$C_{outL} = C_{in}\left[\frac{(1-I_U)(1-\eta_{spL}) + I_U(1-I_L)(1-\eta_{spL})(1-\eta_{spU})}{1-I_U I_L(1-\eta_{spL})(1-\eta_{spU})}\right] \tag{11b}$$

η_{spU} = Average single-pass treatment efficiency for in-well reactor in upper aquifer
η_{spL} = Average single-pass treatment efficiency for in-well reactor in lower aquifer
I_U = Average interflow between upper well screens
I_L = Average interflow between lower well screens
C_{in} = Influent (upgradient) concentration $[M/L^3]$
C_{outU} = Effluent (downgradient) concentration in upper aquifer $[M/L^3]$
C_{outL} = Effluent (downgradient) concentration in lower aquifer $[M/L^3]$

Equations (11a) and (11b) assume there is no vertical flow between two screens of the same well. If vertical flow does occur (perhaps for an isotropic or mildly anisotropic aquifer) there is additional recirculation which results in more passes of contaminated groundwater through the in-well reactor as well as smaller capture zones.

Multiple rows of wells might be required to fully capture a contaminated plume and obtain effluent concentrations within regulatory limits. If multiple rows are placed far enough apart, we can assume their interactions are negligible (Christ, 1997). If each row of treatment wells has the same pumping rate and the same in-well reactor technology, the overall system efficiency is given as (Christ, 1997):

$$\eta = 1 - \left(\frac{C_{out}}{C_{in}}\right)^{M} \qquad (12)$$

where

M = Number of rows of treatment wells
C_{out} = contaminant concentration downgradient of a single row of wells
C_{in} = contaminant concentration upgradient of the same single row of wells

2.7.3 HFTW Systems versus GCW Systems

As an aside, let us clarify the distinction between an HFTW system and the more common groundwater circulation well (GCW) system. Groundwater circulation wells are commonly employed as part of groundwater remediation systems such as the NoVOCs™ or Unterdruck-Verdampfer-Brunnen (UVB) (Sellers, 1999). In these systems, the GCW creates a vertical flow pattern between upper and lower well screens. This vertical pattern results in recirculation of treated groundwater through the treatment system thereby increasing overall efficiency just as we described for the HFTW system. However, a GCW is vulnerable to heterogeneities in the aquifer which result in hydraulic conductivity anisotropy similar to what is shown in Figure 2.7 (Sellers, 1999). Due to these commonly encountered anisotropic conditions, vertical groundwater flow (and hence, fraction of groundwater recirculated) is reduced, thus reducing overall treatment efficiency. Conversely, recirculation to an HFTW system is not adversely affected by anisotropy, and in fact, equations (11a) and (11b) are applicable only under anisotropic conditions.

3.0 METHODOLOGY

3.1 OVERVIEW

This chapter begins with a discussion of how a catalyst/reductant was selected for model analysis in this study. In the second section of the chapter, an abiotic degradation submodel is developed to simulate the kinetics of the in-well reactor. In the final two sections of the chapter, the degradation submodel is coupled with the flow model developed by Christ (1997) in order to simulate injection-extraction and HFTW systems.

3.2 CATALYST/REDUCTANT SELECTION

3.2.1 Metal catalyst/reductant comparisons

Chapter 2 provided an overview of the possible materials currently being researched to achieve degradation of chlorinated contaminants. Comparing the normalized half-lives of each material yields a quantitative foundation to make judgements about each material's suitability for use in-well. As mentioned in Chapter 2, the in-well reactors used in an HFTW system will require relatively rapid degradation kinetics. Tables 3.1 and 3.2 summarize the kinetic information provided in Chapter 2 in order to make this comparison.

Compound	Disappearance Half-Lives (min) Field Data	
	Palladium column	Zero-valent iron wall[3]
PCE	.414[1]	11580[2]
TCE	.510[1]	6540[2]
1,1-DCE	.581[1]	6180[2]
cis-DCE	Not reported	4800[2]
trans-DCE	Not reported	10200[2]
VC	Not reported	Not reported

[1] McNab and others, 2000 (using 300 grams/Pd/19 L)

[2] O'Hannesin and Gillham, 1998

[3] Normalized to 1mL/m^2 iron surface area

Table 3.1 Half-Lives of Pd vs. Fe(0) from Field Column Tests

Material	Laboratory Half-Lives (min)
	Normalized to 1 g Pd/L solution
Pd	1.08[1]
Palladized iron	3.55[2]
	Normalized to 1 g metal/L solution
Fe(0)	$(1.01\text{x}10^5)^5 - (4.14\text{x}10^6)^3$
Zn	$3.82\text{x}10^5$
Sn(0)	$(2.45\text{x}10^6)^3$
Fe(0) and Sn(0)	$(1.17\text{x}10^6)^3$

[1] Lowry and Reinhard, 1999 (using .22 g Pd/L)
[2] Liang and others, 1997b (using 25 g Fe(0) plated by .05% Pd/125 mL)
[3] Su and Puls, 1999 (using Fisher Fe(0) and Sn(0) (15 g/50 mL) at 25 degrees C; Fe(0) has .091 m^2/g; Sn(0) has .139 m^2/g; Fe(0) and Sn(0) combination uses 7.5 grams of each/50 mL)
[4] Arnold and Roberts, 1998 (using 25 g Zn/160 mL; Zn has .035 m^2/g)
[5] Johnson and others, 1996; Tratnyek and others, 1997 (weighted average of several batch studies; normalized half-life=110 min for 1 m^2/mL, average specific surface area = 1.09 m^2/g)

Table 3.2 Normalized Disappearance Half-Lives of TCE by Various Metals in Laboratory Batch Experiments

Based on the normalized half-life information in Table 3.1, it is clear that palladium is superior to zero-valent iron for in-well application. Other materials, such as zero-valent zinc, nickel-iron, and zero-valent tin, were reviewed in Chapter 2 and displayed degradation rates that were as good or better than zero-valent iron. However, none of these materials can attain the degradation rates reported for palladium by McNab and Ruiz (1998) and McNab and others (2000). Table 3.2 compares the kinetics of TCE degradation for palladium-based catalysts versus other metals from laboratory batch experiments. When normalized to one gram of catalyst/reductant per liter of solution, palladium once again reveals its superiority over the other materials. Another factor that contributed to the decision to choose palladium over the other metallic reductants was that the published kinetic data for the other metallic reductants were from batch experiments. Batch experiments are not representative of an HFTW system; therefore, column experiments are preferred. The batch data for zinc, nickel-iron, and tin would have to be adjusted for in-well application. Hopefully, research is on-going to investigate the potential for in-well use of these other catalysts/reductants. Based on currently available data however, the choice is between zero-valent iron and palladium, and palladium is clearly superior for in-well application.

3.2.2 Sonication

Chapter 2 also discussed the use of sonication in conjunction with various metals, and the degradation performance was better than when using the metals alone. However, sonication will not be investigated further in this thesis. The primary reason is because the literature review revealed that research into sonication is not yet far enough along to attempt incorporating it into an in-well reactor. The logistics involved with placing an in-well sonication device might prove to be impractical, or sonication may prove to have some unanticipated impact on catalyst performance. The use of sonication and its potential to increase reactivity of metallic reductants as well as increase the longevity of degradation performance is an intriguing area of research and should receive more attention in the future.

