A Model to Characterize the Kinetics of Dechlorination of Tetrachloroethylene and Trichloroethylene By a Zero Valent Iron Permeable Reactive Barrier

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Abstract:

A one dimensional, multiple reaction pathway model of the dechlorination reactions of trichloroethylene (TCE) and tetrachloroethylene (PCE) as these species pass through a zero valent iron permeable reactive barrier (PRB) was produced. Three different types of rate equations were tested; first order, surface controlled with interspecies competition, and surface controlled with inter and intra species competition. The first order rate equations predicted the most accurate results when compared to actual data from permeable reactive barriers. Sensitivity analysis shows that the most important variable in determining TCE concentration in the barrier is the first order rate constant for the degradation of TCE. The velocity of the water through the barrier is the second most important variable determining TCE concentration. For PCE the concentration in the barrier is most sensitive to the velocity of the water and to the first order degradation rate constant for the PCE to dichloroacetylene reaction. Overall, zero valent iron barriers are more effective for the treatment of TCE than PCE.
Introduction:

Trichloroethylene (TCE), tetrachloroethylene (PCE), and their degradation daughter products are contaminants of concern because of their adverse health effects and widespread persistence in many drinking water sources (EPA). PCE and TCE are used as industrial solvents, dry cleaning detergents, metal degreasers, and are ingredients in lacquer, printing ink, paper, and varnish. The multipurpose uses of those chemicals and their long term perseverance in the environment, combined with improper disposal techniques has led to the widespread groundwater contamination that exists today. PCE and TCE are completely synthetic compounds known to cause central nervous system depression, trigeminal nerve toxicity, liver damage, kidney damage, and increased risk of cancer (Bull et al., 2002; Caldwell et al., 2005). As regulated by the EPA, drinking water maximum contaminant levels (MCLs) for TCE, PCE, and daughter products are as follows:

Table 1: Contaminants and MCLs as defined by the U.S. EPA (816-F-09-004).

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>MCL (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>.005</td>
</tr>
<tr>
<td>PCE</td>
<td>.005</td>
</tr>
<tr>
<td>Trans 1,2 DCE</td>
<td>.1</td>
</tr>
<tr>
<td>Cis 1,2 DCE</td>
<td>.07</td>
</tr>
<tr>
<td>1,1 DCE</td>
<td>.007</td>
</tr>
<tr>
<td>Vinyl Chloride (VC)</td>
<td>.002</td>
</tr>
</tbody>
</table>

Although TCE and PCE are volatile chemicals (Henry's constants of 11 and 20 bar-mol/l at 25° C respectively) once they seep into aquifers, which generally have very low levels of oxygen, they will persist for years (Bedient et al., 1997). The natural attenuation reaction pathways create the daughter products of 1,1 DCE (dichloroethylene), cis 1,2 DCE, trans 1,2 DCE, and VC all of which are hazardous. Many "weathered" plumes consist mainly of cis 1,2 DCE (Bedient et al., 1997). Non-aqueous TCE and PCE are categorized as DNAPLs (dense non-aqueous phase liquids) which means that they will pool at the bottom of an aquifer above a relatively impermeable layer. This condition often makes pump and treat options for remediation fairly ineffective because a pool of DNAPL on the bottom of an aquifer can be difficult to remove, and the DNAPL pool provides a continuous source of aqueous contamination (Bedient et al., 1997; Powell et al., 1998). As DNAPLs infiltrate into the ground they become trapped in the soil pores, causing a smearing effect as they infiltrate. All these tiny droplets in the soil matrix are also a source of continuous aqueous contamination (Selker et al., 1999).

Permeable Reactive Barriers for Groundwater Remediation
Installation and History:

Permeable reactive barriers (PRBs) were first introduced in the 1990s with the installation of a pilot scale barrier in Borden, Ontario, followed by the first full scale barrier installed in 1995 in Sunnydale, CA (Henderson and Demond, 2007). Since then they have become a common practice with nearly 120 applications worldwide, of which 83 are considered full scale (ITRC, 2005). A permeable reactive barrier
is a trench that is dug and filled with reactive material, and situated perpendicular to groundwater flow so that it intercepts the water flow. As the water flows through the barrier, geochemical reactions are used to effectively break down or remove the contaminants of interest (Figure 1). Many different types and blends of materials have been used in these barriers depending on the targeted contaminant. In the case of chlorinated aliphatics, zero valent iron has been found to dechlorinate these compounds relatively quickly via a reaction pathway that also has the benefit of producing non toxic products. Zero valent iron barriers are cost effective and are cheaper than pump and treat options or air sparging (Quander, 2002). In 1995 the EPA assembled the Remediation Technologies Development Forum and Permeable Reactive Barrier (RTDF/PRB) action team to evaluate and further develop this technology (Quander, 2002). The cost of installation of zero valent iron PRBs in the 1990s ranged from $160,000 to $3 million dollars (Quander, 2002). To date, there have been over 40 zero valent iron barriers installed, most meeting design goals of contaminant removal.

Figure 1: Schematic of a permeable reactive barrier.

There are a variety of installation techniques employed to create PRBs: Funnel and gate, continuous wall, reactor vessel, continuous trench, multiple segments/panels, and trench and gate (Quander, 2002). Hydrologic conditions, cost, and site characteristics determine the type of installation that is most appropriate. In funnel and gate design, impermeable slurry or sheet pile walls are installed to "funnel" the groundwater towards the gate where the reactive barrier wall is located. A continuous wall is installed just as the name implies. These walls have been up to 915 ft long (Permeable reactive barrier installation profiles). Some installations have used circular reactive vessels in which the groundwater is by some means diverted to the reactor. This type of configuration can have the advantage of easy maintenance and the ability to easily exchange reactive material. Multiple segments/panels are reactive walls that are not continuous. The trench and gate is similar to the idea of a funnel and gate, except a
trench is used to encourage water motion towards the gate. The width of these walls has ranged from 9 in. to 6 ft (Permeable reactive barrier installation profiles).

Various sand/iron mixes have been used, however the people who evaluated performance at the Seneca Army Depot, Romulus, N.Y. felt that the performance would have been better and for longer with iron only; so as to have the maximum amount of reactive material per unit volume (Permeable reactive barrier installation profiles). Other possible reasons that design goals were not met at the site in Romulus, N.Y. was larger than expected influent concentrations of TCE and faster pore water velocities through the barrier, both conditions made the 14 inch thick barrier too short for complete treatment (Permeable reactive barrier installation profiles).

The Intersil Semiconductor site in Sunnydale, CA effectively used a pre treatment zone consisting of pea gravel to more evenly spread the water over the barrier surface, and it has had the additional benefit of precipitating out of some of the minerals in the water (Permeable reactive barrier installation profiles). Pretreatment areas are adjacent to the barrier on the upstream side of the barrier wall and consist of a material with a higher hydraulic conductivity than both the native soil and the barrier.

The barriers should be installed after a detailed and thorough hydrologic investigation has been completed. Most barriers have failed due to inaccurate estimations of the direction and magnitude of groundwater flow. At the Kansas City Plant in Kansas City, MO poor hydrologic characterization was attributed to the fact that the site had previously been operating an unsuccessful pump and treat remediation scheme, and the groundwater flow gradients and the plume geometry were not allowed to return to their natural state before the hydrologic investigation took place. This led to an inaccurate representation of subsurface water flow and plume size which resulted in poor performance of the barrier wall because parts of the plume were not captured by the barrier (Permeable reactive barrier installation profiles).

Modeling Iron Barriers:
There is a need to understand and model the complex reactions associated with permeable reactive barriers. In order to design and predict performance of barriers modeling of the chemical reactions and physical movement of the species is necessary. In this thesis a one-dimensional model of the chemical reactions and flow through the iron is created and assessed. Flow through porous media with chemical reaction is governed by the conservation of mass equation also known as the advection dispersion equation (in one dimension):

\[
\frac{\partial C}{\partial t} + \frac{u}{R} \frac{\partial C}{\partial x} - \frac{D_i}{R} \frac{\partial^2 C}{\partial x^2} - r = 0
\]

\[
C = \text{Concentration of solute (mass per volume)}
\]

\[
x = \text{Distance (Length)}
\]

\[
R = \text{Retardation coefficient}
\]
The reaction rate variable "r" in equation #1 is defined by a kinetic expression for the chemical of interest. However there is a debate among researchers about which kinetic expression is the most appropriate for the dechlorination reactions. As a surface mediated reaction there are multiple steps each of which have the ability to control the rate of reaction. The kinetic expression used is dependent on the rate limiting step. Another factor is the multiple reaction pathways which are often neglected in modeling efforts. Neglecting these pathways can result in the under prediction of the production of harmful daughter products (DCE isomers, and VC). Using the appropriate kinetic expression and including the multiple reaction pathways will result in more accurate predictions for barrier performance. The details of the kinetics and reaction pathways are discussed in detail further on in this paper.

Iron Properties:
The selection of iron type can have a large impact on the efficiency of a reactive barrier. Purity, surface area, and grain size are three important qualities that have the ability to affect treatment efficiency. Dechlorination reactions happen at the surface of the iron so greater surface area may allow for a greater rate of reaction by providing more surface sites for reaction (Johnson et al., 1996). However, this is not always the case, it was found that surface area corrected reaction rates were slower when using iron sponge as compared to grey cast iron which had a lower surface area (Ebert et al., 2006). This was attributed to possible mass transfer limitations as many of the surfaces of the sponge are through small pore holes. Another possible reason could be that although the surface area is larger, all of the surfaces may not be available for reaction. BET gas adsorption is commonly used for surface area determinations and provides a reliable measure of surface area. However, the actual surface area may not provide an accurate representation of the actual number of sites for reaction on the iron surface, making surface areas determined this way an inaccurate indication of the reactivity of the iron and "surface corrected" rate constants inaccurate (Venkatapathy et al., 2002). The reason that not all surface may be available for reaction is both related to the purity of the iron and preferred sites for reactions. There are different energies associated with the different sites, for example at kinks and cracks (Johnson et al., 1996).
Table 2: Iron types surface areas and density (Su and Puls, 1999; Suk et al., 2009).

<table>
<thead>
<tr>
<th>Iron Type</th>
<th>Surface Area (m²/g)</th>
<th>Density (g/cm³)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fisher (cast iron)</td>
<td>0.091</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Aldrich (cast iron)</td>
<td>0.192</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Fisher (HCL treated, cast iron)</td>
<td>0.334</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Gotthart-Maier (cast iron)</td>
<td>0.51</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Ispat (iron sponge)</td>
<td>0.62</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Peerless (cast iron)</td>
<td>0.66</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Peerless (different source, cast iron)</td>
<td>0.699</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Master Builders (cast iron)</td>
<td>1.164</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Peerless (cast iron, HCL treated)</td>
<td>1.269</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Connelly (cast iron)</td>
<td>1.38</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Aldrich (HCL treated)</td>
<td>1.93</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Master Builders (HCL treated)</td>
<td>2.136</td>
<td></td>
<td>Su and Puls, 1999</td>
</tr>
<tr>
<td>Connely</td>
<td>1.38</td>
<td>3.2</td>
<td>Suk et al, 2009</td>
</tr>
<tr>
<td>Gotthart-Maier</td>
<td>0.51</td>
<td>3.59</td>
<td>Suk et al, 2009</td>
</tr>
<tr>
<td>Peerless</td>
<td>0.66</td>
<td>2.92</td>
<td>Suk et al, 2009</td>
</tr>
<tr>
<td>Ispat</td>
<td>0.62</td>
<td>2.34</td>
<td>Suk et al, 2009</td>
</tr>
<tr>
<td>20-32 mesh iron turnings, fluka, puriss grade</td>
<td>0.018</td>
<td>3.0125</td>
<td>Suk et al, 2009</td>
</tr>
</tbody>
</table>

Cast iron and sponge iron are two types of iron commonly used. Although manufactured by many different companies the process to make these metal products is similar. Cast iron is ferrous iron alloyed with carbon and silicon (Peerless steel). In the process carbon is turned to graphite and incorporated into the product, the amount of graphite is a function of the manufacturing process. Sponge iron, also called direct-reduced iron (DRI), is produced by the direct reduction of iron ore by a gas consisting mainly of H₂ (g) and CO (g) (ISPAT industries). The material becomes very spongy due to the removal of oxygen and is spheroidal with a porous inner structure. The grain size is generally 0.6-1.6 cm in diameter. ISPAT Industries gives the following specifications for their sponge iron; 85% minimum iron, 92% minimum of metallization, 1% to 2% carbon, 0.02% maximum of sulfur, 0.04% maximum of phosphorus, and a 3.5% combined maximum of silicon, aluminum, calcium and magnesium. The type and quality of the iron product will affect the reactivity of the product largely due...
to differences in available sites for reaction. Column and batch studies have revealed that not all types of iron produce the same reaction rates even when the rate constants are corrected for surface area. But as mentioned before, this could be an artifact of the surface area not being representative of the amount of sites available for reaction. Gotthart Maier AG (Rheinfelden, Germany) manufactures grey cast iron that is columnar and platy in form and has a grain size distribution of 0.3-2 cm or 1-3 cm (Ebert et al., 2006). Master Builders Inc. makes a blend which is a 50/50 mix of 1-2 mm and 0.54-1 mm granules with a surface area of 1.5 m²/g (Reardon, 1995). Electrolytic iron powder used in an experiment by Hara et al. purchased from Dowa Iron Powder Co Ltd, Japan and has a specific surface area of 3.9 m²/g determined by BET analysis. Electrolytic iron powder and atomized iron powder from Wako Pure Chemical Industries Ltd. powders has specific surface areas of 0.47, 0.20, 0.13 m²/g determined by BET analysis (Hara et al., 2005). These iron powders are not employed in barriers because they may leach away but rather have shown promise in injection technology where they are injected into the contaminant plume. Each or these irons vary in their purity, surface area, and porosity; and have been shown to have different reaction rates with TCE and PCE.

The grain size and shape has a large influence on expected flow rates through the barrier. Longer residence times will allow for more treatment time but if the grain sizes are too small the porosity may not be large enough to allow for enough flow causing clogging and mass transport problems. A formula developed by Hazen in 1930 related grain size to hydraulic conductivity (Das, 2008).

\[
k(cm/s) = cD_{10}^2
\]

\[
c = a \text{ shape constant that varies from 1 to 1.5}
\]

\[
D_{10} = \text{effective grain size (10% and finer fraction of sample)(mm)}
\]

Other more reliable correlations have been developed to relate grain size to hydraulic conductivity. However, permeability tests are rather simple and inexpensive to carry out in a lab. The design hydraulic conductivity will be a function of the site characteristics. Groundwater flow through existing barriers is variable ranging from less than 0.1 ft/day to 10 ft/day (Permeable reactive barrier installation profiles). Iron comes in a variety of sizes ranging from less than 0.42 mm to 3 cm, giving a designer flexibility for hydraulic conductivity. This equation and others generally predict greater hydraulic conductivity with larger grain sizes. The uniformity of the material will also affect the conductivity of the material. Well sorted materials will usually have a greater conductivity than poorly sorted material due to the geometry of packing. Sand has been mixed with iron in reactive barriers to increase the hydraulic conductivity as well as decrease the cost of the barrier as sand is generally cheaper than iron. So far there is no conclusive evidence that a sand/iron mix is better or worse than a pure iron barrier.
Some concerns about the longevity of these barriers is the possibility of "clogging" and passivation due to precipitation of hardness ions. The geochemical reactions in a barrier favor precipitation of hardness ions which passivate the iron surface and may have the ability to "clog" the barrier (Venkatapathy et al., 2002). The precipitation of oxides, hydroxides, carbonates, and sulfides are of particular interest because they have been observed on iron extracted from operational barriers (Wilkin et al., 2002). At the Lowery Air Force Base, CO₂ porosity in the barrier decreased by 9.7% in 18 months (Permeable reactive barrier installation profiles). Another way in which these barriers can experience a loss of porosity is due to the build-up of H₂ gas that is produced by the corrosion of iron by water. These gas bubbles which have been detected and viewed in column studies can become trapped in the pore spaces and thus effectively block the void spaces (Orth and Gillham, 1996). The installation of gas vents for the hydrogen gas may increase performance. If clogging does in fact happen, that could change the hydrologic conditions and cause the groundwater to flow around the barrier or increase pore water velocities in the barrier.

