Combination of Zero-Valent Iron and Granular Activated Carbon for the Treatment of Groundwater Contaminated with Chlorinated Solvents

by

Donald E. Tillman

M.S., Rural Engineering
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ABSTRACT

This study addressed the long-term economical benefits of adding the innovative zero-valent iron technology to a currently operating granular activated carbon (GAC) system. The concept is based on aboveground vessels, filled with zero-valent iron, which would pretreat the extracted water before it flows through the GAC. This was examined for the remediation of the CS-4 groundwater plume underlying the Massachusetts Military Reservation at Cape Cod. Contaminants to be treated are tetrachloroethylene, trichloroethylene, 1,2-dichloroethylene, 1,1,2,2-tetrachloroethane in concentrations up to 62 ppb. The study was based on data from literature and from reports of previous studies of the site. No laboratory tests were conducted.

The results indicated that the combination of these two technologies is probably not an effective means to reduce long-term treatment costs. The investments of adding an aboveground zero-valent iron vessel do not balance the overall savings. The build up of vinyl chloride (VC) as a result of the degradation of the chlorinated hydrocarbons by the iron was a major concern and was modeled using kinetic expressions. It was shown that an increase of VC over regulatory limits must be expected if contact time of the contaminated water with the iron is more than 0.17 hr. Depending on the degradation rate of VC, a worst case increase up to 50 ppb was modeled. The design of the combined treatment system impeded excessive build up of VC. A required bulk volume of iron of 500 ft³ was estimated to pretreat the water. A bench-scale study should be conducted to verify the results.

Thesis Supervisor: Dr. Philip M. Gschwend
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1. Introduction

1.1 Context

The Cape Cod aquifer is contaminated by various pollutants emanating from the Massachusetts Military Reservation (MMR). One such plume of contaminants, termed Chemical Spill 4 (CS-4), is being contained. At present, a pump-and-treat system has been installed as an interim remedial action to prevent the advancement of the plume. Contaminated water is extracted at the toe of the plume, treated to reduce the contaminant concentrations to regulatory levels, and discharged back into the aquifer. However, operation and maintenance costs of pump-and-treat systems are high. A final remedial plan must be formulated to completely clean up the groundwater.

To develop a final remediation scheme for the CS-4 site was the project objective of a team of six graduate students at the Massachusetts Institute of Technology (MIT). This team-project was completed within the frame of the Masters of Engineering Program of the Department of Civil and Environmental Engineering at MIT. Each team member addressed a different aspect of the overall objective in depth. The findings of these studies were then put together to present a possible, final remediation scheme. The executive summary and the results of the team-project are given in Appendix F.

Within this context and as part of the overall team-project, this thesis focuses on the aboveground treatment of the extracted groundwater.

1.2 Problem

At almost all remediation sites where contaminated groundwater is involved, the prevailing method to achieve cleanup goals is pump-and-treat. Treatment of the extracted groundwater is often achieved by a Granular Activated Carbon (GAC) system (Mackay and Cherry, 1989). This concept may also be considered as a final remedial system for the CS-4 site.
GAC is a proven and reliable technology (Stenzel et al., 1989). However, one of the disadvantages is that the operation and maintenance cost are relatively high. Principal cost contributions are due to the periodical exchange and reactivation of the exhausted carbon, when no more organic compounds can be adsorbed to it. Since typical pump-and-treat remediation requires operation of the system over a long period of time (see chapter 3.4.1; for CS-4 approximately 90 years), this procedure results in high long-term costs. More cost-effective treatment alternatives are needed.

1.3 Objectives

The objective of the present thesis was to answer to the following questions:

- Can the currently operating GAC system at the CS-4 site be optimized in a way which would result in less cost-intensive long-term operation?

- What are the expected savings for such an optimization?

This task was addressed by focusing on a concept of combining the currently operating GAC treatment with another treatment technology. Consequently, the first goal of this study was to get a thorough understanding of the principles, cost and design considerations of the GAC treatment technology. The second goal was to estimate potential cost savings by combining the GAC with an alternative treatment technology.

1.4 Scope

All the used data was based on the review of reports of previous studies at the CS-4 site as part of the Installation Restoration Program (IRP), and on the other theses within the CS-4 team-project. Also, literature data and direct information provided by treatment technology suppliers were consulted.

Chapter 2 and 3 describe briefly the site, its characteristics and the current remedial situation. This part was adapted primarily from the team-project.
Chapter 4, 5, and 6 elucidate the GAC treatment technology, treatment alternatives, and the emerging zero-valent iron technology, respectively. The costs of GAC and zero-valent iron technology were only estimated to an extent which allows comparison of the technologies and estimation of savings or cost due to their combination. Specific evaluation of the construction and design considerations of the combination concept were not examined.

The combination concept was developed to a preliminary stage only. While conclusions regarding its feasibility can be drawn, greater details need to be studied further.
2. Background and Site Description

2.1 Location

Cape Cod is located in southeastern of Massachusetts (Figure 2-1). It is surrounded by Cape Cod Bay on the north, Buzzards Bay on the west, Nantucket Sound to the south, and the Atlantic Ocean to the east. Cape Cod, a peninsula, is separated from the rest of Massachusetts by the man-made Cape Cod Canal.

![Map of the Commonwealth of Massachusetts.](image)

*Figure 2-1: Map of the Commonwealth of Massachusetts.*

The MMR is situated in the northern part of western Cape Cod (Figure 2-2). Previously known as the Otis Air Force Base, the MMR occupies an area of approximately 22,000 acres (30 square miles).
2.2 MMR Setting and History

The MMR has been used for military purposes since 1911. From 1911 to 1935, the Massachusetts National Guard periodically camped, conducted maneuvers, and provided weapons training in the Shawme Crowell State Forest. In 1935, the Commonwealth of Massachusetts purchased the area and established permanent training facilities. Most of the activity at the MMR occurred after 1935, including operations by the U.S. Army, U.S. Navy, U.S. Air Force, U.S. Coast Guard, Massachusetts Army National Guard, Air National Guard, and the Veterans Administration.

The majority of the activities consisted of mechanized army training and maneuvers as well as military aircraft operations. These operations inevitably included the maintenance and support of military vehicles and aircraft as well. The level of activity varied greatly over the operational years. The onset of World War II and the demobilization period following the war (1940-1946) were the periods of most intensive army activity. The period from 1955 to 1973 saw the most intensive aircraft operations. Today, both army training and aircraft activity continue at the MMR, along with U.S. Coast Guard activities. However, the greatest potential for the release of contaminants into the
environment was between 1940 and 1973 (E.C. Jordan, 1989a). Wastes generated from these activities included oils, solvents, antifreeze, battery electrolytes, paint, waste fuels, metals and dielectric fluids from transformers and electrical equipment (E.C. Jordan, 1989b).

2.3 Importance of Aquifer Restoration

2.3.1 Natural Resources

Cape Cod is characterized by its richness of natural resources. Ponds, rivers, wetlands and forests provide habitat to numerous species of flora and fauna. Many of the Cape’s ponds and coastal streams serve as spawning and feeding grounds for a variety of fish (Massachusetts Executive Office of Environmental Affairs, 1994). The Crane Wildlife Management Area, located south of the MMR in western Cape Cod, is home to many species of birds and animals. In addition, throughout the Cape there are seven Areas of Critical Environmental Concern (ACEC) as defined by the Commonwealth of Massachusetts. These were established as areas of highly significant environmental resources and protected because of their central importance to the welfare, safety, and pleasure of all citizens.

2.3.2 Land and Water Use

The majority of the land in Cape Cod is covered by forests or is "open land". One quarter of the land is residential, and less than 1% of the land is used for agriculture or pasture (Cape Cod Commission, 1996).