3.3 ABIOTIC DEGRADATION KINETICS SUBMODEL

Now that palladium-based catalysts have been selected for use in this modeling effort, we must decide how to select the value of the specific first-order degradation rate constant. The first-order degradation assumption simplifies the kinetic submodel by disregarding complicating factors—most notably the complexity of declining catalyst performance over time. This assumption was made because there is not enough information to accurately model catalyst behavior for an extended period of time. The literature review indicated several biogeochemical parameters that could poison palladium-based catalysts, but there are no concrete relationships yet. McNab and others (2000) prolonged catalyst activity by periodically shutting off the hydrogen supply, which allowed for catalyst regeneration. Lowry and Reinhard (2000) pulsed their column of palladium-based catalyst with sodium hypochlorite solution in order to reverse the deactivation process. These two methods were shown to prolong catalyst life, but our understanding of the processes causing deactivation is incomplete and we are as yet unable to incorporate the mechanisms into a submodel.

Studies using palladium-based catalysts to degrade chlorinated ethenes dissolved in water will provide useful data. Among the studies covered in Chapter 2, the most relevant data come from McNab and others (2000), as their research involved an in-well reactor that degraded contaminated groundwater from an actual aquifer as opposed to a laboratory batch or column study. Examination of the half-lives presented in the first column of Table 3.1 shows that the half-lives increase slightly as the level of chlorination decreases in the chlorinated ethene family. In this modeling effort, we will use half-life degradation values for TCE as representative.

Converting the raw data presented by McNab and others (2000) is straightforward. Table 2 in their article summarizes influent and effluent data for the contaminants of interest. For TCE, the influent was 366-370 μg/L and the effluent was < .4 μg/L. Residence time of the reactor was given as 5 minutes. These values were substituted into equation (13)

$$\frac{C(t)}{C_0} = e^{-kt} \tag{13}$$

in order to calculate the first-order degradation constant. An average influent value of 368 μg/L was selected for C_0, and .4 μg/L was selected as a conservative value for C(t), yielding a value for k of 1.36 min^{-1}.

3.4 MODELING OF INJECTION-EXTRACTION SYSTEM

Having obtained a reasonable first-order degradation constant for the palladium-based catalyst, we can now incorporate it into the flow model developed by Christ (1997). In Chapter 2, Christ's concepts were introduced with a pair of injection and extraction wells linked by an aboveground reactor vessel (see Figure 2.4). Modeling for the injection-extraction well system begins by setting the upgradient concentration and downgradient concentrations. These concentrations are used to calculate η, the overall degradation efficiency required of the system, according to equation (9). This parameter is the primary design objective for the injection-extraction well system. The downgradient concentration was set at 5 μg/L, the TCE maximum contaminant level for drinking water. The secondary design objective for the injection-extraction well system is the CZW, which ensures complete capture of the contaminated groundwater plume. With these two design objectives in mind (η and CZW), the next step is to select well parameters (pumping rates and separation distance) using Christ's (1997) model.

Figure 3.1, which plots CZW for various combinations of Q/UB and well separation half-distance (d), was constructed using Christ's flow model for a particular value of α (Christ, 1997).

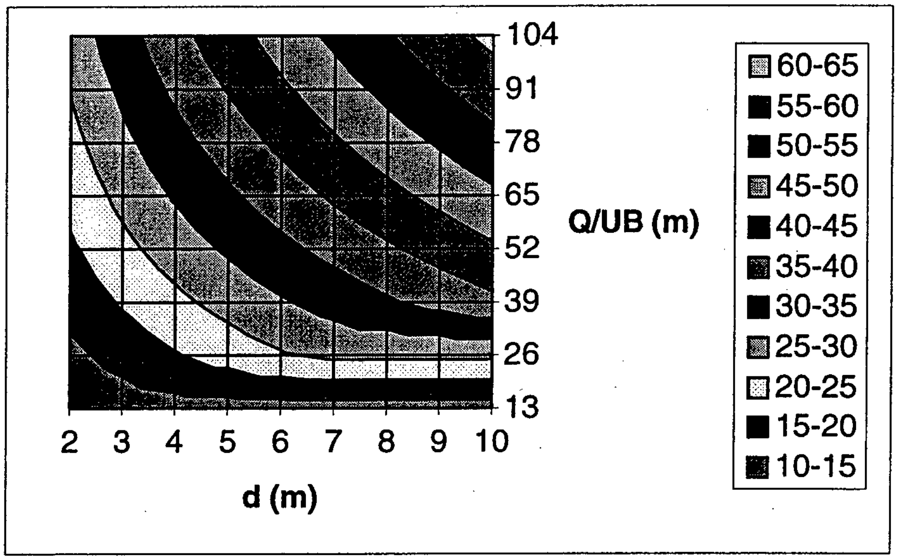


Figure 3.1: Contour Plot of CZW (m) (in 5-m increments) ($\alpha = 67.5°$)

U, B, and α are assumed known and constant for a particular aquifer. Setting the CZW greater than or equal to the width of the contaminant plume, a designer can enter Figure 3.1 along the proper CZW contour, which will correspond to a range of Q/UB values. The upper limit of appropriate Q/UB values is established by calculating Q_{max}, which depends on the maximum allowable drawdown in the aquifer. The resulting Q/UB value generated by Q_{max} will correspond to a specific d, the half-distance between the injection and extraction wells. Knowing Q/UB and d from Figure 3.1, the designer can calculate Q/UBd. The Q/UBd value is a dimensionless parameter indicating the ratio of flow due to pumping (Q/d) relative to regional flow (UB). Knowing Q/UBd and the overall treatment efficiency required, a designer can use Figure 3.2 to determine the in-well reactor volume (V) for a given rate constant (k). Figure 3.2 was constructed using equation (10) to calculate η, with Christ's flow model being used to calculate I_{AVG} for a given Q/UBd, and equation (14), below, being used to calculate η_{sp} for an in-well reactor of volume V, pumping rate Q, rate constant (k), and catalyst porosity (n):