Iron corrosion by water is the chemical reaction that creates the favorable environment for precipitation of minerals. When zero valent iron reacts with water, the pH within the barrier increases rapidly and Eh levels drop to less than -100 volts (Orth and Gillham, 1996). In all zero valent barriers installed the pH increases to around 9.5 within the first foot and often times reaches a final pH of 10 or higher (Ebert et al., 2006; Orth and Gillham, 1996). The high pH and low Eh (reducing environment) favor these precipitation reactions. At the Copenhagen Freight Yard in Denmark, total dissolved solids decreased by 600 mg/l in the water that passed through the barrier (Permeable reactive barrier installation profiles). Some of the possible precipitation reactions are as follows:

\[
\text{CaCO}_3(s) \text{ (Aragonite)} \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \quad (3)
\]

\[
\text{Fe}_2(\text{OH})_2\text{CO}_3 \text{ (s)} \leftrightarrow 2\text{Fe}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (4)
\]

\[
\text{Fe(OH)}_2 \text{ (am)} \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O} \quad (5)
\]
Barriers are sinks for carbon, sulfur, calcium, silicon, magnesium, nitrogen, and manganese (Wilkins et al., 2002). All of these species were completely, or near completely removed in 100% of the barriers that were tested (Permeable reactive barrier installation profiles). However, sodium, potassium, and chloride pass through zero valent iron barriers with minimal change in concentration (Yabusaki et al., 2001). Scanning electron microscope (SEM), X-ray diffraction (XRD), transmission electron microscope (TEM), reflected light microscopy, and X-ray photoelectron spectroscopy (XPS) have been used to analyze the types of precipitates formed on the zero valent iron and some of these precipitates include lepidocrocite ($\gamma$-FeOOH), hematite ($\alpha$-Fe$_2$O$_3$), amorphous iron hydroxide (Fe(OH)$_3$) or (Fe(OH)$_2$), magnetite (Fe$_3$O$_4$), marcasite (FeS$_2$), carbonate minerals (aragonite (CaCO$_3$), brucite (Mg(OH)$_2$), iron carbonate hydroxide, and/or siderite (FeCO$_3$), green rust ([Fe$_4$$^{3+}$-Fe$_2$$^{3+}$](OH)$_{12}$][SO$_4$3H$_2$O]), and iron monosulfide (FeS) (Wilkins et al., 2002; Yabusaki et al., 2001). At a pilot site in Elizabeth City, North Carolina, after four years of operation regular coatings of the precipitates on the iron were 10-50 um thick at the up gradient edge of the barrier (the first 8 cm), and then deceased to discontinuous surface coatings less than 5 um thick (Wilkins et al., 2002). Precipitate concentrations are modeled as exponential decay and the integral is used to find the total mass that stays in the barrier (Wilkins et al., 2002). At the barrier in Elizabeth City, NC a net loss of porosity of 0.032 is estimated for the first 2.5 cm of the barrier after four years of operation (Wilkins et al., 2002). In another barrier a porosity loss of 0.062 in the first 2.5 cm was observed after 3.8 years (Wilkins et al., 2002). This "clogging" can decrease the rate of dechlorination in a number of ways. A lowered porosity will increase the pore water velocity because the same amount of water will have to travel through a smaller area, and the pressure gradient may increase if "pooling" occurs on the up gradient side. Lower porosity or an increased pressure gradient will linearly increase the pore water velocity. This can be seen mathematically with the equation for pore water velocity through porous media:

\[
\nu = \frac{K\n h}{n} 
\]

\[
\nu = \text{Pore water velocity (}$\frac{L}{T}$\text{)}
\]

\[
K = \text{Hydraulic conductivity (}$\frac{L}{T}$\text{)}
\]

\[
n = \text{Porosity}
\]

\[
h = \text{Hydraulic head (}$L$\text{)}
\]

A larger pore water velocity will lower the residence time of the water in the barrier which may not allow enough time for adequate treatment. Another issue is that the precipitates on the surface of the iron passivate the iron by reducing the number of active sites which effectively forces target species to travel further to reach reactive sites (mass transfer limitations) (Venkatapathy et al., 2002).
**Microbial Activity:**

Microbial activity in zero valent iron barriers has been scantly reported on but should not be overlooked as it has been found that microbes which exist in almost all environments, have the ability to increase or decrease the rate of reaction by many orders of magnitude. Dechlorinating organisms are widespread in the subsurface (ITRC, 2005). At Caldwell Trucking, a site in New Jersey, guar gum was used to stabilize the trench walls during construction and inadequate time allowed for the breakdown of the gum caused increased microbial activity (Permeable reactive barrier installation profiles). This type of microbial activity was thought to hinder contaminant break-down however, reasons for this conclusion was not well explained.

There is evidence that zero valent iron barriers may support sulfur reducing bacteria which thrive at low temperature, anoxic reducing conditions, and feed on H₂ (Wilkins et al., 2002). Mass flux of 0.803 kg/m²-yr of sulfur to a reactive barrier is similar to the flux of sulfur to a compost barrier suggesting that compost and zero valent iron may be similar in their capability of supporting sulfate-reducing bacteria. The zero valent iron can provide these microbes with plentiful amounts of hydrogen through the iron corrosion reactions. In Avigliana, Italy, core samples taken in 2007, 3 years after the installation of an iron barrier, showed strong evidence of methanogens and sulfate reducers (Zolla et al., 2009). Sulfate decreased from an average of 177.5 mg/l (average of 2 sampling wells) up gradient of the barrier to 23.45 mg/l down gradient of the barrier. Also no sulfide was detected which would be the reduced version of sulfate. Along with the absence of sulfate or sulfide down gradient of the well, dissolved methane increased from an average of 25.15 ug/l to above 5000 ug/l, both in the barrier and down gradient of the barrier (Zolla et al., 2009). The only explanation for the production of methane is the presence of methanogens. Residual guar gum was detected on the iron left from the installation, this may have increased the microbial activity in this barrier by providing an organic food source. Microbial activity can have a huge effect on the degradation rate of many organic molecules and in some cases has proven to be the most important factor in determining the rate of reaction. To date the role of microbes in iron barriers is not well understood due to a lack of investigation into this very complicated topic.

**Theoretical Background:**

The performance of PRBs is dependent on the relationship between many independent and dependent homogeneous and heterogeneous reactions. TCE and PCE can dechlorinate via multiple reaction pathways. The reaction mechanisms of these pathways are hydrogenolysis, beta-elimination, alpha-elimination, and hydrogenation (Arnold and Roberts, 2000). Other reactions of interest are the precipitation and complexation reactions of the minerals in the groundwater as these reactions have the ability to compete for reaction sites, passivate the reactive material, and "clog" the pore spaces.
Iron Corrosion, Precipitation, and Complexation:
The first reaction of interest is the corrosion of Fe\(^0\) by water. This reaction is what creates the geochemical situation which allows many of the other reactions to proceed. The corrosion of iron can happen in two ways: oxic or anoxic. Aquifers generally have a very low amount of dissolved oxygen in the water so the anoxic corrosion reaction is the one that most often occurs in PRBs. The reaction is as follows:

\[
\text{anoxic conditions: } \text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \quad (7)
\]

The hydrogen produced in this reaction can enter the system in three different ways: The gas phase, the aqueous phase which is solubility limited (7.515*10\(^{-4}\) mol/kg for pure water at 100kPa H\(_2\) at 25\(^{\circ}\)C), and the solid phase, by directly attaching to the iron (Reardon, 1995). Hydrogen can bond to iron at dislocation spots within the iron lattice, and possibly within micro fractures (Reardon, 1995). The buildup of pressure in these lattice structures is hypothesized to cause the embrittlement and blistering of iron that has been observed in anaerobic environments (Reardon, 1995). The rate of hydrogen uptake at the iron surface is proportional to the square root of the hydrogen's partial pressure which indicates that H\(_2\) disproportionates and attaches to the iron as single molecules (Reardon, 1995). As seen in the above reaction, 2 moles of OH\(^-\) ions are produced for every mole of Fe\(^0\) consumed. This reaction quickly affects the water equilibrium reactions and causes an increase in the pH. This is in agreement with data collected from PRBs. Within the first 8 to 10 cm of a PRB the pH rises at least 2 pH units (Permeable reactive barrier installation profiles). The increased amount of OH\(^-\) ions will then react with dissolved carbonic acid, and bicarbonate species to produce carbonate ions (Reardon, 1995).

\[
\text{H}_2\text{CO}_3^- + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + 2\text{H}_2\text{O(l)} \quad (8)
\]

\[
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O(l)} \quad (9)
\]

Buildup of carbonate ions will eventually result in the precipitation of carbonate solid phases (Reardon, 1995). This build-up can passivate iron surfaces and reduce flow rates due to a reduction of porosity and permeability. If the carbonate is exhausted it is possible for the iron itself to precipitate as Fe(OH)\(_2\) which is fairly stable in aquifer conditions of low oxygen and temperature, but is thermodynamically predicted to convert to magnetite (Fe\(_3\)O\(_4\)). In a study by Reardon, Sievert’s Law (R=kP\(_2\)\(^{0.5}\)) was used to predict iron corrosion rates and H\(_2\)(g) evolution. It was found that corrosion rates varied from 0.1-0.7 mmol/kg-d. Corrosion is a self inhibiting process because as corrosion occurs, the resulting precipitates passivate the iron surface, protecting those areas from further corrosion. These surface coatings have the ability to inhibit the dechlorination reactions by preventing the contaminants from coming into contact with the iron. Figures 3 is a theoretical diagram adapted from Pourbaix which display the influence of pH and electrode potential on passivation, corrosion, and immunity of iron in water (Pourbaix, 1966). The derivation of these diagrams were done only considering passivation by Fe(OH)\(_2\) and Fe(OH)\(_3\). Other constituents in groundwater can precipitate out of the water due to pH and electrode potential and would influence these diagrams. However, the different areas of corrosion, passivation, and immunity would not be expected to change that dramatically. It can be seen that at typical barrier conditions of a pH 9-10 and a E of -100mV to -550mV, the iron would be in a state of...
passivation. Considering that the iron is being passivated, the question of kinetics becomes very important. In a model predicting the rates of passivation based on empirical data, it is predicted that at some point the pH would drop back down to ambient pH due to complete passivation and thus the end of the corrosion reaction which causes the increase in pH (Jeen et al., 2007). Their model does not then consider the solubility of the passivating layer, which if dissolved would restart the corrosion passivation cycle again and possibly further the longevity of the barriers effectiveness.

Figure 3: Theoretical conditions for corrosion, passivation, and immunity of iron considering as solid substances only Fe, Fe(OH)$_2$ and Fe(OH)$_3$. Adapted from Pourbaix, 1966.

Characterization of the precipitates found on iron in PRBs is influenced by the treatment of the samples after collection (Phillips et al., 2003). Mineralogical composition of precipitates can change if they are allowed to be oxidized. Samples that are handled improperly may give an inaccurate representation of the precipitates. Green rusts which are double layered Fe$^{2+}$ and Fe$^{3+}$ hydroxysalts are unstable in aerobic conditions and will oxidize very quickly (Genin et al., 2001). In a study of iron samples taken from a reactive barrier, green rusts were only detected in acetone-dried samples that were analyzed immediately (Phillips et al., 2003). The green rusts disappeared from these samples within the first 8 hrs and were not observed in any air and oven dried samples. Green rusts in aerobic conditions transform to goethite ($\alpha$-FeOOH), lepidocrocite ($\gamma$-FeOOH), ferrihydrite (Fe$_2$O$_3$$\cdot$2FeOOH$\cdot$2.6H$_2$O), maghemite ($\gamma$Fe$_2$O$_3$), or magnetite (Fe$_3$O$_4$) (Phillips et al., 2003). Accurate calculations of the mass of green rusts in barriers can be very important because they are known to be reactive and have an effect on the transport of certain constituents in water (Genin et al., 2001).
**Reaction Pathways:**

**Hydrogenolysis:**

One pathway for TCE and PCE degradation is hydrogenolysis. Hydrogenolysis is an important organic chemistry reaction mechanism that involves the cleavage, with hydrogen, of various other bonds (Nishimura, 2001). However hydrogenolysis reactions generally do not happen under ordinary conditions and require high pressures, high temperatures, or a catalyst to make them occur (Nishimura, 2001). In this situation the catalyst is the zero valent iron. Experimentally this has been shown to be the unfavored pathway. The bond that is cleaved in this situation is the C-Cl bond which has a bond energy of 441 kJ/mol (Nishimura, 2001). Aliphatically bound halogens are resistant to hydrogenolysis at acidic or neutral conditions which is not the case in PRBs (Nishimura, 2001). For vinyl chloride degradation, hydrogenolysis is the only observed pathway; in batch tests neither acetylene nor the coupling products affiliated with the reduction of acetylene were observed (Arnold and Roberts, 2000). The hydrogenolysis of cis 1,2 DCE and trans 1,2 DCE produces vinyl chloride. However, in batch studies vinyl chloride only accounts for a maximum of 7% and 1% of the products respectively (Arnold and Roberts, 2000). This is an indication that hydrogenolysis is not the favored pathway for cis and trans 1,2 DCE degradation. Below are the hydrogenolysis reactions involved in a zero valent PRB treating chlorinated hydrocarbons:

\[
\begin{align*}
C_2Cl_4+H_2 & \rightarrow C_2Cl_2H+H^++Cl^- \quad \text{(PCE to TCE)} & (10) \\
C_2Cl_3H+H_2 & \rightarrow C_2Cl_2H_2+H^++Cl^- \quad \text{(TCE to trans, cis 1,2-DCE or 1,1 DCE)} & (11) \\
C_2Cl_2H_2+H_2 & \rightarrow C_2ClH_3+H^++Cl^- \quad \text{(trans or, cis 1,2-DCE to vinyl chloride)} & (12) \\
C_2Cl_2+H_2 & \rightarrow C_2ClH+H^++Cl^- \quad \text{(dichloroacetylene to chloroacetylene)} & (13) \\
C_2ClH+H_2 & \rightarrow C_2H_2+H^++Cl^- \quad \text{(chloroacetylene to acetylene)} & (14) \\
C_2ClH_3+H_2 & \rightarrow C_2H_4+H^++Cl^- \quad \text{(vinyl chloride to ethylene)} & (15)
\end{align*}
\]

There have been many modeling attempts to aid in the understanding of the complex geochemical reactions that occur in a PRB. Many of the models ignore the hydrogenolysis reaction pathway because experimental evidence has shown that it is not the dominate pathway. However, the hydrogenolysis pathway is important to consider because it is by this route that most of the toxic daughter products are produced, possibly making the barrier less effective. By neglecting this pathway a less conservative choice of barrier thickness may be made making residence times inadequate for the treatment of the daughter products.