Water covers over 4% of the surface area of Cape Cod. This water is distributed among wetlands, kettle hole ponds, cranberry bogs, and rivers. Nevertheless, all 15 communities of Cape Cod meet their public supply needs with groundwater. Falmouth is the only municipality that uses some surface water (from the Long Pond Reservoir) as a drinking water source. Approximately 75% of the Cape's residents use water supplied through public works, while the remaining use private wells within their property.
Agriculture constitutes a part of the water use in Cape Cod. Cranberry cultivation is an important part of the economy of the Cape and a water-intensive activity. The fishing industry also provides a boost to the Cape’s economy. Tourism accounts for a substantial part of the Cape’s economy, and therefore the surface water quality is important.
3. Current Situation

3.1 Site Characterization

Site characterization was based on previous studies in the area. Equilibrium sorption (since this factor may greatly affect the fate of the contaminants) however, was tested in the laboratory (Appendix F; Khachikian, 1996).

3.1.1 Hydrogeology

On a regional scale, the geology of western Cape Cod is composed of two glacial moraines deposited along the western and northern edges and a broad outwash plain between the two moraines. The outwash is composed of poorly sorted fine to coarse grained sands, and its thickness varies from approximately 175 ft to 325 ft. Precipitation is the sole source of recharge to the aquifer. Values of recharge are between 18 in/yr and 23 in/yr. A value of 380 ft/day has been accepted as a representative value of average hydraulic conductivity of the outwash sands (regional scale). Effective porosity is estimated to be about 0.39, and average hydraulic gradient is 0.0014 (Lázaro, 1996; López-Calva, 1996).

The groundwater flow model, which was developed for the CS-4 area, showed great sensitivity to the properties of the glacial moraine. The calibrated model (based on head distributions and particle tracking) used an average hydraulic conductivity of 220 ft/day, a seepage velocity of 0.8 ft/day, and recharge of 19 in/yr (Appendix F; Lázaro, 1996; López-Calva, 1996).

3.1.2 Retardation

The organic carbon content in the sediments is very low (in general, less than 0.01%). Because of this low organic content, the degree of sorption of the contaminants is relatively small. The retardation coefficients (R), are 1.04, 1.10 and 1.25 for DCE, TCE and PCE, respectively. For the more strongly sorbing PCE, the retarded longitudinal
macrodispersivity increases by a factor of 2.1. For the least sorptive compound (DCE), the velocity variances introduced by sorption are small as reflected by a small (factor of 1.2) increase in the longitudinal macrodispersivity (Appendix F; Khachikian, 1996).

3.1.3 Chemistry of Groundwater

In order to design treatment processes for the contaminated groundwater, a basic examination of the chemistry of the groundwater must be performed. The properties of the groundwater of particular interest are shown in Table 3-1. The groundwater contains high values of dissolved oxygen (5-10 mg/L) although the values vary with depth (depth < 100 ft below water table). Values for pH range between 5 and 7, and the temperature is approximately 10°C. The range of concentrations of iron and manganese are also of particular interest since high concentrations can influence a treatment system considerably (precipitation, plugging) (E. C. Jordan, 1990; LeBlanc et al., 1991; ABB ES, 1992b).

Table 3-1: Groundwater properties (E. C. Jordan, 1990; LeBlanc et al., 1991; ABB ES, 1992b).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved oxygen (mg/L)</td>
<td>5.0-10.0</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>low</td>
</tr>
<tr>
<td>pH</td>
<td>5-7</td>
</tr>
<tr>
<td>Iron (μg/L)</td>
<td>up to 3,500 (but normally very low)</td>
</tr>
<tr>
<td>Manganese (μg/L)</td>
<td>up to 600</td>
</tr>
<tr>
<td>Temperature</td>
<td>13°C</td>
</tr>
</tbody>
</table>

3.2 Groundwater Plume

3.2.1 Plume Location

The CS-4 plume is located in the southern part of MMR as shown in Figure 3-1, moving southward. According to E. C. Jordan (1990), CS-4 is 11,000 ft long, 800 ft wide and 50 ft thick (5 ppb contour). These dimensions of the plume have been defined using field observations. However, by using the developed contaminant transport model and simulating a continuous input of the contaminants, the plume resulting from the
Simulations had greater dimensions than the plume defined by field observations. Average dimensions were 1,180 ft for the width, 60 ft for the height, and 14,660 ft for the length. However, this model was demonstrated to be sensitive to variations in input values of hydrogeologic parameters (Appendix F; Lázaro, 1996).

Figure 3-1: CS-4 plume and well-fence location.

3.2.2 Contamination

The results of the field sampling are shown in Appendix A (E. C. Jordan, 1990). Because soil contamination has been identified as the source of the groundwater contamination, the table in Appendix A lists not only the maximum concentrations of the chemicals which were found by sampling the aquifer downgradient of the source, but also the levels in the soil at the source location. In the mean time, the contaminated soil has been excavated and thus the source of the groundwater contamination removed.
A comparison of the measured values of each addressed compound with their regulatory limits (Maximum Contaminant Levels, MCL) show that four compounds exceed the MCL:

- Tetrachloroethene (PCE)
- Trichloroethene (TCE)
- 1,2-Dichloroethene (DCE, total of cis- and trans isomer)
- 1,1,2,2-Tetrachloroethane (TeCA)

These four compounds are therefore considered as contaminants of concern, which need to be removed from the groundwater. Table 3-2 summarizes the sampled concentrations. Maximum measured concentrations and average concentrations within the plume as well as an approximate frequency of detection and the individual regulatory limits are given. Average concentration values represent only an approximation, since their determination depends on a definition of the plume border.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Maximum concentration (ppb)</th>
<th>Average concentration (ppb)</th>
<th>Frequency of detection</th>
<th>Regulatory limit (MCL) (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrachloroethylene (PCE)</td>
<td>62</td>
<td>18</td>
<td>14/20</td>
<td>5</td>
</tr>
<tr>
<td>Trichloroethylene (TCE)</td>
<td>32</td>
<td>9.1</td>
<td>14/20</td>
<td>5</td>
</tr>
<tr>
<td>1,2-Dichloroethene (DCE)</td>
<td>26</td>
<td>1.1</td>
<td>11/20</td>
<td>70</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane (TeCA)</td>
<td>24</td>
<td>6.8</td>
<td>1/20</td>
<td>2a</td>
</tr>
</tbody>
</table>

ABB ES, 1992b

a No Federal of Massachusetts limits existent. Therefore, a risk-based treatment level was proposed. This was calculated assuming a $1 \times 10^{-5}$ risk level and using the US EPA risk guidance for human health exposure scenarios.

The total mass of the contaminants, which were discharged from the now removed contaminated soil to the aquifer (source loading), was calculated "backwards" from the concentrations found in the plume (Appendix F; Lázaro, 1996). Due to limitations in the
program code, PCE, TCE and DCE were simulated as one contaminant. Figure 3-2 shows that at least 290 kg (sum of columns) of the compounds of concern were discharged to the aquifer.

The source was modeled as a continuous source input. From groundwater velocity data, it was determined that the contamination must have started at least 15 years ago. The source loading was modeled as seven 5 year intervals (from 1960 to 1993, Figure 3-2).