$$\eta_{sp} = 1 - e^{-\left(k\frac{Vn}{Q}\right)} \tag{14}$$

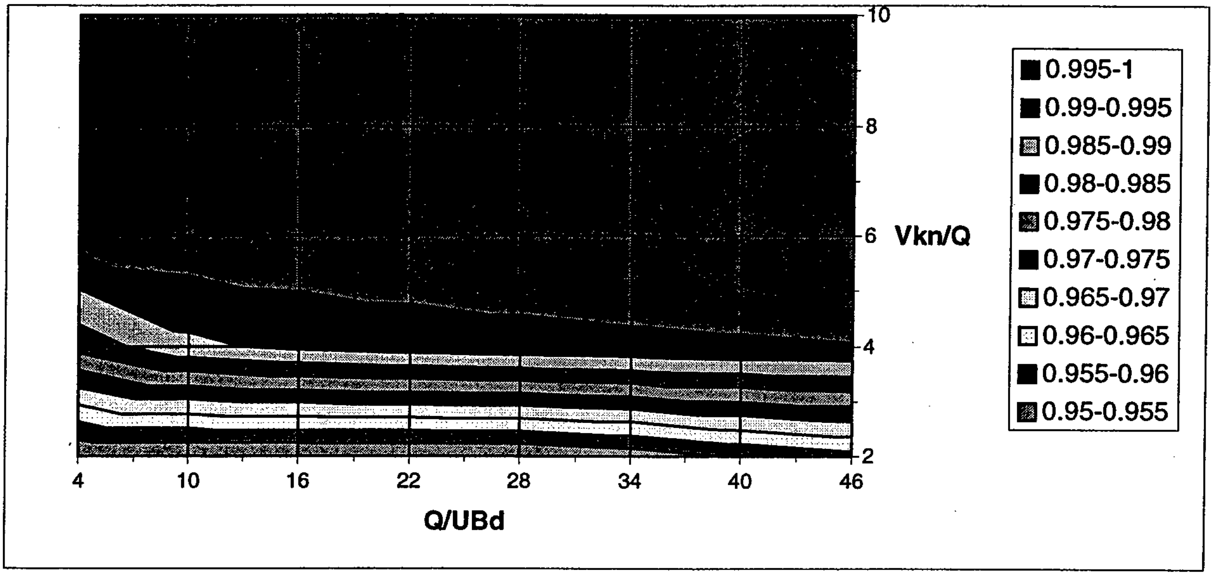


Figure 3.2: Contour Plot of Overall Contaminant Removal Efficiencies (η) (in .005 increments; $\alpha = 67.5°$)

Note that Vn/Q, which appears in equation (14), is simply the hydraulic residence time in the in-well reactor. Any combination of increasing reactor volume and/or decreasing flow rate will result in a longer residence time, which results in more degradation, and a higher η_{sp}.

Use of Figures 3.1 and 3.2 by a designer guarantees that the primary design objectives (η and CZW) are met for various combinations of flow rate (Q), half-distance between wells (d), and reactor volume (V). These combinations translate to design flexibility and facilitate cost comparisons among multiple configurations. In fact, by considering different first-order degradation constants (k), we can compare the effect on design of different catalysts/reductants.

Viable designs are sensitive to the pumping rate (Q). As stated above, calculating Q_{max} for the particular aquifer and using Figure 3.1 can begin an initial design. However, operational considerations might dictate a smaller Q to reduce pumping costs. As an example, let us reexamine Figure 3.1, which is now presented as Figure 3.3 below, at the point where the CZW contour equals 25 m (for a contaminated plume width $\leq$ 25 m) at d = 2 m and Q/UB = 90 m (Box 1). These values indicate that the wells are relatively close together and the pumping rate is quite large, which will result in large interflow. By moving downward along the 25-m CZW contour, d increases and Q/UB decreases. Thus, interflow decreases (Box 2). Eventually, interflow equals zero at the point where d = 7 m and Q/UB = 25 m, and the 25 m CZW contour becomes horizontal (Box 3). It is no coincidence that Q/UB equals the CZW at this point on the graph. The relationship between CZW and Q/UB is explained by examining equation (7), which shows CZW equaling Q/UB when N = 2 and $I_T = 0$. When interflow equals zero it is no longer advantageous (from the point of view of achieving additional treatment through recirculation) to employ an injection-extraction well system because there is no recirculation. From the previous discussion, we see the range of viable flow rates lies between Q_{max} and the point where Q results in zero interflow. Ultimately, if the half-distance between wells becomes large enough, interflow may become negative, which means that regional groundwater is passing between the wells and the contaminant plume is escaping the treatment system.

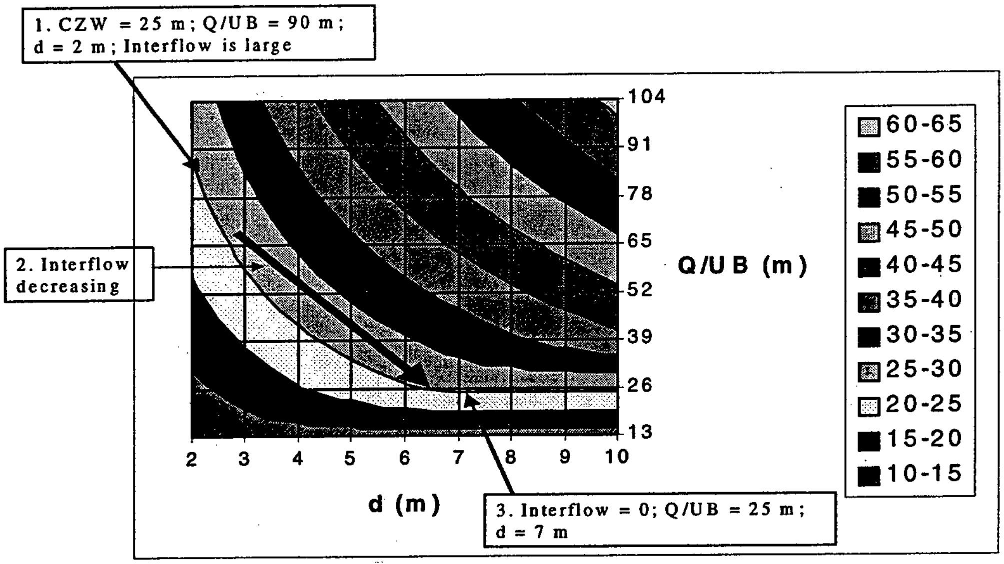


Figure 3.3: CZW Contour Plot (m) of Figure 3.1 Illustrating Dynamics of Interflow

There is a possibility that the contaminated plume width will require a CZW too large for Q_{max} of a given aquifer. If this situation occurs, the modeler must switch to a row of multiple wells to guarantee adequate plume containment. The methodology for this approach is outlined by Christ (1997).

3.5 MODELING OF HFTW SYSTEM

Figure 2.6 depicts the HFTW system to be modeled in this study. Fortunately, the modeling process is identical to that of the injection-extraction well system described in section 3.4. This is because the upper and lower aquifers shown in Figure 2.6 may be treated separately and each modeled like an injection-extraction well system. The reactor in the downflow treatment well simulates an aboveground reactor for the upper aquifer, and the reactor in the upflow treatment well simulates an aboveground reactor for the lower aquifer. By treating the upper and lower aquifers separately, each aquifer's parameters (regional groundwater velocity (U) and aquifer thickness (B)) can be incorporated into Christ's (1997) model to generate interflow values for each aquifer. A significant point to remember is that the value for alpha is different for the upper and lower aquifers because the injection and extraction wells are transposed. The equation for calculating alpha in the lower aquifer is shown below.

$$\alpha_{\text{lower}} = 180° - \alpha_{\text{upper}} \tag{15}$$

α_{lower} = Angle in degrees between the regional flow direction and the axis connecting the injection and extraction wells measured from the injection well in the lower aquifer

α_{upper} = Angle in degrees between the regional flow direction and the axis connecting the injection and extraction wells measured from the injection well in the upper aquifer

Figure 2.6 clearly shows how the injection well in the lower aquifer is the extraction well in the upper aquifer and vice versa.

Using identical catalyst/reductant material in equally sized in-well treatment reactors results in equal single-pass treatment efficiencies (η_{sp}) for the upper and lower aquifers, assuming the flow rates for both wells are equal. The values for interflow and η_{sp} for each aquifer generated by Christ's (1997) injection-extraction well model may be substituted into equations (11a) and (11b) in order to model the HFTW system. Knowing interflow and η_{sp} for each aquifer, a designer can determine if the η and CZW for each aquifer meet design objectives.