**Beta-elimination:**

Beta-elimination involves the exchange of electrons; zero valent iron (a very strong reducer) gives two electrons to the chlorinated species which then releases two chloride ions and Fe$^{0}$ becomes Fe$^{2+}$. This is the pathway that is responsible for the creation of different hydrocarbons. Beta-elimination is the dominate pathway for dechlorination accounting for as much as 87% of PCE, 97% of TCE, 94% of cis 1,2
DCE, and 99% of *trans* 1,2 DCE dechlorination (Arnold and Roberts, 2000). This conclusion is based on the fact that most all of the products resulting from TCE and PCE reacting with iron are ethene, ethane, and smaller amounts of C₂-C₆ hydrocarbons which is consistent with the beta-elimination pathway (Arnold and Roberts, 2000; Orth *et al*., 1996). Very little (3%-3.5% of initial TCE concentration) of the dechlorination byproducts are a DCE isomer or vinyl chloride, which are the expected products of the hydrogenolysis pathway. The products from beta-elimination of PCE and TCE are highly reactive chloro- and dichloro-acetylene (as seen below). 100% of the chloro- and 76% of the dichloro-acetylene undergo the hydrogenolysis reaction described above to become lesser or finally dechlorinated acetylenes (Arnold and Roberts, 2000). The preference of this pathway is independent of water chemistry and iron type. The following reactions are the reductive beta-elimination reactions:

\[
\text{Fe}^0 + \text{C}_2\text{Cl}_4 \rightarrow 2\text{Cl}^- + \text{C}_2\text{Cl}_2 + \text{Fe}^{2+} \quad (\text{PCE to dichloroacetylene}) \tag{16}
\]

\[
\text{Fe}^0 + \text{C}_2\text{Cl}_3\text{H} \rightarrow \text{C}_2\text{ClH} + 2\text{Cl}^- + \text{Fe}^{2+} \quad (\text{TCE to chloroacetylene}) \tag{17}
\]

\[
\text{Fe}^0 + \text{C}_2\text{Cl}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2 + 2\text{Cl}^- + \text{Fe}^{2+} \quad (\text{trans, or cis} \, 1,2 \text{ DCE to acetylene}) \tag{18}
\]

**Alpha-elimination:**

Reductive alpha-elimination is similar to beta-elimination except it is the alpha C-Cl bonds that are affected instead of the beta C-Cl bonds. Through batch studies it was found that modeling the dechlorination reaction of 1,1 DCE as a series of hydrogenolysis reactions (1,1 DCE \rightarrow vinyl chloride \rightarrow ethylene) was not successful when the rate of the vinyl chloride reaction was restricted to rates determined by independent studies of vinyl chloride (Arnold and Roberts, 2000). During alpha-elimination the first step would be a 2 electron reduction of 1,1 DCE to a metal stabilized carbenoid (H₂C=C), followed by the addition of 2 protons to produce ethylene. An alternative would be the rearrangement of the carbonoid to form acetylene (Arnold and Roberts, 2000). In batch studies of 1,1 DCE degradation, acetylene or any affiliated hydrocarbons were not observed so the pathway to ethylene is the favored route.

\[
\text{C}_2\text{Cl}_2\text{H}_2 + 2\text{H}^+ \rightarrow \text{C}_2\text{H}_4 + 2\text{Cl}^- \quad (1,1-\text{DCE to ethylene}) \tag{19}
\]

**Hydrogenation:**

Hydrogenation is another important reaction mechanism in PRBs. Hydrogenation is the addition of hydrogen to a compound by reducing the triple bond between the two carbons (Arnold and Roberts, 2000). In the model it will be assumed that ethane is the only product of ethylene degradation as found by Arnold and Roberts. Acetylene reacts quickly to form ethylene, however other products were also observed in batch reactions of Fe⁰ and acetylene (Arnold and Roberts, 2000). Acetylene is known to couple on reactions on metals in the gas phase. Products from this coupling include: C₃, C₄, C₅, and C₆ hydrocarbons which accounted for about 10% to 15% of the total mass balance of carbon (Arnold and Roberts, 2000). For modeling purposes the formation of this wide array of hydrocarbons will be ignored because they are not major factors in the design of PRBs. As seen below dichloroacetylene will sometimes form *trans* and *cis* 1,2-DCE. Fortunately in batch reactions hydrogenolysis seemed to be the
preferred pathway with chloroacetylene and its subsequent products being the major constituents detected (Arnold and Roberts, 2000). Below are the hydrogenation reactions of interest:

\[
C_2Cl_2 + H_2 \rightarrow C_2Cl_2H_2 \quad \text{(dichloroacetylene to trans, or cis 1,2-DCE) (20)}
\]

\[
C_2H_2 + H_2 \rightarrow C_2H_4 \quad \text{(acetylene to ethylene) (21)}
\]

\[
C_2H_4 + H_2 \rightarrow C_2H_6 \quad \text{(ethylene to ethane) (22)}
\]

Figure 4: Reaction pathways for dechlorination of chlorinated aliphatics and associated kinetic rate constant symbols.

**Kinetics:**

It has been realized that the dechlorination reactions happen at the surface of the iron and therefore the amount of surface area available for reaction can influence the rate of reaction. As a surface mediated reaction there are multiple steps that take place and thus the reaction may be rate limited in any one of these steps. The observed rate constant of a surface mediated reaction will be that of the slowest step when the reactions are in series (Weber and DiGiano, 1996). There are four important steps that have the ability to control the kinetics of the reaction: Mass transfer to the site; adsorption of the species to the reactive site(s); the reaction at the surface of the site(s); and desorption of the products (Arnold and Roberts, 2000; Johnson et al., 1996) (Figure 5). Sorting out which mechanism is controlling the rate of reaction is not an easy task, a further complicating factor is that the rate controlling step may change under different physical situations. For example mass transfer may not be a rate limiting step in a stirred batch reactor at 2000 rpms, but at a lower speed of 200 rpms, mass transfer may limit the rate of reaction. When an apparent rate of reaction switches from one order to
another, it is a good indication that the reaction is surface mediated and is being controlled by the rate of reaction on the surface of the media. This will be demonstrated through a derivation of the Langmuir-Hinshelwood approach.

Figure 5: Surface mediated beta elimination reaction of PCE and zero valent iron. Other beta and alpha elimination reactions occur in a similar way.

From the concepts presented in Figure 5 the Langmuir-Hinshelwood model for rate analysis can be derived. The first three steps describe the disappearance of the reactant. Note subscript "r" denotes reactant and subscript "p" denotes the product.

Mass transfer (mt) out of the bulk solution and into interfacial "film":

$$ r_{mt,r} = -k_{mt,r}a(C_{bulk,r} - C_{film,r}) $$  \hspace{1cm} (23)

Adsorption (ads):

$$ r_{ads} = k_{a,r}C_{bulk,r}(Q_r - q_r - q_p) - k_{d,r}q_r $$  \hspace{1cm} (24)

First order surface reaction (irreversible):

$$ r = -kq_r $$  \hspace{1cm} (25)

The next two steps describe the appearance of the product into the bulk solution:

Desorption (des) of the product:

$$ r_{des} = -k_{a,p}C_{bulk,p}(Q_p - q_r - q_p) + k_{d,p}q_p $$  \hspace{1cm} (26)

Mass transfer (mt) of the product into bulk solution:
When the system is at steady state, the reaction rates may be equated with one another (Fogler, 1999; Weber and DiGiano, 1996):

\[ r_{mt,p} = -k_{mt,p}a(C_{bulk,p} - C_{film,p}) \]  

(27)

\[ k_{mt} = \text{Mass transfer rate constant (t}^{-1}) \]

\[ k = \text{Reaction rate constant (t}^{-1}) \]

\[ k_a = \text{Adsorption constant (t}^{-1}) \]

\[ k_d = \text{Desorption constant (t}^{-1}) \]

\[ Q = \text{Number of sites available for sorption (mass/mass)} \]

\[ q = \text{Amount sorbed (mass sorbed/mass iron)} \]

\[ C_{bulk} = \text{Concentration in the bulk solution} \]

\[ C_{film} = \text{Concentration in film surrounding the iron} \]

\[ a = \text{Specific surface (area/mass) of catalyst} \]

When the system is at steady state, the reaction rates may be equated with one another (Fogler, 1999; Weber and DiGiano, 1996):

\[ r_{mt,r} = r_{ads} = r = r_{des} = r_{mt,p} \]  

(28)

This allows for useful manipulation of the equations so that rate expressions may be written as a function of measurable parameters. This approach to determine the mechanism in heterogeneous catalytic reactions is called the Langmuir-Hinshelwood approach because it was proposed by Hinshelwood and is based on Langmuir principles for adsorption (Hinshelwood, 1940). This approach is also sometimes called the Langmuir-Hinshelwood-Hougen-Watson approach because it was popularized by Hougen and Watson (Fogler, 1999). When equating these rates so that the equations may be manipulated there are quite a few assumptions that need to be made a priori. One assumption is that the surface is uniform and therefore there is the same amount of energy for reaction at each site. This is known to be untrue as it has been proven that there are different energies associated with the surface of iron (i.e. in cracks and dislocation spots) (Ehrlich, 1962). Despite the inaccuracy of this simplification, the general Langmuir isotherm has been shown to fit PCE and TCE sorption and is useful in making approximations for the expected behavior of these two chemicals (Burris et al., 1995). Another issue with the sorption model is that constituents may sorb to the surface in a variety of ways and an assumption of the number of sites the constituent binds to is made before. The general Langmuir competitive model is as follows with adsorption to one site:

\[ q_r = \frac{Q_r \beta_r C_{film,r}}{1 + \beta_r C_{film,r} + \sum_{p=1}^{n_p} \beta_p C_p} \]  

(29)
\[ \beta = \frac{k_a}{k_d} \]  

To simplify the model further the initial rate data will be considered therefore competition with the products may be neglected. Also assuming equilibrium adsorption prevails than \( C_{\text{film},r} = C_{\text{equilibrium},r} \). If it is speculated that mass transfer is the rate limiting step the equations may be solved as such:

First the mass transfer rate is equated with the reaction rate:

\[ r = k_{mt,r} \times a \times (C_{\text{bulk},r} - C_{e,r}) = k_q r = k \frac{Q_r \beta_r C_{e,r}}{1 + \beta_r C_{e,r}} \]  

Next a Damkohler number is defined to relate the maximum surface reaction rate to the maximum mass transfer rate. At these maximum rates the equilibrium concentration of the reactant in the fluid would essentially be zero (Weber and DiGiano, 1996).

\[ \varphi_{da} = \frac{k Q_r}{k_{mt,r} a C_{\text{bulk},r}} \]  

Combining the Damkohler number and equation 31, and then expressed in dimensionless form:

\[ 0 = c_r^2 + c_r (\beta_r^0 + \varphi_{da} - 1) - \beta_r^0 \]  

\[ c_r = \frac{C_{e,r}}{C_{\text{bulk},r}} \]  

\[ \beta_r^0 = (\beta_r C_{\text{bulk},r})^{-1} \]  

The solution to this quadratic equation is as follows:

\[ c_r = \frac{(-\beta_r^0 - \varphi_{da} + 1) \mp \sqrt{[\beta_r + \varphi_{da} - 1)^2 + 4 \beta_r^0]^{0.5}}}{2} \]  

If the boundaries of this solution is examined, when mass transfer is the limiting process \( \varphi_{da} \gg 1 \), and \( c_r \approx 0 \). The rate observed is then given by equation 31 with \( C_{e,r} \) being equal to zero.

\[ r_{\text{observed}} = k_{mt,r} a C_{\text{bulk},r} \]  

If the reaction rate is controlling the observed rate of reaction than \( \varphi_{da} \ll 1 \), and \( c_r \approx 1 \). This means that the bulk and interface concentrations are equal and thus equation 31 can be rewritten as such:

\[ r = k \frac{Q_r \beta_r C_{\text{bulk},r}}{1 + \beta_r C_{\text{bulk},r}} \]  

From the above equations it can be seen that mass transfer control will lead to an observed reaction rate that is first order. If the rate of reaction at the surface is controlling the overall rate then a variable order reaction rate will be observed that is dependent on the bulk phase reactant concentration which
has been observed for TCE degradation (Wust et al., 1999). This apparent shift in reaction order is sometimes called disguised kinetics. By linearizing this equation and by varying the initial concentrations of the reactant, k may be found if Q and $\beta_r$ are known.

A kinetic model for reactions based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) that accounts for interspecies competition and reactions that are limited at the surface will be compared to a pseudo first order kinetic model that is surface corrected with no competition. The LHHW model that was used to determine the rate constants and adsorption parameters was described and tested by Arnold and Roberts (2000):

$$\frac{dC}{dt} = \frac{(\sum_{j=1}^{N_j} ks)KC}{1 + \sum_{m=1}^{N_m} K_mC_m}$$

$$C_{(m)} = \text{concentration, (m) for competing species (mass/vol)}$$

$$k = \text{rate constant (t}^{-1})$$

$$s = \text{abundance of reactive sites (mass/L)}$$

$$K_{(m)} = \text{adsorption constant for Langmuir type adsorption for competing species (mass}^{-1})$$

$$N_j = \text{the number of primary products formed from the parent}$$

$$N_m = \text{the total number of species that inhibit the reaction}$$

It can be seen that equations 38 and 39 are the same where:

$$s = Q, \text{ and } K = \beta$$

"k" and "s" are lumped together and experimentally cannot be solved for independently (Arnold and Roberts, 2000). If inter and intra species competition are neglected the expression becomes:

$$\frac{dC}{dt} = (\sum_{j=1}^{N_j} ks)KC$$

This is analogous to a first order rate reaction because k, s, and K are constants. Data from many other kinetic studies show that these reactions fit a pseudo first order model well (Orth and Gillham, 1996; Su and Puls, 1999; Ebert et al., 2006; Hara et al., 2005; Johnson, 1996). However the pseudo first order kinetics does not always accurately describe the reaction, a few scientists have used mixed order kinetic models (first and zero) because first order alone did not describe the data well enough (Wust et al., 1999). Through comparing a first order model to the a competitive model described above, it will be discernable if the simplification of using a first order model introduces large amounts of error. By ignoring competition between reacting species, the amounts of unwanted daughter products (i.e. VC, and isomers of DCE) may be underestimated.
Scientists whom have employed first order kinetic rate constants acknowledged the effect of the iron by normalizing the rate constants by surface area. Surface area corrected rate constants can then be applied to different sized iron media with different surface areas. However, surface areas may not represent the true amount of sites available for reaction, making reaction rates that are surface corrected inaccurate if a different type of iron is used. BET analysis or other such gas adsorption tools are used to determine surface area. While BET analysis gives an accurate result for the surface area it does not necessarily mean that all of those surfaces are reactive. This is because different types of iron have different amounts of impurities and surface structures, so it is possible for an iron with a smaller surface area to have more sites for reaction than a different type of iron with more surface area. The problem is that it that there are not many reliable techniques that allow for the quantification of reactive sites. One model developed for the quantification of surface sites is called kinetic iron model (KIM) (Delvin, 2009). This model is based on the LHHW model but in its derivation the amount of surface sites and the first order rate coefficient are not lumped together allowing for the determination of each of these values through experimentation. This model is relatively new and therefore there have not been many experiments testing its effectiveness. However surface corrected rate constants should be accurate if the same type of iron is used as was used in the experiment in which the rate constant was derived.