![Figure 3-2: Source loadings for the CS-4 plume (Sum of PCE, TCE and DCE only).](image)

### 3.3 Existing Remedial Action

#### 3.3.1 Interim Remedial Action

The currently operating remedial action was designed as an interim solution, with the objective to contain the plume against further migration. This is achieved by a pump-and-treat system, consisting of the following components:

- Extraction of the contaminated groundwater at the leading edge of the plume by 13 adjacent extraction wells, forming a well-fence as shown in Figure 3-1.
- Transport of the extracted water from the well-fence through pipe to the treatment facility, which is located at the edge of the MMR area.
- Treatment of the water with a Granular Activated Carbon (GAC) system.
- Discharge of the treated water back into the aquifer through an infiltration gallery, which is located next to the treatment facility.
At the time of the implementation of the interim system (1993), it was expected that it would operate about 5 years, until a final remedial system is chosen and implemented. Since the treatment facility started operating in November 1993, the extracted water was predominantly clean. From time to time though, detected concentrations of the contaminants of concern in the water were up to 0.5 ppb (ABB ES, 1996).

### 3.3.2 Pumping Schemes and Treatment Technology

The treatment facility will not be addressed here but discussed in detail in Chapter 4. With regard to the pumping rates, the extraction pumps are currently operated at an overall pumping rate of 140 gpm. Simulations using the current well-fence indicated that this pumping rate is appropriate (Appendix F; López-Calva, 1996). Therefore, for all further calculations in this report, an overall pumping rate of 140 gpm was used.

### 3.4 Objectives for Final Remedy

In contrast to the objective of the current interim remedial action, the final remedial action will address the overall, long-term objectives for the CS-4 Groundwater Operable Unit which are as follows (ABB ES, 1992b):

- Reduce the potential risk associated with ingestion of contaminated groundwater to acceptable levels.
- Protect uncontaminated groundwater and surface water for future use by minimizing the migration of contaminants.
- Reduce the time required for aquifer restoration.

In terms of treatment objectives, the target levels for the treatment of the water are defined through the established Maximum Contaminant Levels (MCL, Table 3-2).

The final remedial system could be chosen to be the same as the existing interim one, or could encompass other remedial concepts.
3.4.1 Expected Performance of Pump-and-Treat: General Review

Since the CS-4 pump-and-treat system was put into operation just recently (November 1993, performance data is lacking. In order to get an estimate of the expected performance, the performances of pump-and-treat systems at other locations were briefly studied by reviewing the literature. At almost all remediation sites, where contaminated groundwater is involved, the prevailing method to achieve cleanup goals is pump-and-treat (Mackay and Cherry, 1989). Specifically, this technology is employed at approximately three-quarters of the Superfund sites where groundwater is contaminated and at most sites governed by the Resource Conservation and Recovery Act (RCRA) (MacDonald and Kavanaugh, 1994).

Numerous authors have raised serious concerns about the ability of existing technology to restore contaminated groundwater to environmentally and health-based sound conditions (Mackay and Cherry, 1989; Doty and Travis, 1991; MacDonald and Kavanaugh, 1994). These and other researchers argue that one of the major disadvantages of pump-and-treat systems is the necessity of pumping over a long period of time. In the case of the CS-4 site, the groundwater transport model (retardation included) predicted continuous pumping for approximately 90 years for the removal of the contaminants from the aquifer (Appendix F). MacDonald and Kavanaugh (1994) however state that it is almost impossible to predict how long pumping and treating will take in order to restore an aquifer.

Other studies have shown that pump-and-treat, in conjunction with other treatment technologies, is able to restore aquifers effectively (Ahlfeld and Sawyer, 1990; Bartow and Davenport, 1995; Hoffman, 1993). However, both sides agree that pump-and-treat is an effective means of controlling the plume migration. Conclusively, the interim CS-4 pump-and-treat system is an appropriate way to quickly respond to the plume migration.

According to a study of the National Research Council (NRC, 1994), groundwater restoration through pump-and-treat may be possible only for sites with relatively simple contamination scenarios. At more complex sites (e.g. most Superfund sites), health-based
drinking water standards may not be achieved. Although thousands of pump-and-treat systems are operating in the United States (the exact number is unknown), comprehensive studies of the performance of individual pump-and-treat systems are rare. In all, the NRC identified 77 sites where sufficient data was available to evaluate the performance of the system (MacDonald and Kavanaugh, 1994). At only 8 of the 77 sites, cleanup goals were reportedly achieved after one to several years of operation. The NRC committee attributed the success of cleanup in part to the relatively simple characteristics of the sites and the rapid initial response. The source of contaminants were quickly controlled and the plume of contaminated groundwater was therefore relatively small. At the other 69 sites, the pumping caused an initial decrease in contaminant concentrations in the extracted water, followed by a leveling of concentration and sometimes a gradual decline. Also, the characteristics of the contaminants play a major role. While for dissolved solutes or LNAPL’s (Light Non-Aqueous Phase Liquids), some success in pumping a significant fraction to the surface has been reported, for DNAPL’s, which are more dense than water, very little success has been achieved in even locating them in the subsurface, let alone removing them.

On the basis of the data from the 77 sites, the NRC committee concluded that cleaning up groundwater to health-based standards using conventional pump-and-treat systems may be feasible at a limited number of sites having relatively simple characteristics. The sites that are simplest to clean up are those where the contaminants are present in dissolved form, the geology is relatively homogenous, and the contamination is recent. However, the committee determined that portions of most sites will remain contaminated above health-based levels even after long-term pumping operation (MacDonald and Kavanaugh, 1994).

Applying these generalizations to the CS-4 situation, it was concluded that a pump-and-treat system will be able to contain the plume as an interim action, in order to finally remediate the aquifer, long duration of pumping must be expected. What appears
favorable to clean-up though is the very low organic matter content of the subsurface, which results in small retardation factors (Khachikian 1996; Appendix F).

3.4.2 Conclusion

The final remedial design of the CS-4 plume has to consider three options:

- Optimize the current pump-and-treat system: Number of extraction wells, pumping rates, flow rates through GAC, configuration of GAC.

- Enhance current pump-and-treat system by combining it with other treatment technology. For example, through the implementation of bioremediation, the concentration of contaminants in the groundwater may get attenuated and therefore the GAC would get loaded with less contaminants (saving in operation costs). Or, the GAC could be combined with another aboveground treatment process, which may result also in less operation cost for the GAC as well.

- Change the pump-and-treat scheme to an in situ scheme, for example implementation of bioremediation (Skiadas, 1996) or a reactive wall (Goo, 1996).

This study focused on the second option. As it can be seen in chapter 6, the zero-valent iron technology was selected to be combined with the GAC.

In the following chapter 4, the GAC technology is presented and the related operation costs estimated. Chapter 6 results in an estimate of capital costs to install the zero-valent iron technology. A comparison between the two cost estimates will indicate whether this option would yield in economic benefits.
4. Expected Performance of GAC

4.1 Description of System

The treatment facility consists of two adsorber vessels in series filled with Granular Activated Carbon (Figure 4-1, Model 7.5 of Calgon Carbon Corporation). Each tank, 7.5 ft in diameter and 10 ft carbon depth, contains 10,000 lb of activated carbon. This system of two downflow, fixed-bed adsorbers in series is the simplest and most widely utilized design for groundwater treatment applications (Stenzel et al., 1989). Two vessels in series assure that the carbon in the first vessel is completely exhausted before it is replaced, thus contributing to the overall carbon efficiency. The removed carbon is then transported off-site for reactivation.

The CS-4 plume water contains little suspended solids (E. C. Jordan, 1990). Therefore, filtration (e.g. sand filtration) of the plume water in order to prevent plugging of the subsequent treatment steps is not required. Although the suspended solid content in the influent is low, the carbon needs to be backwashed periodically. The installed backwash tank, 12 feet in diameter, contains 11,200 gallons of clean water. This allows backwash for 20 minutes with 560 gpm.