4.0 ANALYSIS

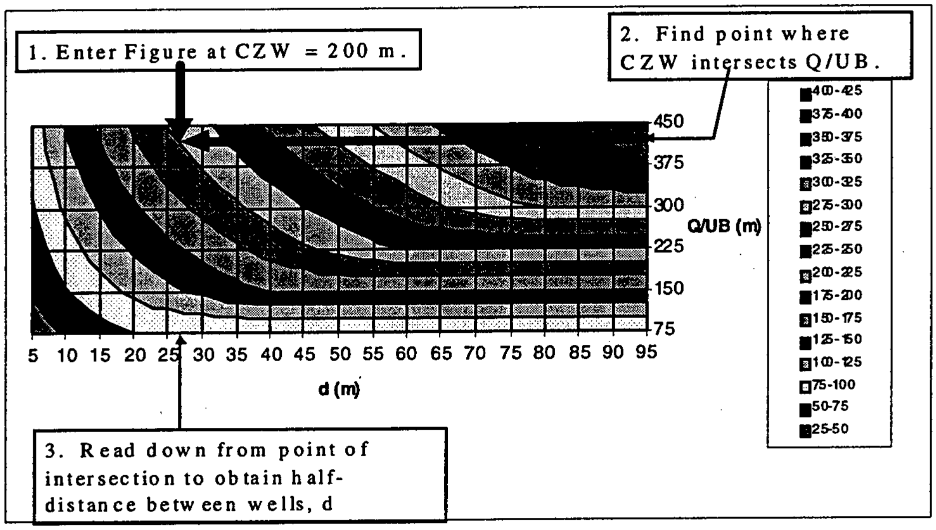
4.1 INTRODUCTION

This chapter includes an analysis using the modeling approach described in Chapter 3. One important goal of the chapter is to demonstrate how project managers can use the model as a screening tool for plume containment. The first section of the chapter uses a hypothetical injection-extraction well system to demonstrate the utility of Figures 3.1 and 3.2. The second section will show how the more complex HFTW system model simulates chlorinated ethene degradation for a real-world plume using data from Edwards AFB. Both of these sections will demonstrate how project managers might use these figures as a screening tool for potential application of this technology.

4.2 INJECTION-EXTRACTION WELL CASE

4.2.1 Injection-Extraction Well in a Hypothetical Scenario

We will now demonstrate how the graphs presented in section 3.4 may be used to design an injection-extraction well system capable of containing a plume contaminated with chlorinated ethenes. First, let us assume the contaminated aquifer has known parameters. For this hypothetical scenario, we will use parameter values from the Edwards AFB upper aquifer, which has a thickness (B) of 8 m, a regional groundwater Darcy velocity (U) of .02056 m/d, and a flow direction defined by an angle α of 67.5° (Christ and others, 1999). Maximum drawdown for wells in aquifers of known hydrogeology can be calculated using a number of well-known methods (e.g. Domenico and Schwartz, 1998). Thus Q_{max} can be determined based upon the maximum allowable drawdown. For this hypothetical example, we will not calculate a value for Q_{max} based on allowable drawdown; rather, we will assume that it is 70 m^3/d. Let us assume that the plume is 200 m wide, contaminated with 1250 μg/L of TCE, and that the downgradient concentration cannot exceed 5 μg/L. Based on a Q_{max} of 70 m^3/d, the Q/UB value is 425 m.

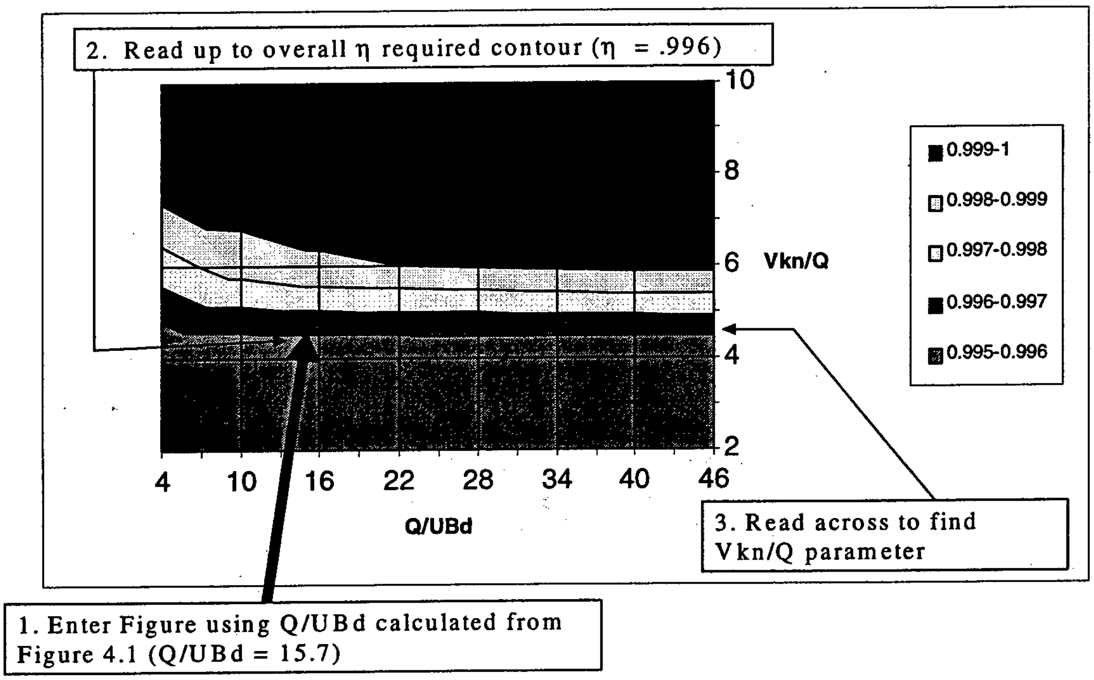

1. Enter Figure at CZW = 200 m.

2. Find point where CZW intersects Q/UB.

3. Read down from point of intersection to obtain half-distance between wells, d

Figure 4.1: Design Methodology for Edwards AFB Upper Aquifer; Q = 70 m^3/d, α = 67.5°, η required = .996, B = 8 m

Using the methodology from section 3.4, we construct Figures 4.1 and 4.2 for the specific α value of interest. We enter Figure 4.1 along the 200-m CZW contour (Box #1) and follow it to where it intersects Q/UB = 425 m. (Box #2). This intersection occurs when d equals approximately 27 m (Box #3). This gives us a Q/UBd value of 15.7, which we will use to enter Figure 4.2.