The debate on whether the reactions are controlled by mass transfer or reaction at the surface has important implications about which kinetic model is most appropriate. There is a body of evidence that indicates that the kinetics of dechlorination (with respect to beta-elimination) is limited by the rate of reaction at the iron surface (Schere et al., 1997; Arnold and Roberts, 2000). The large variability in reaction rates of various chlorinated solvents, when they have similar diffusivities, seemingly points to kinetic limitations related to the reaction and not mass transport (Schere et al., 1997). Conditioning has a large effect on the rate of reaction which is further evidence of surface reaction rate limitations. If a reaction is mass transfer limited, coatings on the surface of the iron would be expected to decrease the rate of reaction a little, but for reaction controlled by the rate of reaction, surface coatings will have a large effect, which is what has been documented for dechlorination reactions (Schere et al., 1997). Effects of initial concentration on rates of reactions also support reaction limitations; pseudo first order rate constants decreased with increasing initial concentrations by a factor of 6 for PCE, 10 for TCE, and 5 for cis 1,2 DCE for initial concentrations between 4 and 175 uM (Arnold and Roberts, 2000). This type of dependence on initial concentrations is indicative of surface reaction limitations as shown in the derivation of the LHHW model.

In an experiment using a Fe⁰ electrolytic plate it was found that the corrosion potential increased positively from -510 mV to -380 mV (+/- 10 mV) when PCE was added. This result was reproducible and shows that PCE is the oxidant in this system (Schere et al., 1997). From these experiments it was shown that the current density on the iron plate only varies slightly with changes in rotation rate when PCE is the major reactant, but varies greatly for reduction of O₂ which has previously been shown to be mass transfer limited (Schere et al., 1997). This is further evidence for surface reaction rate limitations. However, the possibility of mass transfer limitations cannot be completely ignored especially in the situation of a reactive barrier that does not have the advantage of highly controlled mixing rates.
may be why most column studies find that first order kinetics fit the data well (i.e. mass transfer controlled) (Orth and Gillham, 1996; Su and Puls, 1999; Ebert et al., 2006; Hara et al., 2005; Johnson, 1996).

Column studies found very little change in reaction rates for TCE over initial concentration ranges of 1.27 to 61 mg/l, indicating that the reaction is pseudo first order and the rate is independent of the initial concentrations (Orth and Gillham, 1996). Arnold and Roberts did not find the reaction rates to be the same at differing initial concentrations due to intra species competition. In these tests, the highest concentration of TCE and PCE was 0.175 mg/l, way below the concentrations tested by Orth and Gillham. It was also found by comparing different models to dechlorination data that at low TCE concentrations the dechlorination is reaction limited, but at high loading rates (TCE concentration per active site) the reaction is sorption limited due to intra species competition for reactive sites (Venkatapathy et al., 2002). Interspecies competition has also been observed (Allen-King et al., 1996). In batch experiments by Arnold the target species was introduced at a concentration of 4 μM and the competitor at a concentration of 100-200 μM, it was found that the reaction rate of the target slowed down by a maximum factor of two.

Not all of the species involved are controlled by the rate of the reaction. Vinyl chloride and ethylene did not display changes in reaction rates with varying initial concentrations, but rather were adsorption limited (Arnold and Roberts, 2000). For adsorption the following trend was observed: Alkynes > PCE > TCE > DCEs > vinyl chloride and ethylene (Arnold and Roberts, 2000). The more highly chlorinated species have a higher affinity for sorption which can be mistaken for faster reaction rates. If vinyl chloride is sorption limited it may be an important factor in the thickness of a barrier. Even though more highly chlorinated species may degrade rather quickly, it is also important that vinyl chloride, which is toxic, has enough time to be completely degraded.

Reaction rates of chlorinated ethylenes decreased with increasing halogenation (Arnold and Roberts, 2000). In other studies it was found that the reactivity of chlorinated ethylenes increased with increasing halogenation (Mathesen and Tratnyek, 1994; Johnson, 1996). However, the study by Arnold and Roberts was the most rigorous; by using concentrations of species that are comparable to what would be encountered in groundwater (less than 1 mg/l), by including intra species competition in the model for determining rate constants, and by using a more pure iron with little to no carbon impurities. The carbon impurities can act as sorptive sinks for some of the species, if this is not accounted for rate data will be inaccurate (Allen-King et al., 1997; Burris et al., 1995). To this end many of the other experiments could only account for 73% of carbon on their mass balances (Orth and Gillham, 1996). Although some of this carbon may have gone undetected as longer chained hydrocarbons, it is likely that some of the species were sorbed on to carbon sites. In the study by Arnold and Roberts 100% of the carbon was accounted for in the mass balance on carbon. In a study by Burris et al., it was found that sorption was greater for more highly halogenated species and could therefore be mistaken for rapid reaction if sorption is not carefully accounted for (Burris et al., 1995). It is proposed by Arnold and Roberts that the rate limiting mechanism may involve the change of the C-Fe bond from a π-bond to a di-σ-bond (Arnold and Roberts, 2000). A reaction which transfers all the electrons simultaneously is of
very low probability so it is proposed that the TCE or PCE remains "attached" to the surface of the zero valent iron long enough to completely dechlorinate.

The amount of iron per volume may also effect the rate of reaction. It has been shown that there may be a linear proportional relationship between metal loading and the reaction rate. Su and Puls found a positive linear relationship between the TCE reduction rate constant and surface area per liter using Peerless iron (Su and Puls, 1999). This trend was also observed by Matheson and Tratnyek using Fisher iron (Matheson and Tratnyek, 1994). This highlights the importance of providing the largest amount of iron/volume but without compromising mass transport. Results by Arnold and Roberts (2000) found that the pseudo first order rate constants are only proportional to metal loading over a limited range (0-0.5 g per 160 ml). Using Iron as the only material in the barrier provides the maximum amount of reactive surfaces for the dechlorination reactions. In the long term, sand may help to reduce clogging by providing a non-reactive material which may help maintain the integrity of the initial porosity. However, if the iron is passivated the barrier will still become ineffective. Table 3 is a list of reaction rates from Arnold and Roberts kinetic experiments. Table 4 is a list of surface normalized pseudo first order reaction rates. The range in the rate constant for TCE degradation is rather large varying by 3 orders of magnitude.
Table 3: Rate constant variables from Arnold and Roberts 2000.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant k symbol</th>
<th>ks uM/hr Values Used in Model From Arnold, 2000</th>
<th>K symbol</th>
<th>K(uM⁻¹) adsorption constant. Values used in model from Arnold, 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE to TCE</td>
<td>k₃</td>
<td>3.63(+/-0.52)*10⁻³</td>
<td>Kₚ</td>
<td>0.058(+/-0.014)</td>
</tr>
<tr>
<td>TCE to transDCE</td>
<td>k₆</td>
<td>7.72(+/-9.68)*10⁻⁴</td>
<td>Kₜ</td>
<td>0.065(+/-0.009)</td>
</tr>
<tr>
<td>TCE to cisDCE</td>
<td>k₅</td>
<td>5.91(+/-0.53)*10⁻³</td>
<td>Kₜ</td>
<td>0.065(+/-0.009)</td>
</tr>
<tr>
<td>TCE to 1,1 DCE</td>
<td>k₄</td>
<td>4.42(+/-0.45)*10⁻³</td>
<td>Kₜ</td>
<td>0.065(+/-0.009)</td>
</tr>
<tr>
<td>TransDCE to Vinyl Chloride</td>
<td>k₁₂</td>
<td>5.32(+/-15.1)</td>
<td>Kₖ</td>
<td>0.016(+/-0.002)</td>
</tr>
<tr>
<td>CisDCE to Vinyl Chloride</td>
<td>k₁₁</td>
<td>0.14(+/-0.06)</td>
<td>Kₑₑ</td>
<td>0.029(+/-0.003)</td>
</tr>
<tr>
<td>PCE to Dichloroacetylene</td>
<td>k₁</td>
<td>2.48(+/-0.46)*10⁻²</td>
<td>Kₚ</td>
<td>0.058(+/-0.014)</td>
</tr>
<tr>
<td>TCE to Chloroacetylene</td>
<td>k₂</td>
<td>0.33(+/-0.03)</td>
<td>Kₜ</td>
<td>0.065(+/-0.009)</td>
</tr>
<tr>
<td>TransDCE to Acetylene</td>
<td>k₉</td>
<td>4.42(+/-0.45)</td>
<td>Kₖ</td>
<td>0.016(+/-0.002)</td>
</tr>
<tr>
<td>CisDCE to Acetylene</td>
<td>k₁₀</td>
<td>2.18(+/-0.15)</td>
<td>Kₑₑ</td>
<td>0.029(+/-0.003)</td>
</tr>
<tr>
<td>1,1 DCE to Ethylene</td>
<td>k₁₇</td>
<td>3.72(+/-0.25)</td>
<td>Kₖ</td>
<td>0.016(+/-0.002)</td>
</tr>
<tr>
<td>Dichloroacetylene to transDCE</td>
<td>K₈</td>
<td>2.96(+/-1.34)</td>
<td>Kₑₑ</td>
<td>0.051(+/-0.014)</td>
</tr>
<tr>
<td>Dichloroacetylene to cisDCE</td>
<td>K₇</td>
<td>1.02(+/-1.34)</td>
<td>Kₑₑ</td>
<td>0.051(+/-0.014)</td>
</tr>
<tr>
<td>Dichloroacetylene to chloroacetylene</td>
<td>k₁₄</td>
<td>12.97(+/-2.46)</td>
<td>Kₑₑ</td>
<td>0.051(+/-0.014)</td>
</tr>
<tr>
<td>Chloroacetylene to acetylene</td>
<td>k₁₅</td>
<td>6.46(+/-0.94)</td>
<td>Kₑₑ</td>
<td>0.261(+/-0.086)</td>
</tr>
<tr>
<td>Acetylene to ethylene</td>
<td>k₁₆</td>
<td>11.51(+/-1.24)</td>
<td>Kₑₑ</td>
<td>0.109(+/-0.022)</td>
</tr>
<tr>
<td>Vinyl Chloride to Ethylene</td>
<td>k₁₃</td>
<td>6.55(+/-0.93)*10⁻²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene to ethane</td>
<td>k₁₈</td>
<td>2.15(+/-0.25)*10⁻²</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4: Surface corrected rate constants From Ebert et al., 2006; Su and Puls, 1999; and Hara et al., 2005.

<table>
<thead>
<tr>
<th>Source</th>
<th>Iron Type</th>
<th>Surface area m²</th>
<th>k (TCE degradation) (hr⁻¹ m⁻²*10⁻⁵)</th>
<th>k (PCE)</th>
<th>k (cisDCE)</th>
<th>k (transDCE)</th>
<th>k (1,1 DCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ebert et al., 2006</td>
<td>Grey cast iron</td>
<td></td>
<td>8.1</td>
<td>4.5</td>
<td>3.1</td>
<td>9.5</td>
<td>4</td>
</tr>
<tr>
<td>Ebert et al., 2006</td>
<td>Sponge Iron</td>
<td></td>
<td>3.3</td>
<td>2.6</td>
<td>2.6</td>
<td>5.3</td>
<td>4.4</td>
</tr>
<tr>
<td>Su and Puls, 1999</td>
<td>Connelly (cast iron)</td>
<td></td>
<td>1.38</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Su and Puls, 1999</td>
<td>ISPAT sponge iron</td>
<td></td>
<td>0.62</td>
<td>2.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Su and Puls, 1999</td>
<td>Peerless (cast iron)</td>
<td></td>
<td>0.66</td>
<td>3.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Su and Puls, 1999</td>
<td>Gotthart-Maier (cast iron)</td>
<td></td>
<td>0.51</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hara et al., 2005</td>
<td>E 200 (electrolytic iron powder)</td>
<td>3.9</td>
<td>850</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To compare the two kinetic models the rate data will be taken from the study by Arnold and Roberts, 2000. The first order rate constant is obtained by multiplying the adsorption equilibrium constant "K" by the abundance of reactive sites combined with the rate constant "ks", giving units of micro moles. When these terms are combined, this rate is in the range of the surface normalized rate constants once they are multiplied by the surface area per liter of iron. With a porosity of 0.45 (Permeable reactive barrier installation profiles; Suk et al., 2009; Delvin and Barker, 1999), a bulk density of 3 g/cm³ (Suk et al., 2009), and a surface area of 0.79 m² (Suk et al., 2009; Su and Puls, 1999; Arnold and Roberts, 2000), the range of reaction rate constants for TCE is 0.6 h⁻¹ -0.002 h⁻¹ (Table 4) (this does not include the study by Hara in which iron powder was used which is generally not suitable for a reactive barrier). The rate constant obtained from Arnold and Roberts is 0.02 h⁻¹ which is within the range of pseudo first order rate constants reported from other experiments.