![Figure 4-1: GAC configuration at CS-4.](image)

- **Valve open**
- **Valve closed**

**Figure 4-1: GAC configuration at CS-4.**
Metals such as iron or manganese are not present in high concentrations in the plume water (E. C. Jordan, 1990). Hence, a treatment step for metal precipitation is not necessary.

4.2 Theoretical Background

4.2.1 General Considerations

GAC is a technology based on adsorption. The soluble or gas phase contaminants (sorbates, in our case the chlorinated organic solvents) are removed from the water- or gas phase by contact with an interface, e.g. the activated carbon surface. Examination of a microscopic cross-section of activated carbon reveals a porous structure with a large internal surface area, where the sorbates can attach. Activated carbon is available in both powdered and granular form, but the latter is most commonly used for the removal of a wide range of sorbates from water (Metcalf & Eddy, 1991; La Grega et al., 1994).

An important feature is that the treatment of the water with GAC does not destroy the contaminants. The process includes only a transfer of the contaminants from the water to the solid phase. For final destruction of the contaminants, the exhausted carbon (i.e. when the adsorbed contaminants are in equilibrium with the dissolved contaminants in the influent, and thus no more contaminants can be adsorbed with respect to the inflow concentration) needs to be burned, resulting in oxidation of the contaminants.

4.2.2 Preparation and Reactivation of the Carbon

Activated carbon is prepared by producing a char from materials such as almond, coconut, walnut hulls, woods, or coal. This is done by burning the material with insufficient supply of air so that the hydrocarbons are driven off. Then, by exposing the char particle to an oxidizing gas of steam, air and CO₂ at a high temperature, the char develops a porous structure and is now called activated. The porous structure results in a large internal surface area in a range of 650 up to 1800 m²/gram of carbon. The chosen
carbon for the CS-4 treatment facility, Calgon F-300, has an internal surface area of approximately 1000 m²/g (EPA, 1971).

Once exhausted, carbon can be reactivated by dewatering it and then oxidizing the organic matter in a furnace at temperatures of about 870 - 980 °C (1600 - 1800 °F). This results in removing the sorbed contaminants from the carbon surface. But through the reactivation process, about 5-15% of the carbon gets destroyed. Also, the adsorption capacity of reactivated carbon is slightly less than that of virgin carbon (Metcalf & Eddy, 1991). An alternative to thermal reactivation is solvent reactivation (e.g. with acetone, dimethylformamide).

4.2.3 Adsorption Capacity

Adsorption equilibrium is attained when the rate of adsorption onto the solid surface equals the rate of desorption from the solid surface back to the water phase (Neely and Isacoff, 1982). The quantity of adsorbate that can be taken up by an adsorbent (adsorption capacity) is a function of both the characteristics and concentrations of adsorbate as well as the temperature (Metcalf & Eddy, 1991). Thus, the adsorption capacity can be described as an equilibrium relationship between the moles of sorbate (i.e. contaminants) adsorbed per unit mass of sorbent (i.e. carbon) and the concentration of sorbate remaining in solution (Schroeder, 1977). Since these relationships are given for a constant temperature, they are called isotherms.

Equations that are commonly used to describe the experimental isotherm data were developed by Freundlich, by Langmuir and by Brunauer, Emmet and Teller (BET isotherm). While both Langmuir and BET isotherms are based on theoretical developments, the Freundlich isotherm model is an empirical relationship. The latter is used most commonly to frame the adsorption on activated carbon mathematically:
\[ \frac{X}{M} = K \cdot C_i^{1/n} \]  \hspace{2cm} (1)

where \( X \) = mass of contaminant adsorbed (mg)
\( M \) = mass of carbon (g)
\( K, n \) = empirical constants to fit curve to data (Freundlich constants, \( K \) in L/g)
\( C_i \) = concentration in solution after adsorption equilibrium is reached, which equals the influent concentration (mg/L)

note that
\[ X = (C_i - C_e) \cdot V \]  \hspace{2cm} (2)

where \( C_e \) = effluent concentration (mg/L)
\( V \) = volume of solution (L)

Therefore, the required mass of carbon for each liter of treated water can be calculated with information on \( K \) and \( n \).

Compared to batch tests in the laboratory which are used to develop isotherms, full scale units normally don’t reach equilibrium since the contact time of the water in the carbon vessel is too short (Metcalf & Eddy, 1991). Although reported isotherm data may also not reflect equilibria, the contact times there typically are longer. Also, isotherm lab tests are conducted with virgin carbon, under steady conditions (temperature, pH, etc.), and allowing no biological activity building up. These conditions are usually not met in operating units. Therefore, it is important to account for the reduction of the adsorption capacity for field scale units.

4.2.4 Multicomponent Solutions

In water treatment, the ideal case of one adsorbate being removed onto an adsorbent is seldom encountered. The objective of adsorption in most real systems is to remove several adsorbates at the same time. This complicates both the theoretical picture of
equilibrium among adsorbates and adsorbent and the ability of the engineer to apply the
theory in practice (Montgomery, 1985). Typically, there is a depression of the adsorptive
capacity of any individual compound in a solution of many compounds (since the
compounds are competing for sorption sites). However, if the concentrations of the
solute in the mixture are low, one may expect no significant decrease in the adsorption
behavior of the organic molecules, since contaminant molecules are not likely to
encounter competing molecules.

Several mathematical models have been developed to describe multicomponent
adsorption behavior (e.g. Radke and Prausnik, 1972 (IAS model); Baldauf, 1978;
Crittenden and Weber, 1978; DiGiano et al., 1978). The model of DiGiano and co-
workers (1978) allows direct computation of the solute loading from known
concentrations in the mixture:

\[ q_i = k' \left( \frac{n'-1}{n'} \right) \left( k_i C_i^{n_i} \right)^{\frac{1}{n'}} \left[ \sum_{N} \left( \frac{k_i}{k'} C_i^{n_i} \right) \right]^{\frac{1}{n'} n'-1} \]  

(3)

Where \( C_i \) = concentration of solute i in a mixture

\( k_i, n_i = \) Freundlich constants \((K_f, \frac{1}{n})\), describing single solute adsorption

\( k', n' = \) average \( k_i \) and \( n_i \) constants, respectively

\( N = \) number of solutes in mixture

Compared to actual measurements, this model provides a good prediction of the
adsorption behavior of a multicomponent mixture especially if the contaminants are at
low concentrations (DiGiano et al., 1978).
4.2.5 Kinetics of Adsorption

The rate of adsorption is another important issue to address in order to understand and effectively design carbon units. It may influence the required contact time and therefore the influent flowrate to give sufficient time to capture the solutes.

The adsorption of organic contaminants takes place in three steps: 1) macrotransport, 2) microtransport, and 3) adsorption. Macrotransport is referred to as the movement of the molecules through the water to the liquid-solid interface by advection and diffusion. Microtransport involves the diffusion of the molecules through the micropore system of the GAC granule to the adsorption sites. And the third step, adsorption, finally describes the attachment of the organic molecules to the carbon (Faust and Aly, 1987). The overall rate therefore will be controlled by the slowest step. Generally speaking, macrotransport seems to be the rate-limiting step in systems that have poor mixing, dilute concentrations of adsorbate, small particle sizes of adsorbent, and high affinity of adsorbate for adsorbent (Helfferich, 1962). In contrast, microtransport limits the overall transfer for those systems that have good mixing, large particle sizes of adsorbent, high concentration of adsorbate, and low affinity for adsorbent (Helfferich, 1962).