2. Read up to overall η required contour (η = .996)

3. Read across to find Vkn/Q parameter

1. Enter Figure using Q/UBd calculated from Figure 4.1 (Q/UBd = 15.7)

Figure 4.2: Contour Plot of Overall Contaminant Removal Efficiencies (η) (α = 67.5°)

Based on the upgradient and downgradient concentration, the overall η required for this system is 99.6%. If we enter Figure 4.2 along the x-axis at Q/UBd equals 15.7 and move up to the overall η required of .996, the corresponding Vkn/Q is approximately 4.5. To solve for the reactor volume, we simply substitute 70 m^3/d (Q), 1958 day^{-1} (k for palladium), and .3 (n for palladium-based catalyst) into Vkn/Q. This yields a reactor volume of 536 L. As mentioned in section 3.4, we could pick smaller values of Q/UB along the 200-m CZW contour from Figure 4.1 (corresponding to flow rates lower than Q_{max}) that would result in an increased distance between the wells and decrease the amount of interflow. For example, if we had continued down the 200-m CZW contour in Figure 4.1 to where Q/UB = 220 m, d would have been 50 m. The Q/UBd parameter would have been 4.4, and with an overall η required of .996, the Vkn/Q parameter from Figure 4.2 would have been 4.75. The reactor volume for this case is only 293 L and the

Q is approximately 36 m^3/d. This revised design boasts a 49% reduction in flow rate and a 45% reduction in reactor volume to achieve the same overall η required!

Obviously, we cannot reduce Q and V without limit and continue to meet our CZW and overall η goals. Further examination of Figure 4.2 helps us determine what those limits are. Note that the efficiency contour lines are horizontal for larger Q/UBd values. Moreover, the higher the overall η required, the higher the Q/UBd value needed before the contour line becomes horizontal. As long as the contour line is horizontal, decreasing Q/UBd values (as well as decreasing interflow, since each Q/UBd value corresponds to a specific interflow) decreases reactor volume (V). This is because Vkn/Q is constant along the horizontal portion of an overall efficiency contour, so V must decrease with Q. The Q corresponding to the left-most Q/UBd value along the horizontal portion of an overall efficiency contour represents a dominant solution (i.e. $Q_{dominant}$) relative to the Q values located to the right along the horizontal portion of the overall efficiency contour. However, depending on cost tradeoffs, the optimum design solution may be at a Q/UBd value located further to the left. These smaller Q/UBd values are where the contour line begins to turn upward. This effect is due to the fact that as Q/UBd decreases, interflow decreases. With less recirculation, higher single-pass efficiencies (η_{sp}) are needed to maintain the overall efficiency of the system. Once the Q/UBd values become small enough, the increased residence time (due to reduced Q) is no longer enough to ensure adequate η_{sp}, and the reactor volume must increase to account for the decreased interflow. This relationship is clearly seen in Figure 4.2 on the .999 η contour. When Q/UBd gets below 22, the contour begins to rise (Note that the Q associated with Q/UBd

= 22 is the "$Q_{dominant}$."). In order to achieve this high level of overall degradation, the system requires much more interflow than the .996 η system. After Q/d decreases enough so that Q/UBd is less than 22, the corresponding interflow is too low to achieve the required overall η, so the reactor volume must increase to achieve the design objective. Therefore, we can quickly determine the maximum Q/UBd value by examining the overall efficiency contour plot. The largest Q/UBd value would be located at the left-most end of the horizontal portion of the overall efficiency contour.

4.2.2 Comparison of Injection-Extraction Well Case with Zero-Valent Iron

Because Figure 4.2 contains a dimensionless degradation parameter, Vkn/Q, we can easily substitute a first-order degradation constant for zero-valent iron and compare it to the palladium-based catalyst. From Table 3.1, the half-life of TCE degradation by zero-valent iron measured in the field is 6540 minutes. This corresponds to a first-order rate constant (k) of .153 d^{-1}. For the previous case, with Vkn/Q = 4.75 and Q = $36 m^3/d$, utilization of zero-valent iron as the in-well reductant would require a reactor volume of 3.73×10^6 L (assuming porosity (n) equals .3). If this reactor volume were placed in a 15.24-cm diameter well, it would need to be 204 km long!

4.3 HFTW SYSTEM ANALYSIS

4.3.1 Model Analysis with CZW and η as Design Objectives

Application of a model to real-world data is a useful way to gain confidence in the model. In this study, we are modeling an innovative technology that has only been applied once in the field (McNab and others, 2000). The field test involved a single groundwater circulation well, somewhat different than the HFTW system proposed here. Thus, validating the model cannot be accomplished at the present time, since field data are not available to compare to model results. However, the model can be applied to an actual field situation to demonstrate its capability to serve as a screening tool for this new technology. The tool can help project managers gain insight as to whether or not an HFTW system using an in-well catalyst is appropriate for application at a given site with chlorinated ethene-contaminated groundwater.

Similar to the injection-extraction well case discussed in section 4.2.1, screening a contaminated site with the model to determine applicability of an HFTW system involves determination of parameters. Parameters that are known for a site include the first-order degradation constant (k) (assuming a catalyst has been preselected), the regional groundwater velocity (U), the thickness of the aquifer (B), the direction of groundwater flow relative to the row of wells (defined by the angle α), the upgradient contaminant concentration (C_{up}), and the required downgradient concentration (C_{down}). Figures 2.6 and 2.7 show cross-sectional views of an HFTW system. In Figure 2.6, an aquitard creates an upper and lower aquifer, both of which are assumed to be contaminated. Each aquifer can have individual values for U, B, α, and C_{up}. Figure 2.7 shows an HFTW system for a single anisotropic aquifer. In this case, U, C_{down}, and C_{up} will be the same for the upper and lower well screens. However, B will depend on screen length and α on the injection/extraction configuration of the upper and lower screens. Engineered parameters for the systems are reactor volume (V), flow rate (Q), and the half-distance between the wells (d). In the most general case, where the designer is not constrained to use a particular catalyst, the first-order degradation constant (k) may also be varied.

For the following example, we will refer to a TCE-contaminated site at Edwards AFB that is similar to the depiction in Figure 2.6. The Edwards AFB aquifer properties are as follows: hydraulic conductivity of 3.4×10^{-3} cm/sec, regional gradient of .007, the upper aquifer is 8 m thick, and the lower aquifer is 5 m thick (Christ, 1997). The regional Darcy velocity, which is the hydraulic conductivity multiplied by regional gradient, is .02056 m/day. In the upper aquifer, the angle α is 67.5°, and in the lower aquifer α is 112.5° (note that these are supplementary angles, as they must be, based on the definition of α and the fact that the direction of regional groundwater flow is the same in both aquifers) . The TCE concentrations in the Edwards AFB aquifers ranged from 500 – 1200 μg/L; however, for this modeling effort, in order to investigate the applicability of the technology at a highly contaminated site, we will arbitrarily set the TCE concentration at 15 mg/L. The TCE downgradient concentration must be 5 μg/L, so the overall η required is 99.97%. In this example, we will design for a plume that is 200-m wide. We will use a palladium-based catalyst for the treatment reactors, which has a k of 1958 day^{-1} and a porosity (n) that is assumed to be .3. Thus, we now have values for η, U, B, α, k, and n to substitute into the model. Selection of the engineered parameters begins by recalling the prior discussion regarding the concept of Q_{dominant} along the horizontal portion of the overall efficiency contour plot. According to Figure 4.3, when $\eta = .9997$, Q_{dominant}, which occurs roughly at Vkn/Q = 7, corresponds to the Q/UBd value of approximately 8. This Q/UBd solution dominates other solutions on the horizontal contour. These other solutions result in higher values of both Q and V, but only achieve the same overall treatment efficiency.