Without competition the rates of reaction will be modeled as (using data from Arnold and Roberts):

**PCE:**

\[ r_{PCE} = (-k_3 - k_1) \times K_p \times [PCE] \]  \hspace{1cm} (42)

**TCE:**

\[ r_{TCE} = \left((-k_4 - k_5 - k_6 - k_2) \times K_c \times [TCE]\right) + \left(k_3 \times K_p \times [PCE]\right) \]  \hspace{1cm} (43)
trans-DCE:

\[ r_{\text{trans-DCE}} = \{(-k_9 - k_{12}) \times K_d \times \text{[transDCE]} + [k_6 \times K_t \times \text{TCE}] + k_8 \times K_{dc} \times \text{[Dichloroacetylene]} \} \] (44)

\text{cis-DCE:}

\[ r_{\text{cis-DCE}} = \{(-k_{10} - k_{11}) \times K_{cd} \times \text{[cisDCE]} + [k_5 \times K_t \times \text{TCE}] + k_7 \times K_{dc} \times \text{[Dichloroacetylene]} \} \] (45)

1,1 DCE:

\[ r_{1,1 \text{DCE}} = \{-k_{17} \times K_d \times \text{[1,1 DCE]} \} + [k_4 \times K_t \times \text{TCE}] \] (46)

\text{VC:}

\[ r_{VC} = \{-k_{13}[VC] + k_{12} \times K_d \times \text{[transDCE]} \} + [k_{11} \times K_{cd} \times \text{[cisDCE]}] \] (47)

\text{Dichloroacetylene:}

\[ r_{\text{Dichloroacetylene}} = \{-k_{14} \times k_7 - k_8 \times K_{dc} \times \text{[Dichloroacetylene]} \} + [k_1 \times K_p \times \text{[PCE]}] \] (48)

\text{Chloroacetylene:}

\[ r_{\text{Chloroacetylene}} = \{-k_{15} \times K_c \times \text{[Chloroacetylene]} \} + [k_2 \times K_t \times \text{TCE} + k_{14} \times K_{dc} \times \text{[Dichloroacetylene]}] \] (49)

\text{Acetylene:}

\[ r_{\text{Acetylene}} = \{-k_{16} \times K_a \times \text{[Acetylene]} \} + [k_{15} \times K_c \times \text{[Chloroacetylene]} + k_9 \times K_d \times \text{[transDCE]} + k_{10} \times K_{cd} \times \text{[cisDCE]}] \] (50)

\text{Ethylene:}

\[ r_{\text{Ethylene}} = \{-k_{18}[Ethylene] + k_{13}[VC] \} + [k_{17} \times K_d \times \text{[1,1 DCE]} + k_{16} \times K_a \times \text{[Acetylene]}] \] (51)

\text{Ethane:}

\[ r_{\text{Ethane}} = \{k_{18}[Ethylene]\} \] (52)

With the addition of interspecies competition the rates will be modeled by the equations below. To include intra species competition the rate equations below would simply need the addition of the reacting species times the appropriate adsorption constant in the denominator.
PCE:

\[ r_{PCE} = (-k_3 - k_4) \times K_p \times [PCE] \times (1 + K_t \times [TCE] + K_d \times [transDCE] + K_{dc} \times [Dichloroacetylene] + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene]) \]  

(53)

TCE:

\[ r_{TCE} = \left\{ (-k_4 - k_5 - k_6 - k_2) \times K_t \times [TCE] \times (1 + K_p \times [PCE] + K_d \times [transDCE] + K_{dc} \times [Dichloroacetylene] + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene]) \right\} + \left\{ k_2 \times K_p \times [PCE] \times (1 + K_t \times [TCE] + K_d \times [transDCE] + K_{dc} \times [Dichloroacetylene] + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene]) \right\} \]  

(54)

trans-DCE:

\[ r_{trans-DCE} = \left\{ (-k_9 - k_{12}) \times K_d \times [transDCE] \times (1 + K_p \times [PCE] + K_t \times [TCE] + K_{dc} \times [Dichloroacetylene] + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene]) \right\} + \left\{ k_6 \times K_t \times [TCE] \times (1 + K_p \times [PCE] + K_d \times [transDCE] + K_{dc} \times [Dichloroacetylene] + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene]) + k_8 \times K_{dc} \times [Dichloroacetylene] \times (1 + K_p \times [PCE] + K_d \times [transDCE] + K_t \times [TCE] + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene] + K \times [Acetylene]) \right\} \]  

(55)

cis-DCE:

\[ r_{cis-DCE} = \left\{ (-k_{10} - k_{11}) \times K_{cd} \times [cisDCE] \times (1 + K_p \times [PCE] + K_t \times [TCE] + K_{dc} \times [Dichloroacetylene] + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene]) \right\} + \left\{ k_5 \times K_t \times [TCE] \times (1 + K_p \times [PCE] + K_d \times [transDCE] + K_{dc} \times [Dichloroacetylene] + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene]) + K_{cd} \times [cisDCE] + K_d \times [1,1 DCE] + K_c \times [Chloroacetylene] + K_a \times [Acetylene] \right\} \]  

(56)
1,1 DCE:

\[ r_{1,1\text{DCE}} = \left\{ -k_{17} \times K_d \times [1,1\text{DCE}] / (1 + K_t \times [TCE] + K_p \times [PCE] + K_d \times [\text{transDCE}] + K_{dc} \\
\times [\text{Dichloroacetylene}] + K_{cd} \times [\text{cisDCE}] + K_c \times [\text{Chloroacetylene}] + K_a \times [\text{Acetylene}] \right\} \]

VC:

\[ r_{VC} = -\left\{ k_{13} [VC] + k_{12} \times K_d \times [\text{transDCE}] / (1 + K_p \times [PCE] + K_t \times [TCE] + K_{dc} \times [\text{Dichloroacetylene}] + K_{cd} \times [\text{cisDCE}] + K_d \times [1,1\text{DCE}] + K_c \times [\text{Chloroacetylene}] + K_a \times [\text{Acetylene}] \right\} \]

Dichloroacetylene:

\[ r_{\text{Dichloroacetylene}} = \left\{ -k_{14} - k_7 - k_9 \times K_d \times [\text{Dichloroacetylene}] / (1 + K_p \times [PCE] + K_t \times [TCE] + K_{dc} \times [\text{transDCE}] + K_{cd} \times [\text{cisDCE}] + K_d \times [1,1\text{DCE}] + K_c \times [\text{Chloroacetylene}] + K_a \times [\text{Acetylene}] \right\} \]

Chloroacetylene:

\[ r_{\text{Chloroacetylene}} = \left\{ -k_{15} \times K_c \times [\text{Chloroacetylene}] / (1 + K_t \times [TCE] + K_{dc} \times [\text{Dichloroacetylene}] + K_{cd} \times [\text{cisDCE}] + K_d \times [1,1\text{DCE}] + K_p \times [PCE] + K_a \times [\text{Acetylene}] \right\} \]
Acetylene:

\[
\begin{align*}
\dot{r}_{\text{Acetylene}} = & \left[ -k_{16} \times K_a \times [\text{Acetylene}] / (1 + K_p \times [\text{PCE}] + K_t \times [\text{TCE}] + K_d \times [\text{transDCE}]ight. \\
& + k_{cd} \times [\text{cisDCE}] + K_d \times [1,1 \text{ DCE}] + K_c \times [\text{Chloroacetylene}] + K_{dc} \\
& \times [\text{Dichloroacetylene}] + k_{15} \times K_r \times [\text{Chloroacetylene}] / (1 + K_t \times [\text{TCE}]ight. \\
& + K_d \times [\text{transDCE}] + K_{dc} \times [\text{Dichloroacetylene}] + K_{cd} \times [\text{cisDCE}] + K_d \\
& \times [1,1 \text{ DCE}] + K_p \times [\text{PCE}] + K_a \times [\text{Acetylene}]) \\
& \left. + \{ k_9 \times K_d \times [\text{transDCE}] / (1 + K_p \times [\text{PCE}] + K_t \times [\text{TCE}] + K_{dc} \\
& \times [\text{Dichloroacetylene}] + K_{cd} \times [\text{cisDCE}] + K_d \times [1,1 \text{ DCE}] + K_c \\
& \times [\text{Chloroacetylene}] + K_a \times [\text{Acetylene}]) + k_{10} \times K_{cd} \times [\text{cisDCE}] / (1 + K_p \\
& \times [\text{PCE}] + K_t \times [\text{TCE}] + K_{dc} \times [\text{Dichloroacetylene}] + K_d \times [1,1 \text{ DCE}] + K_c \\
& \times [\text{Chloroacetylene}] + K_a \times [\text{Acetylene}]) \right]. 
\end{align*}
\]

Ethylene:

\[
\begin{align*}
\dot{r}_{\text{Ethylene}} = & \left[ -k_{18} [\text{Ethylene}] + k_{13} [\text{VC}] + k_{17} \times K_d \times [1,1 \text{ DCE}] / (1 + K_t \times [\text{TCE}] + K_p \\
& \times [\text{PCE}] + K_d \times [\text{transDCE}] + K_{dc} \times [\text{Dichloroacetylene}] + K_{cd} \times [\text{cisDCE}] \\
& + K_c \times [\text{Chloroacetylene}] + K_a \times [\text{Acetylene}]) \
& \left. + \{ k_{16} \times K_a \times [\text{Acetylene}] / (1 + K_p \times [\text{PCE}] + K_t \times [\text{TCE}] + K_d \\
& \times [\text{transDCE}] + k_{cd} \times [\text{cisDCE}] + K_d \times [1,1 \text{ DCE}] + K_c \times [\text{Chloroacetylene}] \\
& + K_{dc} \times [\text{Dichloroacetylene}]) \right]. 
\end{align*}
\]

Ethane:

\[
\dot{r}_{\text{Ethane}} = k_{18} [\text{Ethylene}] 
\]

**Thermodynamics of Dechlorination:**

From a thermodynamic prospective (according to Gibbs free energy calculations) all of the reactions in Table 5 will occur spontaneously at 298K. Although lower ground water temperatures may increase these numbers slightly, the fact that all the reactions will occur spontaneously is expected to be the same.
Solute Transport:
The rate of transport of solutes through porous media is governed by multiple physical and chemical phenomenon. Molecular diffusion, advection, mechanical dispersion, sorption, and reaction all have the ability to influence the movement of a constituent in water and in porous media. Each of these mechanisms will be discussed with respect to their relative importance for modeling the performance of a permeable reactive barrier.

Advective transport is the fluid velocity component of mass transport. It can be calculated by the dot product of the velocity vector, \( \mathbf{u} \), and the unit normal vector, \( \mathbf{n} \), to the area \( dA \), all multiplied by the concentration of the solute, \( C \).

\[
\text{Advective mass transport through } dA = (\mathbf{u} \cdot \mathbf{n})CdA = (j_{\text{adv.}} \cdot \mathbf{n})dA \quad (64)
\]

\[
 j_{\text{adv.}} = UC \quad (65)
\]

\( \mathbf{u} = \text{velocity vector} \left( \frac{L}{t} \right) \)
The magnitude of the velocity vector (pore water velocity) in one dimension is determined by Darcy's law where:

\[ v = \frac{K_x \nabla(h)}{\varepsilon} \]  

\( K_x = \text{Hydraulic conductivity in the x direction} \) \( \left( \frac{L}{t} \right) \)  

\( h = \text{Total head} \)  

\( \varepsilon = \text{Porosity} \)

Molecular diffusion is governed by Fick's Law which states that the net rate of diffusive mass transport is proportional to the negative gradient of the concentration, normal to the area \((dA)\) (Selker et al., 1999). Mathematically it may be expressed as follows:

\[ \text{Diffusive mass transport through } dA = -D \frac{\partial C}{\partial n} dA = (j_{\text{diffusion}} \cdot n) dA \]  

Where:

\[ j_{\text{diffusion}} = -D \nabla C \]

\( C = \text{Solute concentration} \) \( \left( \frac{\text{mass}}{\text{volume}} \right) \)

\( D = \text{diffusion coefficient} \) \( \left( \frac{\text{area}}{\text{time}} \right) \)

\( n = \text{unit normal vector over boundary surface } dA. \)

Diffusion coefficients can be found in various reference texts, and there are correlations that have been developed to estimate the coefficients. Table 6 gives diffusion coefficients for TCE, PCE, 1,1 DCE, cisDCE, transDCE, and vinyl chloride (Crittenden et al., 2005; Ebert et al., 2006).

**Table 6: Diffusion coefficients for chlorinated species (Crittenden et al., 2005; Ebert et al., 2006).**

<table>
<thead>
<tr>
<th>Source</th>
<th>Solute</th>
<th>Diffusion Coefficient ( (m^2/s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crittenden et al., 2005</td>
<td>Trichloroethylene</td>
<td>( 8.4 \times 10^{-10} )</td>
</tr>
<tr>
<td>Crittenden et al., 2005</td>
<td>Tetrachloroethylene</td>
<td>( 7.5 \times 10^{-10} )</td>
</tr>
<tr>
<td>Crittenden et al., 2005</td>
<td>Vinyl Chloride</td>
<td>( 1.1 \times 10^{-9} )</td>
</tr>
<tr>
<td>Ebert et al., 2006</td>
<td>1,1 DCE, cisDCE, trans DCE</td>
<td>( 1.04 \times 10^{-9} )</td>
</tr>
</tbody>
</table>

Mechanical dispersion is another phenomenon that affects the transport of solutes in the water. In porous media fluids will travel faster or slower than the average flow velocity depending on the path.
taken. Tortuosity or how "tortured" the flow path is causes local accelerations and decelerations as liquid flows around particles and through different size pores. In actuality dispersion is due to the correlation between variations in solute concentrations and fluid velocities (Selker et al., 1999). This means that dispersive flux depends on the area over which the average is taken due to the fact that there is generally more heterogeneity over a larger volume thus a larger amount of dispersion. The proper approach is to calculate the dispersion coefficient based on the size of the plume being modeled with attention to any heterogeneity on the site (Selker et al., 1999). In practice, the effects of dispersion look much like that of diffusion and as such it is modeled in an analogous way.

\[
\dot{J}_{\text{disp}} = -\theta D \nabla C
\]

(68)

\[
\theta = \text{volumetric water content } \left[ \frac{\text{vol}}{\text{vol}} \right]
\]

\[
D = \text{dispersion coefficient } \left( \frac{L^2}{t} \right)
\]

\[D\] is a second ranked tensor and is often aligned with fluid velocity so that the off diagonal terms go to zero. Dispersion in the longitudinal direction (in the direction of fluid velocity) is always larger than transverse dispersion (perpendicular to flow). The dispersion coefficient depends on the fluid velocity and because fluid flow in the ground is almost always laminar, a longitudinal and transverse dispersivity (\(\alpha_L\), \(\alpha_T\) respectively) is defined with units of length that is a function of the media. As velocity increases so does dispersion because dispersion is the variation from the mean velocity, so a greater velocity will incur larger variations from the mean.

\[
D_L = \alpha_L |\mu|
\]

(69)

\[
D_T = \alpha_T |\mu|
\]

(70)

\[D = \text{dispersion coefficient } \left( \frac{L^2}{t} \right)\]

\[\alpha = \text{dispersivity } (L)\]

Estimates commonly used for dispersivity at the small scale are (Selker et al., 1999):

\[
\frac{\alpha}{\sqrt{f}} = 25 \text{ to } 50
\]

(71)

\[f = \text{intrinsic permeability } = \frac{K \times v}{g}\]

\[v = \text{kinematic viscosity } \left( \frac{L^2}{t} \right)\]

\[g = \text{gravitational acceleration } \left( \frac{L^2}{t} \right)\]
Now the advective-dispersion equation can be written over a control volume that includes advection, diffusion, dispersion, and a term for sources and sinks (σ).

\[
\frac{\partial C}{\partial t} = \nabla \cdot (\theta \mu C) - \nabla \cdot (\theta(D + D)\nabla C) - \sigma = 0
\]  

(72)

The diffusion and dispersion coefficient appear together so it is convenient to combine these terms into one coefficient of hydrodynamic dispersion:

\[
D + D = E
\]

(73)

\[E = \text{coefficient of hydrodynamic dispersion} \ (m)\]

In order to evaluate the relative importance of each, the Peclet number is used which is a dimensionless parameter used to evaluate the relationship between diffusion, dispersion, and pore water velocity. The Peclet number is a ratio of the pore water velocity times a characteristic length expressed as the mean grain size, to the molecular diffusion coefficient, D. Although the Peclet number does not explicitly include the dispersion coefficient it has been found that as the velocity increases so does the longitudinal dispersion coefficient because as seen in equations 69 and 70 above, dispersion is a function of the pore water velocity.

\[
Pe = \frac{ud}{D}
\]

(74)

The relationship between D and D is a function of Pe and can be divided into several regions. For Pe ≤ 0.4, molecular diffusion dominates. In this zone the liquid velocity is so slow that the time for a solute to diffuse through the pore is equal to or greater than the velocity. Where 0.4 ≤ Pe ≤ 5, diffusion processes are as important as dispersion. Where 5 ≤ Pe ≤ 10, the main spreading is due to mechanical dispersion combined with transverse molecular diffusion which has the impact of reducing longitudinal dispersion. When 4 Pe ≥ 10, mechanical dispersion dominates and diffusion is negligible (Selker et al., 1999).