The required contact time of the contaminated water with the GAC (empty bed contact time, EBCT) is a function of these parameters. Generally, after an initial rapid decrease in carbon usage rate with increasing EBCT, the curve flattens and no significant reduction in usage rate is gained with increasing contact time (Faust and Aly, 1987). The shape of the curve depends on the particular carbon, the contaminant concentrations, and contaminant characteristics. Most EBCT studies are conducted with contact times up to 1 hour, since EBCTs over 1 hr are considered impractical for field units (Faust and Aly, 1987).
4.3 Adsorption Capacity of GAC at CS-4

4.3.1 Isotherms for Single Components

Different researchers report different values for the Freundlich constants $K_f$ and $1/n$ (Dobbs and Cohen, 1980; Weber, 1981; Benedict, 1982; Love and Eilers, 1982; Crittenden et al., 1985). A list of them can be found in Appendix B. Table 4-1 gives values for each of the contaminants of interest. These values (Dobbs and Cohen, 1980) are chosen as they are often cited in the literature and also represent the values with which the existing GAC was designed. For a given inflow concentration of the contaminant (for the calculations in Table 4-1 the maximum encountered values at CS-4 are chosen), the adsorption capacity at equilibrium can be estimated by using equation 1, chapter 4.2.3.

From isotherms for the F-300 carbon of the carbon supplier, Calgon Carbon Corporation (Appendix C), $K_f$ and $1/n$ values were estimated and are also included in Table 4-1 in order to compare the literature values. The adsorption capacity at equilibrium with influent concentration is calculated using equation (1) and the influent concentration as shown in the following example (for PCE, literature values):

$$\frac{X}{M} = K_f \cdot C_i^{1/n} = 50.8 \cdot 0.062^{0.56} = 10.7 \text{mg/g}$$


<table>
<thead>
<tr>
<th>Contaminant (concentration mg/L)</th>
<th>Literature</th>
<th>Calgon Carbon Corporation (isotherms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCE (0.062)</td>
<td>50.8</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>(L/g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption capacity at equilibrium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>with influent conc.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mg/g)</td>
</tr>
<tr>
<td></td>
<td>44.1</td>
<td>Adsorption capacity at equilibrium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mg/g)</td>
</tr>
<tr>
<td>TCE (0.032)</td>
<td>28</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>0.62</td>
<td>(L/g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption capacity at equilibrium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mg/g)</td>
</tr>
<tr>
<td></td>
<td>9.9</td>
<td>134.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption capacity at equilibrium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mg/g)</td>
</tr>
<tr>
<td>DCE (0.026)</td>
<td>3.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>(L/g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption capacity at equilibrium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mg/g)</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption capacity at equilibrium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mg/g)</td>
</tr>
<tr>
<td>TeCA (0.024)</td>
<td>10.6</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>(L/g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption capacity at equilibrium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mg/g)</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption capacity at equilibrium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mg/g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>(L/g)</td>
</tr>
</tbody>
</table>
4.3.2 Scenarios of Influent Concentration

The size of every GAC facility depends on two major parameters. The first one is the flowrate of water that has to be treated. As seen in Appendix F, the selected flowrate is 140 gpm. The second major parameter is the range of inflow concentrations of contaminants of concern. Since only about 20 samples determine the range of contaminant concentrations, this range is uncertain. To get a better feel about how the treatment system behaves with respect to different inflow concentrations, the following estimations of carbon usage are made for two different scenarios of plume concentrations:

The two scenarios are defined as follows (Table 4-2):

- **Scenario 1:** Assuming the maximum concentrations (e.g. PCE @ 62 ppb) throughout the whole plume. This scenario represents the worst case.
- **Scenario 2:** Assuming average concentrations (e.g. PCE @ 18 ppb) throughout the whole plume.

The concentrations for scenarios 1 and 2 are the maximum and average values from the field observations, respectively, as presented in chapter 3.2.2.

**Table 4-2: Two scenarios for influent concentrations.**

<table>
<thead>
<tr>
<th>Contaminant of concern</th>
<th>Scenario 1: maximum concentration (ppb)</th>
<th>Scenario 2: average concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>62</td>
<td>18</td>
</tr>
<tr>
<td>TCE</td>
<td>32</td>
<td>10</td>
</tr>
<tr>
<td>1,2-DCE</td>
<td>26</td>
<td>2</td>
</tr>
<tr>
<td>1,1,2,2-TeCA</td>
<td>24</td>
<td>7</td>
</tr>
</tbody>
</table>

While Table 4-2 represents the concentrations in the plumewater, the actual contamination of the extracted water which will flow into the treatment system, is
smaller. Through modeling of the behavior of the well fence, López-Calva (1996) (Appendix F) determined that for the overall pumping rate of 140 gpm, only 43% of the extracted water is coming from the plume. The rest is clean water, coming from clean parts of the aquifer. Therefore, the inflow concentrations to the treatment facility are the concentrations of Table 4-2 multiplied by a factor of 0.43 (Table 4-3).

### Table 4-3: Inflow concentrations to treatment facility, scenarios 1 and 2.

<table>
<thead>
<tr>
<th>Contaminant of concern</th>
<th>Scenario 1: maximum concentration (ppb)</th>
<th>Scenario 2: average concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>27</td>
<td>8</td>
</tr>
<tr>
<td>TCE</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>1,2-DCE</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>1,1,2,2-TeCA</td>
<td>10</td>
<td>3</td>
</tr>
</tbody>
</table>

#### 4.3.3 Loading Rate

In order to determine the multicomponent loading rate (LR), i.e. the loading rate of the four contaminants together, and following the general consideration in chapter 4.2.4, the loading rate was calculated using different methods. The loading rate (lb carbon/1000 gal of water) is the amount of carbon which is used for the treatment of 1000 gallons of extracted water. Following equation 2, chapter 4.2.3, the theoretical loading rate with respect to influent concentrations of each contaminant was estimated. For that, adsorption capacities at equilibrium (mg/g, Table 4-1) are needed. As an example, the loading rate for PCE are calculated below, using literature Freundlich constants.

1. Calculation of adsorption capacity at equilibrium with influent concentrations (0.062 mg/L), using Freundlich values of 50.8 for $K_f$ and 0.56 for $1/n$:

$$\frac{X}{M} = K_f \cdot C_i^{1/n} = 50.8 \cdot 0.062^{0.56} = 10.7\text{mg/g}$$
2. To calculate the loading rate LR, an acceptable effluent concentration (at equilibrium) needs to be assumed (e.g. 0.005 mg/L, MCL). In order to approximate field conditions where effluent concentrations are zero at the beginning of the treatment process, but then increase with time until the design effluent concentration is reached (assume linear increase), equation (2) is modified to equation 2a.

\[ X = \left( C_i - \frac{C_e}{2} \right) \cdot V \]  

(2a)

The loading rate LR can thus be calculated as

\[ LR = \frac{1}{X/M} \left( C_i - \frac{C_e}{2} \right) = \frac{1}{10.7 \text{mg/g}} \cdot \left( 0.062 - \frac{0.005}{2} \right) \text{mg/L} \cdot \frac{1L}{0.264 \text{gal}} \cdot \frac{1000 \text{gal}}{g} \cdot \frac{0.0022 \text{lb}}{g} \]

\[ LR = 0.047 \text{lb/1000gal} \]

Following the discussion in chapter 4.2.4, the loading rate of the multicomponent mixture of solutes must be estimated. What needs to be considered is the fact that the contaminants do not adsorb equally well. The least sorbable will break through first. A high loading rate for a contaminant (which corresponds to a low adsorption capacity at equilibrium with influent concentrations) indicates that the contaminant will break through early. The overall loading rate is thus determined by the contaminant with the highest loading rate. Since for given influent concentrations and effluent target levels the LR is a function of the adsorption capacity at equilibrium (X/M), this measure of how much of the contaminant can be adsorbed to the carbon needs to be calculated.