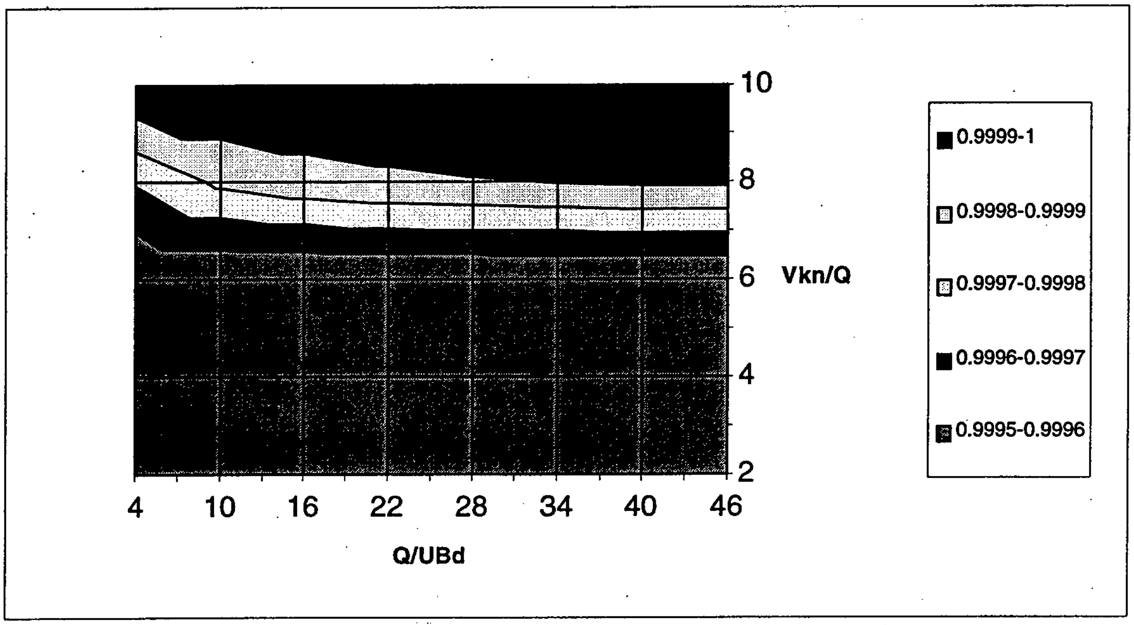


Figure 4.3: Contour Plot of Overall Contaminant Removal Efficiencies (η) for Edwards AFB Upper Aquifer (α = 67.5°)

Figures 4.4 and 4.5 are the CZW contour plots of the upper and lower aquifers from Edwards AFB. Two graphs are needed to account for the differences in aquifer thickness and α.

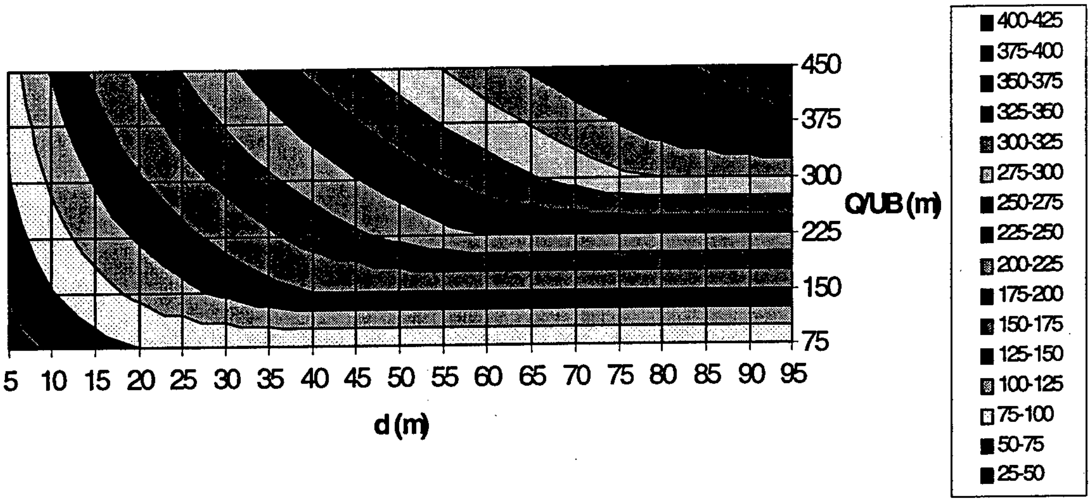


Figure 4.4: Contour Plot of CZW (m) for Edwards Upper Aquifer (α = 67.5°, B = 8 m)

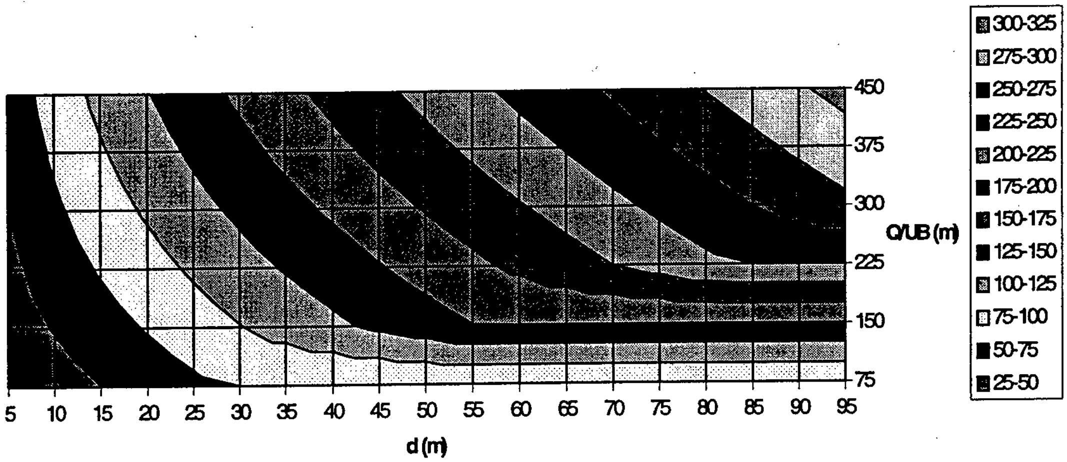


Figure 4.5: Contour Plot of CZW (m) for Edwards Lower Aquifer (α = 112.5°, B = 5 m)

We need to enter Figure 4.4 along the 200-m CZW contour. We also know from the previous analysis using Figure 4.3 that we need to be along the line Q/UB = 8d. These conditions are met at the intersection of Q/UB = 320 and d = 40. Knowing U and B, we can calculate Q is approximately 53 m^3/d and the CZW is about 212 m. Substituting Q back into Vkn/Q = 7 to solve for V gives us a reactor volume of 632 L. The required length for this reactor volume in a 15.24-cm diameter well is 35 m. Although the upper aquifer is only 8 m thick, a reactor designed to be 35 m long might be feasible depending on the total depth of the well.