In a permeable reactive barrier the mean grain size can range from 0.23 mm to 20.0 mm, Table 7 lists commonly used types of iron and their grain size. As can be seen from the Peclet number, the grain size of the media has a large influence on the relative importance of dispersion. The grain size will also affect the hydraulic conductivity of the media and thus the pore water velocity. To get an idea of how the grain size will affect the Peclet number, the third column lists the Peclet number for a constant pore water velocity of 0.5 m/d and a diffusion coefficient of \(7.26 \times 10^{-5} \text{ m}^2/\text{d}\) (the diffusion coefficient for TCE).
Table 7: The effect of grain size on Peclet number. Pore water velocity is 0.5 m/d and the diffusion coefficient is $7.26 \times 10^{-5}$ m$^2$/d.

<table>
<thead>
<tr>
<th>Iron Type</th>
<th>Grain size range (mm)</th>
<th>Peclet number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Sponge</td>
<td>0.42-1.0</td>
<td>2.89-6.88</td>
</tr>
<tr>
<td>20-32 mesh iron turnings, fluka, puriss grade</td>
<td>0.5-0.85</td>
<td>3.44-5.85</td>
</tr>
<tr>
<td>Iron Sponge (different source)</td>
<td>0.6-1.6</td>
<td>4.13-11.02</td>
</tr>
<tr>
<td>Grey cast iron</td>
<td>3-20</td>
<td>20.66-137.74</td>
</tr>
<tr>
<td>Gotthart-Maier metallpulver GmbH</td>
<td>85% was 0.23 to 0.3 mm all less than 5mm</td>
<td>1.55-2.07</td>
</tr>
</tbody>
</table>

Dispersivity is very system specific so a range of values that are appropriate for a zero valent barrier were generated using a variety of correlations and experimental results. The boundaries of this range will then be used to access whether hydrodynamic dispersion may be neglected for the simulation. Hydrodynamic dispersion is proportionally related to the pore water velocity (eqs. 68 and 69) therefore there may be a range of water velocities where dispersion is not important above which it does become important. This can occur because dispersion is the amount of deviation from the mean pore water velocity, if the average velocity is high than there will usually be larger deviations away from the mean producing larger dispersion of the solute. However, it has also been shown that dispersivity is generally greater in materials with lower hydraulic conductivity because of a larger chance of preferential flow through "worm holes" or cracks in compacted soils, thus greater "smearing" of the solute front (Fried, 1975). That is contradictory to larger pore water velocities having greater dispersion but this is because there are two different physical phenomenon affecting dispersion in each case. In a material with low pore water velocities, it is the effect of macropores that can cause a large increase in dispersion this is affecting the $\alpha$ or dispersivity of the soil and in the case with high pore water velocities it is the velocity part of the dispersion equation being affected which is related to statistics and deviation from the mean as mentioned above.

Although dispersivity is a function of the media, it has been realized that length of travel affects the dispersivity. Therefore, many of the correlations for dispersivity are related to the length of travel because it has been found that the longer the flow path the greater the dispersivity due to greater heterogeneity (Weber and DiGiano, 1996; Gelhar et al., 1992; Fogler, 1999; Bear, 1979). However the accuracy of these correlations have been criticized because these correlations ignore the properties of the geologic material which also influence dispersivity (Gelhar et al., 1992). Gelhar et al. compared 59 different field site dispersivity tests and ranked them by reliability of the results ("3" being the most reliable). This data was used to gain results that may be comparable to dispersivity in a barrier (Gelhar et al., 1992). All studies that had a flow path of less than 5 m, received a score of 3 for reliability, and had a hydraulic conductivity that was comparable to the conductivity of a barrier were selected (Figure 6). Six studies met these requirements and the range of dispersivity was from 0.01 m to 0.55 m. Table 8 shows the results from correlations and from three tracer tests. These values are lower than those from tests done in natural material. This may be due to the smaller scale and/or homogeneous packing of material (i.e. engineered systems). The highest value obtained is 0.55 m and the arithmetic average of
all values from the graph and table is 0.11 m. A dispersivity of 0.55 m is most likely higher than in a real barrier, as natural material is more heterogeneous than a barrier which can be carefully engineered to have a specific grain size range and uniform packing. However the upper bound of 0.55 m will be used, so that if there are deviations from ideal plug flow, the maximum amount of error will be generated.

Figure 6: Graph of measured dispersivity in natural media vs. flow path length:

A: Pickens and Grisak 1981, Sand with a hydraulic conductivity of $2 \times 10^{-5}$ to $2 \times 10^{-4}$ m/s.
B: Leland and Hillel 1981, fine sand and glacial till with a hydraulic conductivity of $2.4 \times 10^{-5}$ to $3 \times 10^{-5}$ m/s.
C,D,E: Hoehn and Santschi 1983, Layered gravel and silty sand with a hydraulic conductivity of $9.2 \times 10^{-4}$ to $6.6 \times 10^{-3}$ m/s.
F: Wilson 1971, unconsolidated gravel, sand, and silt with a hydraulic conductivity of $5.75 \times 10^{-3}$ m/s.
H: Rousselot et al 1977, clay, sand, and gravel with a hydraulic conductivity of $1.5 \times 10^{-2}$ m/s.
Table 8: Values for dispersivity.

<table>
<thead>
<tr>
<th>Source</th>
<th>Equation/ Method</th>
<th>Limits</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neuman (1990)</td>
<td>$\alpha_l = 0.0175L^{1.46}$</td>
<td>$L &lt; 3500 \text{ m}$</td>
<td>0.0027m</td>
</tr>
<tr>
<td>Jeen (2007)</td>
<td>Bromide tracer test in a column. Curve fitting to breakthrough curves</td>
<td></td>
<td>0.00099m</td>
</tr>
<tr>
<td>Keith (2006)</td>
<td>Breakthrough curves of Li$^+$ in an iron PRB</td>
<td>0.8 m iron barrier</td>
<td>0.06m-0.513m, avg of 0.275m</td>
</tr>
<tr>
<td>Selker (1999)</td>
<td>$\frac{\alpha_l}{\sqrt{K}} = 25 \text{ to } 50$ K= intrinsic permeability</td>
<td>&quot;micro scale&quot;</td>
<td>.0002m-.0004m</td>
</tr>
<tr>
<td>Devlin and Barker (1999)</td>
<td>Pump tests and curve fitting of breakthrough curves.</td>
<td>1 m iron barrier</td>
<td>0.128m to $2*10^{-4}$m avg=0.021m</td>
</tr>
</tbody>
</table>

Another factor influencing the movement of solutes in the water is the rate of reaction. All of the dechlorination reactions have been fairly well modeled by a first order reaction rate (Orth and Gillham, 1996; Su and Puls, 1999; Ebert et al., 2006; Hara et al., 2005; Johnson et al., 1996). Other models have been employed to more closely represent the reaction at the surface and other details of the reaction. However, an overwhelming majority of the literature has reported the degradation of PCE, TCE, DCE, and VC as following first order kinetics because it does fit the data well and therefore the first order degradation rate assumed in the analytical solutions to the advection dispersion equation is an accurate representation of the system.

Retardation or sorption is another process incorporated into many groundwater transport models. In the simplest case, linear isotherms are used to calculate a $K_d$ which is a proportionality constant relating the adsorbed solute to the solute concentration in the fluid. As mentioned earlier, the dechlorination reactions happen at the surface of the media, however this phenomenon is accounted for in the rate of reaction which includes a surface area term. Sorption without reaction is a separate phenomenon and is directly related to the amount of carbon impurities in the iron. The type of iron used will determine the amount of carbon but many retailers report less than 4% carbon or other impurities (Connelly, Peerless, ISPAT Industries). These carbon impurities can act as sorption sites as evinced by the fact that during many column studies mass balances on carbon was sometimes as low as 60% due in part to sorption (Johnson, 1996). The other possibility is that the carbon is tied up in larger chained hydrocarbons that were not tested for. When there is no sorption the retardation factor is 1. Table 9 lists retardation coefficients determined experimentally, one by a column test and the other a tracer test through an iron barrier, calculated retardation coefficients very close to 1. Retardation is calculated with:

$$R = 1 + \frac{\rho_b K_d \theta}{\rho}$$  \hspace{1cm} (75)

$$\rho_b = \text{Bulk density of media} \left(\frac{\text{mass (dry media)}}{\text{volume}}\right)$$
\[ K_d = \text{Proportionality constant } \left( \frac{\text{conc. sorbed}}{\text{conc. in fluid}} \right) \]

\[ \theta = \text{Volumetric moisture content } \left( \frac{\text{vol. of water}}{\text{total vol.}} \right) \]

Table 9: Retardation coefficients determined experimentally.

<table>
<thead>
<tr>
<th>Source</th>
<th>Type of study</th>
<th>Retardation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keith et al, (2006)</td>
<td>Tracer test of Li(^+) in an iron PRB</td>
<td>0.09 to 1.33</td>
</tr>
</tbody>
</table>

A retardation coefficient of 1 will be used in this modeling work as experiments have shown that it is approximately 1 (Lai et al., 2006; Keith et al., 2006).

Now putting all of the terms together, a more complete form of the advection and dispersion equation can be written in 1 dimension, assuming there are no sources or sinks within the barrier.

\[
\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} - \frac{D_t}{R} \frac{\partial^2 C}{\partial x^2} - r = 0
\]

\[ C = \text{Concentration of solute } \left( \frac{\text{mass}}{\text{vol}} \right) \]

\[ x = \text{Distance(Length)} \]

\[ R = \text{Retardation coefficient} \]

\[ r = \text{Rate of reaction } \left( \frac{\text{mass}}{\text{time}} \right) \]

\[ D_t = \text{Hydrodynamic dispersion coefficient } (L^2/\text{time}) \]

There are many analytical solutions to this equation in 1 dimension. These solutions vary in the boundary conditions, initial conditions, and assumptions used. For this model pseudo steady state will be assumed. The second simplification to this equation would be to neglect dispersion. However, to do this, it has to be determined if the dispersion term does in fact affect the solution to this problem. To evaluate the importance of dispersion, a range of dispersivity, pore water velocity, and degradation rates will be used in an analytical solution to the advection dispersion equation and compared to a solution for an ideal plug flow with no dispersion, considering the degradation of only one contaminant, TCE. Table 10 lists the range of values that will be used as the inputs for the advection dispersion model.
Table 10: Range for input variables for modeling equations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore water velocity</td>
<td>0.6m/hr-0.01m/h</td>
</tr>
<tr>
<td>Dispersivity</td>
<td>0.55m-0.0002m</td>
</tr>
<tr>
<td>Reaction rate constant</td>
<td>0.6h⁻¹-0.002h⁻¹</td>
</tr>
<tr>
<td>Retardation</td>
<td>1</td>
</tr>
</tbody>
</table>

For these trials the range of first order degradation rates will be based on the range reported in Table 4 neglecting the study by Hara which uses electrolytic "powder" iron which is not typically appropriate for barrier installations due to the size of the iron particles. All of the reaction rate constants are surface area corrected, to convert them to a "observed" rate of reaction the following equation must be used:

\[
 k_{\text{observed}} = k_{sa} \times \text{surface area per mass} \times \text{mass loading rate} \tag{77}
\]

To obtain a mass loading rate the following equation is used:

\[
 \text{Mass loading rate} = (1 - \text{porosity}) \times \text{bulk density of iron} \tag{78}
\]

The range of porosity reported is from 0.4 to .5 so a value of 0.45 will be used (Permeable reactive barrier installation profiles; Suk et al., 2009; Delvin and Barker, 1999). The average bulk density reported from Table 2 is 3 g/cm³ (Suk et al., 2009), the average surface area is 0.79 m² (Suk et al., 2009; Su and Puls, 1999; Arnold and Roberts, 2000), and the range of surface corrected reaction rates is from \(1.8 \times 10^{-6} \text{h}^{-1} \text{m}^{-2}\) to \(4.4 \times 10^{-4} \text{h}^{-1} \text{m}^{-2}\) (Table 4). Inputting these values into the equation above gives an effective reaction rate constant range of 0.6 h⁻¹ -0.002 h⁻¹.

Below are two solutions to the advection-dispersion equation for a continuous point source injection with an infinite length, and first order decay. The initial condition is that the concentration is zero everywhere except at \(x=0\). The rate of injection is \(C_0\) at \(x=0\). The first equation is derived by Selker et al., (1999) and the second is from Bear, (1979):

\[
 C(x,t) = \frac{C_0}{2} \exp \left( \frac{x}{2\alpha_L} \right) [\exp \left( \frac{-xy}{2\alpha_L} \right) erfc \left( \frac{x - vty}{2\sqrt{\alpha_L vt}} \right) - \exp \left( \frac{xy}{2\alpha_L} \right) erfc \left( \frac{x + vty}{2\sqrt{\alpha_L vt}} \right) ] \tag{79}
\]

\[
 C(x,t) = \frac{C_0}{2} \left[ \exp \left( \frac{vx}{2D} \left( 1 - \sqrt{1 + \frac{4kD}{v^2}} \right) \right) \times erfc \left( \frac{Rx - vty}{2\sqrt{D} \sqrt{vt}} \right) \right] \tag{80}
\]

\[
 \alpha_L = \text{longitudinal dispersivity, (L)}
\]

\[
 v = \text{pore water velocity, (L/}t) \]

36
These solutions give identical results, and thus overlap one another when graphed. Because both solutions give the same result the Selker equation was chosen because it decouples velocity from dispersion and thus uses dispersivity in the equation. This makes it easier to manipulate the variables. These solution will be compared to solutions from an ideal plug flow model which can be modeled as follows:

**Advection equation at steady state:**

\[
\frac{u}{R} \frac{dC}{dx} - r = 0
\]  

(81)

*Where r is a first order reaction:*

\[
r = -kC
\]

(82)

*Substituting and rearranging:*

\[
\frac{dC}{dx} = -kCR \frac{1}{v_x}
\]

(83)

The velocities used reflect the high and low data reported from actual barriers. The highest reported value is 0.6 m/h and one of the lowest is 0.01 m/h (Permeable reactive barrier installation profiles; Devlin and Barker, 1999). The largest error is generated from the combination of the largest reaction rate with the slowest velocity at the highest dispersivity. In this case a 60% error in relative concentration is generated it the first 0.5 m of the barrier (Figure 10). At 0.5 m the solutions are the same as the concentration has decreased to zero for both equations. With a maximum velocity of 0.6 m/hr and a maximum reaction rate of 0.6 hr\(^{-1}\), the largest percent error generated is 12% at a dispersivity of 0.55 m (Figure 7). When the dispersivity is at the average of 0.1 m the greatest deviations from the analytical solution is 40%. Again this is in the case of a low pore water velocity and high reaction rate (Figure 10). However in the other three simulations the largest difference is in solute
concentrations is 3.5% in Figure 7 which is the maximum pore water velocity and maximum reaction rate.

Figure 7: The percent difference in relative concentrations of the analytical solution to the advection dispersion equation vs. ideal plug flow; t=5000hrs (steady state), velocity =0.06m/hr, retardation=1, reaction rate constant=0.6/hr, dispersivity is varied.

Figure 8: The percent difference of relative concentration for the 1-D analytical solution to the ADE vs. ideal plug flow; t=5000 hrs (steady state), retardation=1, velocity=0.01m/hr, reaction rate=0.002/hr, dispersivity is varied. The flow path is lengthened to view maximum difference.
Figure 9: Percent difference in relative concentrations of 1-D solution to the ADE vs. ideal plug flow; t=5000hrs, retardation=1, velocity=0.6m/hr, reaction rate=0.002/hr, dispersivity is varied. The percent difference maximum is about 0.2% at about 500m.