The estimation of the adsorption capacity at equilibrium (mg/g) of the contaminants in the mixture was approached by using four different methods and comparing them. The methods are:
1. Assuming that the contaminants are not influencing each other since their concentrations are low, the capacities are calculated using equation 1, chapter 4.3.2. Freundlich values from literature were used (Table 4-1).

2. The adsorption capacities of the contaminants are determined by using the competitive model as described in chapter 4.2.4 (equation 3). Freundlich values from literature are used.

3. Similar to method 1, but using Freundlich values calculated from the Calgon isotherms (Table 4-1).

4. Similar to method 2, but using Freundlich values calculated from the Calgon isotherms.

The overall loading rate is determined by the contaminant which breaks through first. Table 4-4 shows the results of the calculations for the four methods with the inflow concentrations of scenario 1. In method 1, DCE is expected to break through first (lowest adsorption capacity at equilibrium), but this is not important because the influent concentration and therefore also the effluent concentration is below the MCL. Then, TeCA will break through at 2 ppb. While at the same time also TCE may break through (similar X/M as TeCA), PCE is probably still fully "captured" by the carbon (high X/M).

The overall loading rate is thus determined by either TeCA or TCE, and was approximated to be approximately 0.05 lb/1000 gal (Table 4-4).
### Table 4-4: Calculation of loading rates with different methods for scenario 1.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>C_i (mg/L)</th>
<th>X/M (mg/g)</th>
<th>C_e (mg/L)</th>
<th>LR (lb/1000 gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method 1: Single component, literature Freundlich data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCE</td>
<td>0.027</td>
<td>6.75</td>
<td>0.005</td>
<td>0.031</td>
</tr>
<tr>
<td>TCE</td>
<td>0.014</td>
<td>1.99</td>
<td>0.005</td>
<td>0.049</td>
</tr>
<tr>
<td>DCE*</td>
<td>0.011</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TeCA</td>
<td>0.010</td>
<td>1.93</td>
<td>0.002</td>
<td>0.039</td>
</tr>
<tr>
<td>approximate overall loading rate for mixture</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Method 2: Multicomponent equation, literature Freundlich data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCE</td>
<td>0.027</td>
<td>6.22</td>
<td>0.005</td>
<td>0.033</td>
</tr>
<tr>
<td>TCE</td>
<td>0.014</td>
<td>0.58</td>
<td>0.005</td>
<td>0.167</td>
</tr>
<tr>
<td>DCE*</td>
<td>0.011</td>
<td>0.016</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TeCA</td>
<td>0.010</td>
<td>0.58</td>
<td>0.002</td>
<td>0.139</td>
</tr>
<tr>
<td>approximate overall loading rate for mixture</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Method 3: Single component, Freundlich data from Calgon isotherms</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCE</td>
<td>0.027</td>
<td>31.6</td>
<td>0.005</td>
<td>0.007</td>
</tr>
<tr>
<td>TCE</td>
<td>0.014</td>
<td>6.72</td>
<td>0.005</td>
<td>0.014</td>
</tr>
<tr>
<td>DCE*</td>
<td>0.011</td>
<td>1.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TeCA</td>
<td>0.010</td>
<td>0.71</td>
<td>0.002</td>
<td>0.107</td>
</tr>
<tr>
<td>approximate overall loading rate for mixture</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Method 4: Multicomponent equation, Freundlich data from Calgon isotherms</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCE</td>
<td>0.027</td>
<td>124</td>
<td>0.005</td>
<td>0.002</td>
</tr>
<tr>
<td>TCE</td>
<td>0.014</td>
<td>6.18</td>
<td>0.005</td>
<td>0.016</td>
</tr>
<tr>
<td>DCE*</td>
<td>0.011</td>
<td>0.234</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TeCA</td>
<td>0.010</td>
<td>0.078</td>
<td>0.002</td>
<td>0.865</td>
</tr>
<tr>
<td>approximate overall loading rate for mixture</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In method 2, DCE is also going to breakthrough first, but this is again not relevant. TeCA or TCE break through next (similar capacities), while according to the PCE adsorption capacity, PCE will still be adsorbed. The overall loading rate for the mixture is again determined by TeCA of TCE and was approximated to be 0.2 lb/1000 gal. In
method 3, TeCA had the lowest adsorption capacity and was expected to break through first and thus determining the loading rate of about 0.1 lb/1000 gal. In method 4, the adsorption capacities follows a similar trend to that observed in method 3. The overall LR is thus about 0.9, which is much higher than the one for the other three methods.

All but the fourth method show similar overall loading rates between 0.05 and 0.2 lb/1000 gal. For the following calculations of the carbon usage rate of the GAC, it was therefore assumed that the overall loading rate is approximated by 0.1 lb/1000 gal.

For scenario 2, analogous loading rate estimations were made. The values of the calculations are shown in Appendix E. The overall loading rate is expected to be 0.05 lb/1000 gal.

### 4.3.4 Design Loading Rates

Considering the nonideal situation of a field scale carbon unit compared to a lab test as described in chapter 4.2.3, the adsorption capacity of the full-scale column is some percentage of the theoretical adsorption capacity found from the isotherms. The time needed by the water to flow through one vessel was calculated to be 18 minutes (EBCT, Calgon Carbon Corporation, Appendix D). Since this typical contact time gives only limited time to the contaminants to adsorb, the effective capacity can be assumed to be approximately 25 to 50 % of the theoretical one (Metcalf & Eddy, 1991). The design loading rate was hence assumed to be the theoretical loading rate multiplied by the factor 2.5, which corresponds to 40% (Table 4-5).

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Theoretical LR (lb/1000 gal)</th>
<th>Design LR (lb/1000 gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 4-5: Calculation of design loading rates LR for the two scenarios.
4.3.5 Carbon Exchange Rate

The carbon usage rate dictates how often one vessel containing the carbon has to be replaced. The vessel contains 10,000 lb of activated carbon. The flowrate of extracted water, which has to be treated, is 140 gpm. Table 4-6 summarizes the calculations. It can be seen that in the case with the maximum inflow concentrations (scenario 1), one carbon vessel has to be exchanged approximately every two months. Therefore, 1.8 vessel changes are required every year. For scenario 2, it was expected that only every 13 months a carbon vessel is exhausted. This results in 0.9 vessel changes per year.

Table 4-6: Carbon usage rate for two different scenarios of plume concentrations.

<table>
<thead>
<tr>
<th></th>
<th>Scenario 1</th>
<th>Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design loading rate (lb/1000 gal)</td>
<td>0.25</td>
<td>0.13</td>
</tr>
<tr>
<td>Daily carbon use (lb/day)</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>Exchange of carbon after (month)</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>Number of vessel exchanges per year</td>
<td>1.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

4.4 Cost Estimation

This chapter encompasses an estimation of carbon exchange cost if the GAC will be operated until the CS-4 area is completely remediated, which, according to the results of the team-project, is in approximately 90 years.

Due to the carbon exchange/reactivation cost, operation and maintenance (O&M) costs of GAC systems are generally relative high. Typically, O&M cost of $0.48 - $2.52 per 1,000 gallons of treated water must be expected and depend mainly on the influent concentrations and characteristics of the contaminants. Reducing influent concentrations is thus a most efficient way to reduce O&M costs.

In order to transform long-term carbon exchange cost to today's values, the net present worth was calculated, using equation (4):
\[ PW = A \cdot \left[ \frac{(1+i)^n - 1}{i(1+i)^n} \right] \]  

where  
\( n \) = Number of years  
\( i \) = Interest rate (assumed to be 5\%)  
\( PW \) = Present worth  
\( A \) = Annual cost

For the assumed pumping duration of 90 years, the factor to calculate the present worth (parenthesis in equation 4) equals 19.8. The costs for 90 years (PW) are thus calculated by multiplying the annual cost (A) by 19.8.