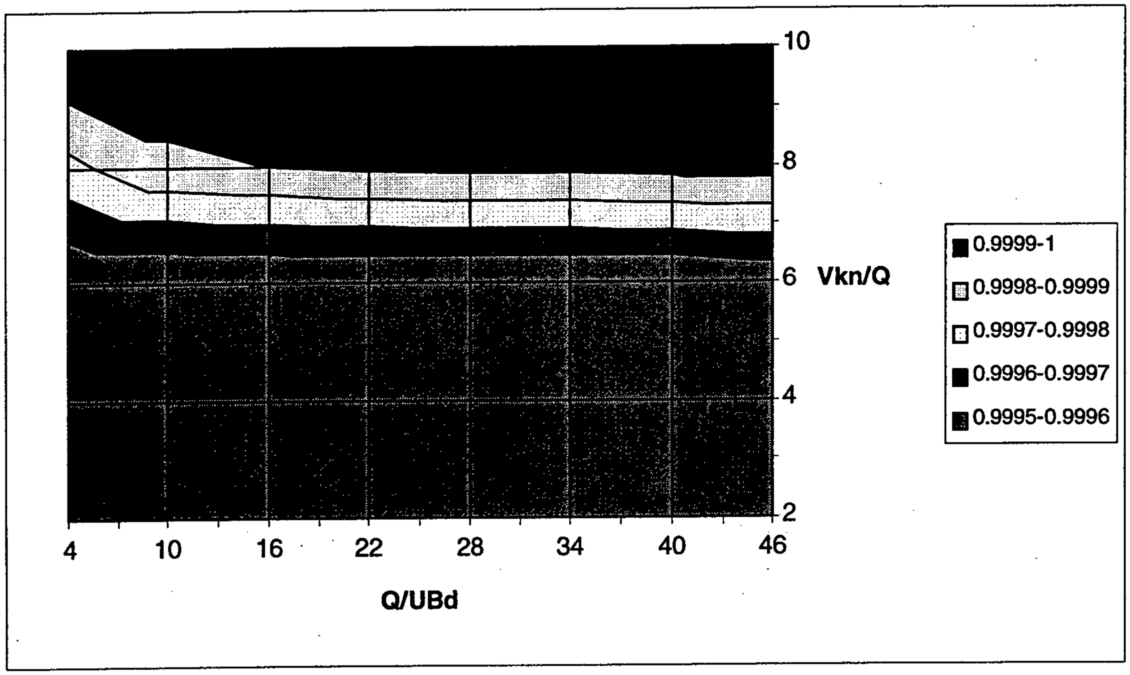


Figure 4.6: Contour Plot of Overall Contaminant Removal Efficiencies (η) for Edwards AFB Lower Aquifer ($\alpha = 112.5°$)

Analysis of the lower aquifer is also necessary to ensure adequate overall treatment efficiency. Entering Figure 4.6 along the approximately horizontal portion of the η = .9997 contour (at Vkn/Q = 6.9), we find the left-most (i.e. dominant) Q/UBd value is 7. From Figure 4.5, when Q/UB = 420 and d = 60, the corresponding Q is 43 m^3/d and the

CZW is 225 m. Substituting Q into Vkn/Q = 6.9 to solve for V yields a reactor volume of 505 L; which requires a reactor length of 28 m assuming the diameter is 15.24 cm. The final step is to analyze the upper and lower aquifers simultaneously and redesign the system for equal flow rates (Q) and half-distances between the wells (d). This will provide us with a two-well HFTW system designed to pump water equally within each well. Evaluating the aquifers independently was necessary to decide which aquifer would be limiting. If our design accommodates the limiting aquifer, we can be assured of adequate overall efficiency with the HFTW system. For this example, we will adjust the upper aquifer design parameters (Q and d) to match the lower aquifer. The motivation for this decision is evident by looking at Figures 4.4 and 4.5 and comparing the effects of changing d. If we shift the lower aquifer d from 60 m to 40 m (Figure 4.5), it would be impossible to meet the 200-m CZW criterion. However, if we increase d in the upper aquifer from 40 m to 60 m, we can simultaneously increase CZW while decreasing Q (Figure 4.4). Specifically, if we set the upper aquifer d to 60 m and Q/UB to 275, the flow rate decreases from 53 to 45 m^3/d and the CZW increases from 212 m to 250 m. Figure 4.3 must be reevaluated with these changes to analyze the effect of a new Q/UBd value. In this case, Q/UBd is now 4.58, which increases the reactor volume from 632 L to 651 L, and the reactor length from 35 m to 36 m.

The previous example focused on a design that met the objectives of overall treatment efficiency and CZW. Although our example resulted in a specific V, Q, and d, the model can generate multiple combinations of V, Q, and d that achieve the overall design objectives. Also, when designing an HFTW system for the limiting aquifer, maintaining an equal flow rate in each treatment well is not a strict requirement. Using the figures provided thus far allows the designer to ascertain which Q, V, and d combinations meet requirements. Based on cost considerations, an optimal design can be selected.

A final note on the above design example involves a polishing step to verify that $Q_{dominant}$ is less than Q_{max} for wells operating in a given aquifer. If $Q_{dominant}$ is greater than Q_{max}, then a designer should reiterate using Q_{max}. We also need to point out that an HFTW system enables greater flow rates within the treatment wells compared to single extraction wells. This is due to the reduction of drawdown at the extraction well, due to the presence of the injection well.

4.3.2 Model Analysis with Reactor Volume Constrained to Aquifer Thickness

The large discrepancy between aquifer thickness (8 m) and designed reactor lengths (28 and 36 m in the previous two-well HFTW system example) raises another consideration for a design approach. That is, there may be a requirement to constrain reactor volume (V) based on aquifer thickness. If V is constrained, our application of the design figures is different than before, as we cannot initially specify a CZW. We will now demonstrate how a designer might approach this problem using Figures 4.3 and 4.4. First, let's assume the total reactor length cannot exceed 8 m. A 15.24-cm diameter reactor will therefore have a volume of 146 L. For this problem, we will design for treatment of a 100-m wide plume with an upgradient TCE concentration of 15 mg/L and a required downgradient concentration of 5 µg/L (corresponding to $\eta = .9997$).

We begin by locating the .9997 contour on Figure 4.3. As before, the left-most point on the horizontal portion of the contour represents our $Q_{dominant}$ for viable solutions. On Figure 4.3, this particular location occurs when Vkn/Q = 7 and Q/UBd = 7. Knowing our constrained volume (V = 146 L) enables us to solve for $Q_{dominant}$, which is 12.3 m^3/d. With Q now known and Q/UBd = 7, we can solve for Q/UB and d, which are approximately 75 m and 10.6 m, respectively. Using these values for Q/UB and d, we can use Figure 4.4 to see if we meet the CZW criterion. Figure 4.4 shows that the CZW is approximately 50 m, which is much less than the required 100 m CZW. Note that by using $Q_{dominant}$ in the analysis, we find that the 50-m CZW is the maximum CZW for this particular HFTW configuration. Further reductions in Q could produce viable design combinations that satisfy the overall treatment efficiency (due to increased residence time); however, these reductions in Q will result in a decreased CZW. Therefore, we can conclude that for this particular volume constraint, it is impossible to achieve an overall treatment efficiency of .9997 for a 100-m wide plume. Analysis of the lower aquifer is not necessary as we have determined from the upper aquifer analysis that we cannot attain design objectives within constraints.