Figure 10: Percent difference in relative concentrations of the 1-D analytical solution to the ADE vs. ideal plug flow; t=5000hrs, retardation=1, velocity=0.01m/hr, reaction rate=0.6/hr, dispersivity is varied.
From the graphs above, it can be seen that dispersion may be neglected if careful consideration about the parameters are made. For example the greatest deviation occurs in the scenario of a low velocity and a high reaction rate. This error may become propagated when multiple reactions instead of just one is considered. If dispersion is neglected in this case, then a barrier that is way too thin may be constructed because in ideal plug flow, the concentration drops to zero much more quickly when dispersion is neglected. From these graphs a dimensionless variable can be introduced that can be used to estimate the maximum error that may be produced by neglecting dispersion.

\[ D_0 = \frac{v}{\alpha I k} \]  

\[ v = \text{Pore water velocity} \left( \frac{L}{t} \right) \]

\[ k = \text{Observed reaction rate constant} \left( t^{-1} \right) \]

\[ \alpha I = \text{longitudinal dispersivity} \left( L \right) \]

As this number increases, the maximum percent difference of concentration goes down. However, where this maximum error occurs can be at very different locations along the flow path. Generally the larger maximum percent errors in concentration of the solute occur within the first meter where as lower maximum percent errors peak out at lengths way beyond any practical barrier width (i.e. 500 m).

For most barriers that are constructed with uniform grain sizes and uniform packing dispersivity should be low (at the average of 0.11 m or less). However larger dispersivites may result from poor packing of the materials leading to preferential flow through macropores. From the above results, dispersion may be neglected if dispersivity is 0.01 m or less, this results in a maximum error of less than 15% (Figure 10) which is acceptable, and in most cases it is much less than that. According to the dimensionless parameter, this would mean that \( D_0 \) must be 1.6 or greater.

The Model:

The model of these reactions will be governed by coupling the kinetic expressions (eqs 42-63) with, the conservation equation for an ideal plug flow reactor, and porous media flow equations. For porous media flow Darcy's law will be used. Assumptions are that the porous media (the iron) is isotropic and spherical in shape.

Neglecting dispersion and retardation, assuming steady state:

\[ \frac{dC}{dx} = \frac{r}{v_x} \]  

\[ v_x = \text{pore water velocity} \left( \frac{L}{t} \right) \]

\[ r = \text{reaction rate} \left( t^{-1} \right) \]
The initial concentrations of all the species are zero in the barrier and there were three different trials with different influent concentrations. All three trials compared the different kinetic models (first order, intra species competition, and intra/inter species competition). The first trial had PCE only entering the barrier; the second was TCE only; and the third was a mix of PCE, TCE, cisDCE, and VC. The third trial with a mix of chlorinated species was closer to reality because plumes of chlorinated aliphatics usually contain a mix of contaminants (Bedient et al., 1997). Sometimes this is because multiple contaminants were released into the ground or because when chlorinated species naturally attenuate in the subsurface the pathway of sequential dechlorination is followed (Bedient et al., 1997). This means that PCE→TCE→DCE (isomers)→VC. Usually the cisDCE isomer is more persistent because it does not degrade as fast as the other DCE isomers (Bedient et al., 1997). If PCE is released into the subsurface after years of weathering the plume will be a mix of PCE, TCE, DCE isomers, and VC. The concentrations of each constituent is variable depending on the mass of the initial contaminate and subsurface conditions (pore water velocity, soil material, etc). At the Shaw air force base in South Carolina there was about 9 times as much TCE than cisDCE, at the federal highway administration in Colorado there was 5 times as much TCE than cisDCE, and 170 time more TCE than VC (Permeable reactive barrier installation profiles). Table 11 is a list of the influent concentrations for the three trials:

Table 11: Influent concentrations for contaminants entering a zero valent permeable reactive barrier.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Species</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCE</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>TCE</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>PCE</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>cisDCE</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>VC</td>
<td>.5</td>
</tr>
</tbody>
</table>
Figure 11: First order kinetic model of a PCE contaminant plume through a permeable reactive barrier. PCE influent concentration is 10 mg/l and the pore water velocity is 0.01 m/h. DCE isomers, VC, chloroacetylene, and acetylene are not shown because concentrations never get higher than 0.01%.

There was very little change in concentrations for the inter and intra/inter species competition models because there are not many other species to compete with. No graphs are presented because they are similar to Figure 11. As predicted by the rate constants used, PCE treatment efficiency is not high, only reducing the concentration by about 15%.
Figure 12: First order kinetic model of a TCE contaminant plume through a permeable reactive barrier. TCE influent concentration was 10 mg/l and the pore water velocity was 0.01 m/h. DCE isomers, VC, chloroacetylene, and acetylene are not shown because concentrations never were higher than 0.01%.

Figure 13: First order kinetic model of a TCE contaminant plume through a permeable reactive barrier. View of the products of concern. TCE influent concentration was 10 mg/l and the pore water velocity was 0.01 m/h.

The first order kinetic model found a 90% reduction of TCE in a 1 meter thick barrier with very minimal production of DCE isomers or vinyl chloride. From Figure 13 the maximum production of daughter products are shown; cisDCE was 0.025 mg/l, 1,1 DCE was 0.018 mg/l, transDCE was 0.0036 mg/l, VC was
0.0014 mg/l. All of these concentrations except 1,1 DCE are below EPA drinking water standards. At one meter into the barrier 1,1 DCE has degraded to 0.006 mg/l which is just below drinking water standards which is 0.007 mg/l. With interspecies competition the degradation of TCE decreased to 78% reduction (Figure 14).

Figure 14: Interspecies competitive kinetic model of a TCE contaminant plume through a permeable reactive barrier. TCE influent concentration was 10 mg/l and the pore water velocity was 0.01 m/h. DCE isomers, VC, chloroacetylene, dichloroacetylene, and acetylene are not shown because concentrations were not greater than 0.01%.

Figure 15: Interspecies competitive kinetic model of a TCE contaminant plume through a permeable reactive barrier. View of products of concern. TCE influent concentration was 10 mg/l and the pore water velocity was 0.01 m/h.
From Figure 15 it can be seen that the maximum production of daughter products increased; the maximum cisDCE concentration was 0.044 mg/l, 1,1 DCE was 0.035 mg/l, transDCE was 0.005 mg/l, VC was 0.0014 mg/l. The predicted concentrations of these species were within EPA drinking water standards except for 1,1 DCE. For these predictions 1,1 DCE remains above EPA drinking water standards by 0.004 mg/l. These levels are the highest, with inter species competition the concentration of unwanted daughter products was less with inter and intra species competition. With inter and intraspecies competition, removal rates decreased dramatically to only 33% TCE removal (Figure 16).

![Figure 16: Interspecies and intraspecies competitive kinetic model of a TCE contaminant plume through a permeable reactive barrier. TCE influent concentration was 10 mg/l and the pore water velocity was 0.01 m/h. DCE isomers, VC, chloroacetylene, and acetylene are not shown because concentrations never got higher than 0.01%.](image)

With a mix of species and first order rates of reaction, TCE attained 90% removal in 1 meter, VC and cis DCE are fully degraded within 0.5 m, and PCE achieves minimal treatment.
Figure 17: First order kinetic model of a PCE, TCE, cisDCE, and VC contaminant plume through a permeable reactive barrier. PCE influent concentration was 5 mg/l, TCE was 10 mg/l, cisDCE was 2mg/l, and VC was .5 mg/l and the pore water velocity was 0.01 m/h. Trans, 1,1 DCE, chloroacetylene, dichloroacetylene, and acetylene are not shown because concentrations were less than 0.01%.

Figure 18: Interspecies competition kinetic model of a PCE, TCE, cisDCE, and VC contaminant plume through a permeable reactive barrier. PCE influent concentration was 5 mg/l, TCE was 10 mg/l, cisDCE was 2mg/l, and VC was .5 mg/l and the pore water velocity was 0.01 m/h. Trans, 1,1 DCE, chloroacetylene, dichloroacetylene, and acetylene are not shown because concentrations never get higher than 0.01%.
Interspecies competition dramatically decreases TCE removal rates to 45% removal. VC and cisDCE removal rates are also considerably less with 43% of cisDCE removed and about 50% of VC removed in 1 meter.

Figure 19: Inter and intra species competition kinetic model of a PCE, TCE, cisDCE, and VC contaminant plume through a permeable reactive barrier. PCE influent concentration was 5 mg/l, TCE was 10 mg/l, cisDCE was 2mg/l, and VC was .5 mg/l and the pore water velocity was 0.01 m/h. Trans, 1,1 DCE, chloroacetylene, dichloroacetylene, and acetylene are not shown because concentrations were below 0.01%.

Inter and intra species competition further decreases the removal rate efficiency. TCE is only degraded by 25%, PCE is not treated, cisDCE, and VC maintain the same amount of removal as inter species competition only.
Figure 20: Percent difference of the first order kinetic model vs. the interspecies kinetic model. Non toxic products not included. Other DCE isomers not included because percent difference was less than 5%. PCE influent concentration was 5 mg/l, TCE was 10 mg/l, cisDCE was 2mg/l, and VC was .5 mg/l and the pore water velocity was 0.01 m/h.

As can be seen on Figure 20, the different kinetic models give very different concentrations for TCE. In order to choose the best model, a comparison to real data would help to decide which model will give the most accurate results. In all of the trial runs, toxic daughter products are not produced in any significant amounts. This is in line with data from column studies and from permeable reactive barriers where ethylene and ethane make up almost all of the byproducts.

Model Validation:
The first order kinetic model, the interspecies competition model, and the inter and intra species competitive model are compared to two different field sites, an industrial site in South Carolina and a Dupont site in North Carolina. Both barriers were installed in the late 1990's and were then monitored periodically to gage performance (Permeable reactive barrier installation profiles).

In South Carolina, the barrier is 1 ft thick and is a 50/50 mix of sand and Iron (Permeable reactive barrier installation profiles). The average concentrations of the inflowing contaminants is 25 mg/l TCE, 3.5 mg/l cisDCE, and .9 mg/l VC (Permeable reactive barrier installation profiles). The pore water flow rate is about 0.5 ft/day. The average removal for TCE was 68%, 80% for cisDCE, and 69% for vinyl chloride (Permeable reactive barrier installation profiles). In North Carolina the barrier is 4 inches thick, and the contaminant plume consisted of 155 ug/l of TCE (Permeable reactive barrier installation profiles). The groundwater in the region has a interstitial velocity of 0.1 ft/day. The iron used was granular cast iron.
These variables were entered into the model and compared to average removal rates experienced at these sites.

Table 12: Comparison of real results to three different kinetic models.

<table>
<thead>
<tr>
<th>Location</th>
<th>Contaminant</th>
<th>% removal (actual)</th>
<th>Predicted % removal (First Order)</th>
<th>Predicted % removal (Interspecies competition)</th>
<th>Predicted % removal (Inter and intra species competition)</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Carolina</td>
<td>TCE</td>
<td>68%</td>
<td>70%</td>
<td>23%</td>
<td>7%</td>
</tr>
<tr>
<td>South Carolina</td>
<td>cisDCE</td>
<td>80%</td>
<td>95%</td>
<td>19%</td>
<td>20%</td>
</tr>
<tr>
<td>South Carolina</td>
<td>VC</td>
<td>69%</td>
<td>94%</td>
<td>19%</td>
<td>17%</td>
</tr>
<tr>
<td>North Carolina</td>
<td>TCE</td>
<td>92%</td>
<td>90%</td>
<td>89%</td>
<td>88%</td>
</tr>
</tbody>
</table>

Figure 21: Graph of percent removal from a site in South Carolina (SC) and a site in North Carolina (NC) compared to three different kinetic models.

From the table and graph it can be seen that the first order model does the best in predicting results. However, the first order model usually predicts greater removal of the contaminant than seen in the field. Neglecting dispersion in the model may be one cause for the calculation of higher removal rates. Using the dimensionless variable introduced in equation 83, the dispersivity for the North Carolina site would have to be less than 0.002 m for a less than 15% error between a model with dispersion and one without. In South Carolina for TCE the dispersivity would have to less than 0.01 m, 0.002 m for cisDCE, and 0.06 m for VC for the percent error to be less than 15% for neglecting dispersion.

Reaction rate constants from kinetic studies have a fairly large degree of variability, making it hard to know if the reaction rate constants used in the simulations are the reaction rate constants for the iron used at these sites (Arnold and Roberts, 2006). It has been shown that the type of iron used can have an
The amount of contaminant removed is affected by the amount of iron per volume, type of iron, and the pore water velocity. Although these input values are based on the data from these sites, the data is sparse. For example in the simulation, the input velocity in the barriers is based on data of the groundwater velocity on the site. The velocity in the barrier and in the natural soils in the area should be close, but will not be exactly the same. Also, there was no information about the reaction rate constants that were expected for the type of iron used at these sites. All these approximations about the conditions at these sites likely affected the model predictions.

The competitive models under predicted performance by up to 61%. Although there is evidence for competition between sorbing species, it probably does not have such a pronounced effect on the reaction rates (Arnold and Roberts, 2000; Lu et al, 2011). From these examples the more simple pseudo first order model is the most appropriate model to use with a maximum error of 25% for vinyl chloride.

One dimension analysis obviously simplifies the system to a great degree. The solute may not necessarily travel through the barrier in a straight path, but rather may travel vertically for a while or in some other direction. This will make the effective flow path length much larger, which would allow for more time for degradation. On the other hand some solute will travel through the barrier faster than expected due to dispersion or flows through macro pores which would be an artifact from construction. However, the first order model gives fairly good predictions with a less than 25% error. Given the simplicity and ease of use, more complicated, higher dimensional analysis may be unnecessary because the accuracy of the predictions may not be that much improved. Even in the case of loss of porosity or loss of surface area for reaction, this model may be adjusted to quantify these effects. In the case of a loss of porosity, the new faster velocity may be entered in as the velocity variable. In the case of a loss of surface area, being as the rate constants are surface normalized, the rate constant can be calculated with a lower surface area (eq 76), which would in effect lower the kinetic rate constant. This model is very useful as long as the input variables (reaction rates and velocity) are accurate.

**Sensitivity Analysis:**

With all the uncertainty in rate coefficients and the natural variation of groundwater flow, it is important to know how variations in the model inputs will affect the output concentrations. The packing of the iron and the type of iron will result in differences in the rate coefficients for the dechlorination of PCE and TCE. How important these changes are will help elucidate the importance of iron type. If differences in some of the rate coefficients are not that important than the cheapest iron would be the one to select for a barrier. If the reaction rate constants are very important, then the selection of iron would be based on the one that has the faster reaction rate and cost may not be as influential. A "global" approach to the sensitivity test was taken.