The total carbon exchange/reactivation costs involve the exchange of the carbon, transport off site, reactivation and transport back to the treatment facility. The following rates were assumed (Calgon Carbon Corporation, 1996):

- Reactivation/Replacement: $1.13 per lb of carbon (10,000 lb to be exchanged each time).
- Transport to regeneration plant: $2.48 per mile round-trip. The nearest regeneration facility to Cape Cod/CS-4 is located about 700 miles away in Pittsburgh or New Jersey. This results in about $2,000 each round-trip.

With these assumptions, the carbon exchange cost for the required pumping years are presented in Table 4-7. It should be emphasized at this point that these values do not represent the total operation and maintenance costs. For that, additional cost would have to be added for monitoring, backwash, and energy requirements.
Table 4-7: Total estimated carbon exchange cost (net present value) over expected duration of pumping.

<table>
<thead>
<tr>
<th></th>
<th>Scenario 1</th>
<th>Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Changes of vessel per year</td>
<td>1.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Carbon exchange cost per year ($)</td>
<td>25,000</td>
<td>12,000</td>
</tr>
<tr>
<td>Required pumping years</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Present worth factor</td>
<td>19.8</td>
<td>19.8</td>
</tr>
<tr>
<td><strong>Total carbon exchange cost ($)</strong></td>
<td><strong>484,000</strong></td>
<td><strong>242,000</strong></td>
</tr>
</tbody>
</table>

The difference in total carbon exchange cost between scenario 1 (maximum inflow concentrations) and scenario 2 (average inflow concentrations) is about $250,000 or a factor of 2. These results show the importance of a good knowledge of the average contaminant concentrations in the plume in order to predict the long-term carbon exchange cost and also the operation and maintenance cost in general.
5. Technology Review

Considering the cost estimates for carbon exchange as shown in chapter 4, the question of alternatives to the existing technology or its economical optimization and enhancement was addressed. The first section (chapter 5.1) summarizes how the GAC was selected as an interim remedial technology, while in the second section (chapter 5.2), different types of technology which might be suitable alternatives for the CS-4 clean-up are briefly presented.

5.1 GAC Evaluation

5.1.1 Evaluation Criteria for GAC Selection

At this point, it is important to be aware of the nine evaluation criteria, which were used to select the CS-4 interim GAC technology (E. C. Jordan Co., 1990; ABB ES, 1992a):

1. Overall protection of human health and the environment
2. Compliance with ARARs (Applicable or Relevant and Appropriate Requirement)
3. Long-term effectiveness and permanence
4. Reduction of mobility, toxicity or volume through treatment
5. Short-term effectiveness
6. Implementability
7. Cost
8. State acceptance
9. Community acceptance

5.1.2 Other Technologies Considered

The other technologies considered for the interim remedial technology are briefly reviewed. Of the 13 remedial technologies screened in the Feasibility Study (E. C. Jordan, 1990), five were selected and retained for detailed analysis. For further evaluation, they were compared against the above nine criteria.
1) **Air stripping followed by activated carbon**

By bubbling air through the contaminated water, the VOCs partition into the air, causing contaminant transfer from the water to the gaseous phase. The gas is then treated by vapor-phase carbon adsorption to meet with the regulatory limits. The advantage of this concept is that carbon adsorption is sometimes more efficient in treating gases than liquids, depending on inflow characteristics (O’Brien and Stenzel, 1984; McKinnon and Dyksen, 1984).

2) **UV Oxidation**

An oxidant (e.g. peroxide, ozone) is added to the water which thus oxidizes the contaminants, yielding less harmful chemicals. The reaction rate of this process is enhanced by exposing the water to ultraviolet (UV) light.

3) **Spray aeration**

Spray aerators sprinkle the extracted water through the air, forming tiny droplets. Thus by extending the air-water contact area, the contaminants can evaporate into the air at a faster rate. As a result, the VOCs don't get actually destroyed but only vaporized and dissipated into the atmosphere.

4) **Otis Wastewater Treatment Plant**

The contaminated groundwater is treated at the Otis Wastewater Treatment Plant (WWTP), where it is subject to the same biological treatment as municipal sewage water. Although the WWTP was not designed to treat VOC-contaminated groundwater, existing processes may be able to remove the VOCs (Smith et al., 1993). Volatilization in the various process steps would be the predominant removal mechanism to air.

These alternatives were not only compared against the above nine criteria, but also against the "no action" alternative. The contaminant plume would not be removed from the aquifer and only a monitoring program implemented (E. C. Jordan Co., 1990; ABB
ES, 1992a). The removal of the contaminants would be due to natural processes - such as dilution, volatilization, biodegradation, adsorption to and reaction with subsurface materials. Using dilution and volatilization effects as remedial means is debated, not only at hazardous waste sites, but also in the area of wastewater management (e.g. outfall pipes).

5.2 Innovative Treatment Alternatives

The US-EPA Superfund Innovative Technology Evaluation (SITE) Program evaluates innovative technologies for the remediation of contaminated Superfund and RCRA sites. Historically the use of innovative treatment technologies has been hindered due to the lack of reliable cost and performance data. To overcome these impediments and respond to the increased demand for validated hazardous waste treatment technologies, the SITE program was created.

From its inception in 1986 through the fiscal year 1994, the SITE Program has evaluated 72 technologies for field demonstration. The results are published, which have lead to an increase in the number of innovative technologies applications at waste sites (EPA, 1993; EPA, 1995a; EPA 1995b). None of these technologies can yet ensure the achievement of the clean up goals, but they nevertheless have a rather big potential for the future.

Some of the technologies that could be able to clean up the extracted water of the CS-4 plume were examined briefly and encompass the following types of treatment:

- Metal-enhanced abiotic degradation of halogenated VOC’s
- In situ bioremediation
- Thermal- and photothermal oxidation
- Membrane separation
- Photocatalytic oxidation

After the general review of these technologies, it was decided to focus on the metal-enhanced abiotic degradation technology. The next chapter will thus describe the technology and evaluate it usefulness to enhance the GAC.
6. Abiotic Dehalogenation with Zero-Valent Iron

6.1 Description of Technology

The use of zero-valent metals for enhanced degradation of halogenated organic compounds has been the subject of increasing interest in recent years (e.g. Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Orth and Gillham, 1996; Weber, 1996). It has been shown that certain metals, in particular iron, are highly effective in promoting the breakdown of these organic compounds in aqueous solution. Iron is chosen in particular because of its effectiveness, availability, and relatively low cost.

The results of several laboratory column tests, field studies, and operating full scale units show the successful and efficient degradation of several VOC's, including PCE, TCE, DCE, Vinyl Chloride, and TeCA (e.g. Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Orth and Gillham, 1995; Mackenzie et al., 1995). The process may be applied either in situ or aboveground. The in situ method involves a permeable treatment wall, containing the reactive granular iron media. This reactive wall is installed across the path of the plume, so that the plume will have to migrate through the reactive wall under naturally occurring flow conditions. At the same time, the contaminants get degraded. An optimization of this system configuration is the so-called “funnel and gate” system, where the reactive wall width can be minimized by installing impermeable walls (sheet piles, slurry walls, etc.) on each side of the reactive wall and thus serve to funnel the plume through the reactive part of the barrier.