Based on the above analysis, it appears a 2-well HFTW system is insufficient to achieve sufficient contaminant destruction for a 100-m wide plume contaminated with 15 mg/L TCE. A modified design, consisting of 4, 6, or 8 wells in a row or multiple rows of wells, may be needed to achieve the overall design objectives. One row of 4, 6, or 8 wells might achieve the design objectives. The analytical model presented by Christ and others (1999) can be used to calculate interflow for a multi-well row, thereby allowing construction of plots for multi-well configurations similar to the two-well plots presented in this chapter. Using these plots, it can be determined if design objectives can be achieved. If objectives are unachievable using a single row of wells, then multiple rows of wells may be needed. Equation (12) can be applied to determine how many rows of wells are needed based on the overall efficiency required. Although our example above concluded with the upper aquifer analysis, we must remember to include the lower aquifer before settling on an HFTW design. The aquifer that most constrains the system must guide the design process.

4.4 GENERIC APPLICATION OF ABIOTIC DEGRADATION KINETICS SUBMODEL

Equation (14), which is the equation for single-pass treatment efficiency, shows that we might not be restricted to first-order degradation kinetics. We might be able to model any order kinetics, so long as we know contaminant concentrations before and after the treatment reactor. Knowing the single-pass treatment efficiency, we can use equation (14) to obtain a generic, lumped Vkn/Q parameter. It is important to note that the parameter k in this case does not represent a first-order degradation rate. Regardless of the actual degradation kinetics, by knowing the single-pass treatment efficiency we can still use equation (14) to obtain values for Vkn/Q that can be used to construct the dimensionless plots presented in this study.

5.0 CONCLUSIONS

5.1 SUMMARY

In this thesis a screening model was developed to show how containment of a chlorinated ethene groundwater plume could be achieved using an HFTW system with in-well catalysts. The screening model incorporated an abiotic degradation kinetic submodel into the groundwater flow model developed by Christ (1997). Graphical contour plots were generated using the model. These contour plots may be used as a preliminary design tool as well as to help determine the applicability of this technology at a particular contaminated site.

5.2 CONCLUSIONS

- **Palladium-based catalysts offer first-order degradation kinetics suitable for use in an in-well reactor.** The extensive literature review discussed many different materials that have been used to degrade chlorinated ethenes. However, except for palladium-based catalysts, the kinetics of the other metals are too slow for in-well application.

- **Catalyst regeneration might overcome the detrimental effects of groundwater biogeochemistry.** Groundwater with elevated levels of carbonate, sulfite, or sulfide species had significant detrimental effects on the catalyst activity. Cycling off the hydrogen supply or pulsing the reactor with sodium hypochlorite seemed to be effective at regenerating the catalyst.

- **The figures presented in this study are useful for quickly screening a contaminated site to see if *in situ* degradation of chlorinated ethenes using an HFTW system is appropriate.** Using the overall treatment efficiency and CZW contour plots in concert gives a designer an idea if this technology will work. With knowledge of certain parameters (groundwater velocity and direction, aquifer thickness, upgradient contaminant concentration, downgradient contaminant concentration requirement, catalyst degradation rate constant, and catalyst porosity), one can quickly determine potential combinations of treatment well pumping rate, separation half-distance, and reactor volume that meet the overall design objectives (overall treatment efficiency and capture zone width).

- **Under typical conditions, this modeling effort has indicated that the HFTW system with in-well catalytic reactors can lower the concentration of a highly contaminated plume (15 mg/L) to within acceptable regulatory levels (5 µg/L).** Designing an HFTW system with an unconstrained reactor volume using the contour plots presented in this study is a relatively straightforward process that reinforces the utility of this model as an initial screening tool.

- **HFTW systems allow for a greater Q_{max} in an aquifer than would be allowable for a single extraction well.** The injection well reduces drawdown at the extraction well, thus enabling greater pumping rates.

- **Constrained conditions require iterative analysis and might lead to a modified design.** Constraints on parameters (e.g. maximum allowable pumping rate or reactor volume) may result in the need for more than 2 wells in a row (to ensure plume containment) or multiple rows of wells (to obtain adequate overall treatment efficiency). If the aquifer being studied is modeled with an upper and lower portion, each must be analyzed independently to determine the limiting aquifer, which must be used to guide the design.

- **The abiotic degradation kinetics submodel could incorporate alternate kinetic models if single-pass treatment efficiencies are known.** Laboratory experiments might provide single-pass treatment efficiencies that might not conform to first-order degradation kinetics. Using equation (14), a designer can obtain a lumped value for Vkn/Q and complete a screening analysis according to the methods outlined in this study.

5.3 RECOMMENDATIONS

- **Investigate long-term reactivity of palladium-based catalysts.** The use of palladium-based catalysts to degrade chlorinated ethenes has not yet progressed beyond the pilot scale testing stage. More research is needed to determine how biogeochemistry interferes with the catalyst, how much the first-order rate constant slows over time, and how effective regeneration techniques are over time.

- **Investigate sonication in conjunction with metallic reductants.** The use of sonication is another emerging field of research that will warrant future study for possible application in-well. The apparent benefits of sonication include prolonged reactivity of the metallic reductants as well as increased rate constants.

- **Perform analysis with a numerical model.** The analytical model used in this study incorporated simplifying assumptions to facilitate analysis. For design purposes a three-dimensional numerical model should be developed which incorporates aquifer heterogeneities and anisotropy.

- **Develop an optimization algorithm.** The range of viable designs for various Q, V, and d (and perhaps, k) will result in a range of operating costs. For large plumes or plumes with high concentration, it is not clear whether it is more cost effective to operate several rows of relatively small reactors or one row of large reactors. An optimization methodology that can account for the cost versus performance trade-offs is needed in order to advance commercialization of this technology.

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REPORT DOCUMENTATION PAGE	Form Approved OMB No. 074-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
March 2000

3. REPORT TYPE AND DATES COVERED
Master's Thesis

4. TITLE AND SUBTITLE

IN SITU TREATMENT OF CHLORINATED ETHENE-CONTAMINATED GROUDWATER USING HORIZONTAL FLOW TREATMENT WELLS

5. FUNDING NUMBERS

6. AUTHOR(S)

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8. PERFORMING ORGANIZATION REPORT NUMBER

AFIT/GEE/ENV/00M-05

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10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

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12a. DISTRIBUTION / AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

12b. DISTRIBUTION CODE

ABSTRACT (*Maximum 200 Words*)

In this study, the literature is reviewed to determine which metal reductants/catalysts might be appropriate for in-well use in a proposed Horizontal Flow Treatment Well (HFTW) system. The HFTW system involves use of two or more dual-screened wells to capture and treat chlorinated solvent contaminated groundwater without the need to pump contaminated water to the ground surface. A model is then presented which couples a chemical degradation submodel, simulating destruction of chlorinated ethenes in an in-well metal reactor, with the steady-state flow field imposed by the HFTWs. Natural and engineered parameters are varied to see how they affect HFTW system performance. Performance is quantified by simulating overall treatment efficiency (comparing contaminant concentrations downgradient and upgradient of the HFTW system) and the width of the contaminant plume captured by the system. Model results are displayed in a format that will facilitate use by designers who need to determine if this innovative technology is applicable for use at a specific contaminated site.

14. SUBJECT TERMS
Groundwater contamination, reductive dehalogenation, catalyst, chlorinated hydrocarbons, *in situ* degradation, abiotic

15. NUMBER OF PAGES
94

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102