The method of "Sobol" was used to do the sensitivity analysis. This method uses Monte Carlo estimations to quantify the variance produced by each variable or combinations of variables. This type of analysis is called a global analysis because instead of varying one variable at a time, all the variables are altered according to a predefined distribution and then the variance created by each variable is analyzed (Saltelli et al., 2004).
Each of the reaction rates were made to range one order of magnitude larger and smaller from the reaction rates determined by Arnold and Roberts (Arnold and Roberts, 2000). The exceptions are; TCE which has a slightly higher upper bound due to other sources of data (Table 4), pore water velocity has a smaller range which is more realistic according to previous barrier installation data, and three reaction rates (o,p,and q see Table 13) were set constant because these reaction pathways do not affect the concentrations of any of the targeted species (PCE, TCE, DCE isomers, and VC). Table 13 shows the description, range, and distribution used for each variable. A uniform distribution was used to allow each variable to fluctuate within their respective ranges without preference for a mean value.

The first step is the input of two sample matrices. The columns range from \( x_1 \) to \( x_n \), \( x \) being the variables. There are \( N \) number of rows which is the number of Monte Carlo simulations that are run. \( N \) can vary from a few hundred to thousands. In this study 3000 was used. The second matrix is the same structure as the first except it is a random re-sampling of the input distributions and is thus called the "re-sample matrix" see equations 86 and 87 (Saltelli et al., 2004).

\[
M_1 = \begin{bmatrix}
    x_1^{(1)} & x_2^{(1)} & \cdots & x_k^{(1)} \\
    \vdots & \vdots & \ddots & \vdots \\
    x_1^{(N)} & x_2^{(N)} & \cdots & x_k^{(N)}
\end{bmatrix}
\]

\[
M_2 = \begin{bmatrix}
    x_1^{(1')} & x_2^{(1')} & \cdots & x_k^{(1')} \\
    \vdots & \vdots & \ddots & \vdots \\
    x_1^{(N')} & x_2^{(N')} & \cdots & x_k^{(N')}
\end{bmatrix}
\]

From these two matrices a third matrix \( N \) can be made. \( M_1 \) is the sample matrix and \( M_2 \) is the resample matrix and \( N \) is the matrix where all factors are taken from the re-sample matrix (eq. 87) except for the \( x_j \) which would be the variable being analyzed, its values would be taken from the sample matrix (eq. 86). From matrix \( M_1 \) or \( M_2 \) the unconditional variance (\( V(Y) \)), and unconditional mean (\( E(Y) \)) may be estimated (\( Y \) being the results obtained from the model) (Saltelli et al., 2004).

\[
N = \begin{bmatrix}
    x_1^{(1')} & \cdots & x_j^{(1')} & \cdots & x_k^{(1')} \\
    \vdots & \ddots & \vdots & \ddots & \vdots \\
    x_1^{(N')} & \cdots & x_j^{(N')} & \cdots & x_k^{(N')}
\end{bmatrix}
\]

\[
E(Y) = \frac{1}{N} \sum_{r=1}^{N} f(x_1^r, x_2^r, \ldots, x_k^r)
\]

\[
V(Y) = \frac{1}{N-1} \sum_{r=1}^{N} f^2(x_1^r, x_2^r, \ldots, x_k^r) - E^2(Y)
\]

Now the first order sensitivity measure may be computed using the following equations:
U is obtained from values of Y corresponding to the sample matrix and the "N" matrix:

\[
S_j = \frac{V(E(Y \mid x_j))}{V(Y)}
\]  \hspace{1cm} (91)

\[
V(E(Y \mid x_j)) = U_j - E^2(Y)
\]  \hspace{1cm} (92)

So U is the product of the sample matrix times the "N" matrix which is where all the factors are re-sampled except for the \(j^{th}\) component. The \(j^{th}\) component is the variable which is being analyzed for the variance that it will produce in the results. For factors that have a large influence, the sensitivity measure \(S_j\) will be large. However \(S_j\) will only vary from 0 to 1 and the sum of \(S_j\) will be equal to 1 for an additive model and less than 1 for a model that is not additive. Sometimes small negative numbers are calculated due to numerical errors and indicate little to no influence. Another note is that these estimates will only work for orthogonal or non-correlated variables. If the variables are correlated these measures must be calculated in a different way to account for correlations between variables. Another important note is that when using equations 91 and 92 which calculates the variance produced by the \(j^{th}\) factor, \(E^2\) should be calculated as follows (Saltelli et al., 2004):

\[
E^2 = \frac{1}{N - 1} \sum_{r=1}^{N} f(x_1^{r'}, x_2^{r'}, \ldots, x_k^{r'}) \times f(x_1^{r'}, x_2^{r'}, \ldots, x_k^{r'})
\]  \hspace{1cm} (94)

If second or higher ordered indices are desired, the same procedure is followed except in the "N" matrix all the factors are re-sampled except for the \(j^{th},i^{th}\) and so on.
Table 13: Ranges and distributions used for the sensitivity analysis.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Range (h⁻¹)</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>k</td>
<td>TCE to chloroacetylene</td>
<td>2.15×10⁻³ - 0.6</td>
<td>Uniform</td>
</tr>
<tr>
<td>e</td>
<td>TCE to transDCE</td>
<td>5.52×10⁻⁶ - 5.02×10⁻⁴</td>
<td>Uniform</td>
</tr>
<tr>
<td>h</td>
<td>TCE to cisDCE</td>
<td>3.37×10⁻³ - 3.37×10⁻²</td>
<td>Uniform</td>
</tr>
<tr>
<td>z</td>
<td>TCE to 1,1 DCE</td>
<td>2.87×10⁻³ - 2.87×10⁻¹</td>
<td>Uniform</td>
</tr>
<tr>
<td>a</td>
<td>PCE to dichloroacetylene</td>
<td>1.44×10⁻⁴ - 1.44×10⁻²</td>
<td>Uniform</td>
</tr>
<tr>
<td>b</td>
<td>PCE to TCE</td>
<td>2.11×10⁻⁴ - 2.11×10⁻³</td>
<td>Uniform</td>
</tr>
<tr>
<td>g</td>
<td>transDCE to vinyl chloride</td>
<td>8.51×10⁻³ - 8.51×10⁻³</td>
<td>Uniform</td>
</tr>
<tr>
<td>f</td>
<td>transDCE to acetylene</td>
<td>7.07×10⁻³ - 0.707</td>
<td>Uniform</td>
</tr>
<tr>
<td>w</td>
<td>cisDCE to vinyl chloride</td>
<td>4.06×10⁻⁴ - 4.06×10⁻²</td>
<td>Uniform</td>
</tr>
<tr>
<td>l</td>
<td>cisDCE to acetylene</td>
<td>6.32×10⁻³ - 0.632</td>
<td>Uniform</td>
</tr>
<tr>
<td>m</td>
<td>1,1 DCE to ethylene</td>
<td>5.95×10⁻³ - 0.595</td>
<td>Uniform</td>
</tr>
<tr>
<td>n</td>
<td>Vinyl chloride to ethylene</td>
<td>6.55×10⁻³ - 0.655</td>
<td>Uniform</td>
</tr>
<tr>
<td>o</td>
<td>Dichloroacetylene to trans DCE</td>
<td>1.51×10⁻² - 1.51</td>
<td>Uniform</td>
</tr>
<tr>
<td>p</td>
<td>Dichloroacetylene to cisDCE</td>
<td>5.20×10⁻³ - 0.520</td>
<td>Uniform</td>
</tr>
<tr>
<td>q</td>
<td>Dichloroacetylene to chloroacetylene</td>
<td>0.661</td>
<td>Constant</td>
</tr>
<tr>
<td>r</td>
<td>Chloroacetylene to acetylene</td>
<td>1.69</td>
<td>Constant</td>
</tr>
<tr>
<td>s</td>
<td>Acetylene to ethylene</td>
<td>1.25495</td>
<td>Constant</td>
</tr>
<tr>
<td>v</td>
<td>Pore water velocity</td>
<td>0.01 - 0.6 (m/h)</td>
<td>Uniform</td>
</tr>
</tbody>
</table>

The sensitivity measures were calculated for two different location in the barrier, 0.4 m and 1 m. This was done to explore the influence of the variables change at different locations. 0.4 m and 1 m were chosen because some of the narrowest barriers were about 1 ft thick and 1 m is a common thickness. Tables 14 show the two most important variables affecting the concentration of each of the targeted species (PCE,TCE, DCE isomers, VC) at 0.4 m and at 1 m for two different influent concentrations. In the first trial an influent concentration of 10 mg/l of PCE was simulated. In the second trial an influent concentration of 10 mg/l TCE, 5 mg/l PCE, 2 mg/l cisDCE, and 0.5 mg/l VC was simulated. The N, number of rows or the amount of times the model was run to calculate these indices was 3000 times. Appendix A contains tables with all of the sensitivity measures.

Table 14: The two most important variables (most important 1st) in determining the concentration of the respective species at different places in the barrier and for different influent concentrations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Influent concentration: PCE 10 mg/l</th>
<th>Influent concentration: PCE 5 mg/l, TCE 10 mg/l, cisDCE 2 mg/l, VC 0.5 mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4 m</td>
<td>1 m</td>
</tr>
<tr>
<td>PCE</td>
<td>v,a</td>
<td>a,b</td>
</tr>
<tr>
<td>TCE</td>
<td>k,v</td>
<td>k,a</td>
</tr>
<tr>
<td>cisDCE</td>
<td>l,v</td>
<td>l,v</td>
</tr>
<tr>
<td>transDCE</td>
<td>f,v</td>
<td>f,v</td>
</tr>
<tr>
<td>1,1 DCE</td>
<td>n,k</td>
<td>n,k</td>
</tr>
<tr>
<td>VC</td>
<td>o,w</td>
<td>o,v</td>
</tr>
</tbody>
</table>
As can be seen from Table 14 the most important variables in determining the concentration of each species does not change under differing conditions. The most important factor determining the concentration of TCE at both 0.4 m and 1 m and with differing influent concentrations is the rate constant "k". This is not surprising as this is the pathway where TCE reacts to become chloroacetylene and is the highest rate constant for the TCE degradation pathways. Changing this rate constant created a larger variance in the resulting TCE concentrations. For PCE the rate constant "a" (PCE to dichloroacetylene) has the largest effect on the concentration of PCE at 1 m and the pore water velocity is more important at 0.4 m. This is also an expected result as this is the degradation pathway of PCE with the fastest rate. Some of the results that are a bit more unexpected was the fact that the velocity of the pore water does not play as large of a role as many of the rate constants. This is not to say it is unimportant as it is the second most important factor for many of the species. For vinyl chloride, the most important variable is the rate constant "o" which is the dichloroacetylene to transDCE reaction. This is an unexpected result because "o" is not explicitly in the equation for VC but rather transDCE has a pathway which creates VC. This means that the production of transDCE which can then turn into VC is the most influential step in determining VC concentrations. For cis and transDCE, the variance in the concentrations is related to their degradation pathways to acetylene and not to the pathways which form them. This may be related to the fact that the degradation rate constants are larger than the rate constants which create them. 1,1 DCE sensitivity measure is the most perplexing by being most sensitive to "n" and "k". These reaction pathways are not directly related to the production or degradation of 1,1 DCE. This sensitivity analysis attests to the fact that the rate constant for degradation of TCE is the most important variable to have an accurate numbers for if TCE treatment is the desired goal. In the creation of a barrier, lab tests with the particular iron material to be used along with the water being treated should be conducted so that simulations may be run with accurate rate constants for TCE.

To further investigate the most important variables affecting the concentration of TCE, the effect of these variables is tracked through 1 m of barrier. To do this the influence of the reaction rate k on the TCE concentration is plotted in Figure 22 for the length of a 1m thick barrier. The "k" value is most influential at about 0.3 m into the barrier. At this point approximately 0.73 or 73% of the error in TCE concentrations could be mitigated with an accurate value for "k".
Figure 22: Sensitivity measure the first order rate constant “k” on TCE concentration through a PRB. The influent concentration was PCE only at 10 mg/l.

The pore water velocity is the second most influential variable on TCE concentration. The pore water velocity becomes more influential at about 0.5m.

Figure 23: Sensitivity measure of the influence of pore water velocity on TCE concentration through the barrier. The influent concentration was PCE only at 10 mg/l.
When designing a barrier estimates in changes in pore water velocity or in the rate constant "k" due to passivation of the iron or clogging of the pore spaces need to be considered in for a good estimation of the longevity of the barrier.

Conclusions:

From the models it is clear that this technology is not the best approach to treat PCE. However removal of TCE, DCE isomers, and VC are promising. This technology has in fact been successful at many sites. The first order kinetic model is the best model to use when simulating the dechlorination reactions in a barrier. This is further evidence that mass transfer is the limiting step in the reactions.

When designing a PRB it is important to do batch studies to get an accurate rate constant for the degradation of TCE and PCE. Although batch studies do not simulate an iron barrier as well as column studies, the rate constants generated in batch are within the range of those generated by column, and batch studies are faster and easier to perform. The pore water velocities also play an important role in determining the thickness of the barrier. Although from the sensitivity studies the pore water velocity often times comes second in importance, it still plays a major role in determining the concentration of every constituent in the barrier.

Through this evaluation it is clear that the pathways that create the undesired products (DCE isomers, and VC) do not play major roles in iron barriers. This adds to the effectiveness of these barriers as these undesired products are produced in very small amounts. To get a good grasp of the amount of cis and transDCE that may accumulate in a barrier their degradation pathways should be investigated as they are the ones that will produce the largest variance in these DCE isomer concentrations. In order to estimate the expected life of a barrier, empirical estimations of precipitate build-up from existing barriers may be incorporated into the model. The rate of degradation of TCE precipitate-coated iron would be the most important to determine. These change in rate constants and pore water velocities can be put into this model and the resulting treatment efficiency predicted.

Future studies for iron barriers should investigate the longevity of these barriers by studying the precipitation reactions that will eventually lead to passivation of the iron. There may be ways to flush the barrier to help remove these coatings from the surface of the iron to reactivate the material. If reactivation of the iron is possible the effectiveness of these barriers will be increased as the life expectancy of them would increase radically. Overall the use of iron to treat these chlorinated solvents is a good technology as it is safe, effective, and degrades the chemicals rather than transferring them to another location.
Works Cited


Lui, Y., G.V. Lowry. Effect of particle age (Fe⁰ content) and solution pH on NZVI reactivity: H₂ evolution and TCE dechlorination. Environmental Science and Technology. 2006. 40, 6085-6090.


Appendix A - Results from sensitivity analysis:

Results from sensitivity analysis at 0.4 m with an influent concentration of PCE at 10 mg/l.

<table>
<thead>
<tr>
<th>Variable</th>
<th>TCE</th>
<th>PCE</th>
<th>transDCE</th>
<th>cisDCE</th>
<th>1,1DCE</th>
<th>VC</th>
<th>Dichloroacetylene</th>
<th>Chloroacetylene</th>
<th>Acetylene</th>
<th>Ethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>0.73184</td>
<td>0.000614</td>
<td>4.65E-05</td>
<td>3.52E-05</td>
<td>0.16995</td>
<td>0.00015</td>
<td>0.000575</td>
<td>0.002454</td>
<td>0.002042</td>
<td>0.003352</td>
</tr>
<tr>
<td>k</td>
<td>-6.47E-05</td>
<td>0.000619</td>
<td>6.06E-05</td>
<td>5.74E-05</td>
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Results from sensitivity analysis at 0.4 m with an influent concentration of PCE at 5 mg/l; TCE 10 mg/l; cisDCE 2 mg/l; VC 0.5 mg/l.

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Results from sensitivity analysis at 1 m with an influent concentration of PCE at 5 mg/l; TCE 10 mg/l; cisDCE 2 mg/l; VC 0.5 mg/l.

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