In the aboveground version of the metal-enhanced dehalogenation process, the groundwater is pumped out of the aquifer and flows gravity-driven through the reactor tanks, containing the granular iron. The EPA SITE (Superfund Innovative Technology Evaluation) Program evaluated such an aboveground reactor in New Jersey. Initial contaminant concentrations up to 16 ppm (PCE) were degraded below the corresponding MCL of 5 ppb (flowrate 0.5 gpm, EPA, 1995a).
The applicability of the metal-enhanced degradation process is further encouraged by the fact that the process does not appear to be significantly inhibited through the use of commercial grade iron, solvents, and by the fact that once installed, the treatment system should be entirely passive. Though encouraging, it must be recognized that corrosion of the iron through dissociation of water undoubtedly consumes iron at a greater rate than the dechlorination reaction. Although corrosion rates of iron were not investigated in depth so far, it is quite reasonable to expect that, especially aboveground, reactors could be constructed such that the iron would persist for many years to decades (Gillham and O'Hannesin, 1994).

**6.2 Degradation Process**

In order to use zero-valent iron in remediation processes, an understanding of the reaction mechanisms is necessary. Although the process of degradation is widely accepted as reductive dechlorination (Matheson and Tratnyek, 1994; Schreier and Reinhard, 1994; Gillham and O'Hannesin, 1994; Sivavec and Horney, 1995), details of the mechanism remain uncertain. From degradation studies of carbon tetrachloride, Matheson and Tratnyek (1994) suggested three different possible pathways for the degradation. These reaction pathways involve either direct electron transfer from zero-valent iron at the surface of the iron metal or reaction with dissolved Fe\(^{2+}\) or H\(_2\), which are products of iron corrosion.

a) The first pathway involves the metal directly and implies that reduction occurs by electron transfer from the Fe\(^0\) surface to the adsorbed organo halide:

\[
\begin{align*}
\text{Fe}^0 & \quad \Rightarrow \quad \text{Fe}^{2+} + 2\, e^- \quad E_{\text{h}^-}^0 = 0.44 \, \text{V} \\
\text{R-Cl} + H^+ + 2e^- & \quad \Rightarrow \quad \text{R-H} + \text{Cl}^- \quad E_{\text{h}^-}^0 = 0.5 - 1.5 \, \text{V (pH 7)} \\
\text{Fe}^0 + \text{R-Cl} + H^+ & \quad \Rightarrow \quad \text{Fe}^{2+} + \text{R-H} + \text{Cl}^- \quad (5)
\end{align*}
\]

The estimated standard reduction potentials are from Bratsch (1989), and from Vogel et al. (1987), respectively. They indicate that the net reductive dehalogenation reaction (5)
is thermodynamically very favorable under most conditions (Matheson and Tratnyek, 1994).

b) The second pathway involves the Fe$^{2+}$ that is an immediate product of corrosion in aqueous systems:

\[
\begin{align*}
2\text{Fe}^{2+} & \Rightarrow 2\text{Fe}^{3+} + 2e^- \\
\text{R-Cl} + \text{H}^+ + 2e^- & \Rightarrow \text{R-H} + \text{Cl}^- \\
\hline
2\text{Fe}^{2+} + \text{R-Cl} + \text{H}^+ & \Rightarrow 2\text{Fe}^{3+} + \text{R-H} + \text{Cl}^- \quad (6)
\end{align*}
\]

where Fe$^{2+}$ is the product of the oxidation of iron by water or dissolved oxygen:

- \( \text{Fe}^0 + 2\text{H}_2\text{O} \Rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \quad (7) \)
- \( 2\text{Fe}^0 + \text{O}_2 + 4\text{H}^+ \Rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O} \quad (8) \)

c) The third model for reductive dehalogenation by iron involves hydrogen, which is produced as a product of the above described corrosion of iron with water:

\[
\begin{align*}
\text{H}_2 + \text{2OH}^- & \Rightarrow \text{2H}_2\text{O} + 2\text{e}^- \\
\text{R-Cl} + \text{H}_2\text{O} + 2\text{e}^- & \Rightarrow \text{R-H} + \text{2OH}^- + \text{H}^+ + \text{Cl}^- \\
\hline
\text{H}_2 + \text{R-Cl} & \Rightarrow \text{R-H} + \text{H}^+ + \text{Cl}^- \quad (9)
\end{align*}
\]

This last reaction needs an effective catalyst to contribute to dehalogenation (excessive H$_2$ accumulation at the metal surface is known to inhibit the continuation of corrosion and of reduction reactions).

Further studies by Orth and Gillham (1996) indicate that mainly two of the above reactions are important: The direct reductive dechlorination (5) and the oxidation of iron by water (7). Similarly, the studies of Weber (1996) support the conclusion, that the process is a surface-mediated process. Nevertheless, it is not quite clear how the primary reactions, as well as the secondary reactions, influence each other.
6.2.1 Kinetic Considerations

Numerous laboratory tests (batch tests and column tests) have been conducted over the past four years in order to determine the rate of degradation for various chemicals. It is now generally considered that the degradation process is best described by the pseudo first-order model with respect to the substrate (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994). The rate constant appears to be directly proportional to the surface area-to-volume of solution ratio (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994). Also, the rate declines with decreasing degree of chlorination and the rate constant is independent of the initial substrate concentration (Orth and Gillham, 1996; Gillham and O'Hannesin, 1994).

\[
\frac{dC}{dt} = -k_{obs} \cdot \langle C \rangle = -k_{rxn} \cdot (Fe_{surface-area}) \cdot \langle C \rangle
\]  

Since the reaction is a surface process, one would anticipate that, although the overall reaction is pseudo first-order, at some upper limit in substrate concentration the reactive sites would be saturated, and thus at higher concentrations the reaction would not appear to be first order any more. But this upper limit exceeds the concentrations normally found in groundwater plumes and thus the pseudo-first order model appears to be appropriate for the design of field-scale remediation systems (Orth and Gillham, 1996).

The rate limiting step of the degradation is either the reaction itself or the diffusion of the solutes through the liquid film around the iron granules. Matheson and Tratnyek (1994) have found that the reaction rate is unaffected by temperatures from 4 to 35 °C. Since reaction rates that are limited by diffusion typically have low dependence on temperature, it could be concluded that the diffusion of the mass to the reaction sites are rate limiting (besides surface area) (Matheson and Tratnyek, 1994). Consequently, as the flow rate through the iron medium increases, the profile of the solutes concentration through the column becomes more elongated (Gillham and O'Hannesin, 1993).
For the present contaminants PCE, TCE and DCE, the overall reaction sequence can be given as follows:

\[ PCE \xrightarrow{k_1} TCE \xrightarrow{k_2} DCE \xrightarrow{k_3} VC(Vinyl \cdot Cloride) \xrightarrow{k_4} Ethylene \]  

(11)

The rates of degradation are:

\[ \frac{d(PCE)}{dt} = -k_1 \cdot (PCE) \]  

(12)

\[ \frac{d(TCE)}{dt} = +k_1 \cdot (PCE) - k_2 \cdot (TCE) \]  

(13)

\[ \frac{d(DCE)}{dt} = +k_2 \cdot (TCE) - k_3 \cdot (DCE) \]  

(14)

\[ \frac{d(VC)}{dt} = +k_3 \cdot (DCE) - k_4 \cdot (VC) \]  

(15)

The effects of pH on the reaction rate remain relatively minor until the pH approaches about 9.5 (Gillham et al., 1993). Then, the reaction rate declines with increasing pH. An indirect effect of increasing pH is precipitation of minerals, present in the treated water. The precipitates so formed could coat the reactive surfaces, causing reduced reaction rates.

Biological activity does not affect the process directly, based on several labtests. However, the possibility of indirect effects through the accumulation of biological coatings on the active iron surfaces, or changing geochemical conditions causes by biological activity, can not be excluded (Gillham et al., 1993).
6.2.2 Half-life Data

Since the half-life $t_{1/2}$ is proportional to the iron surface area to volume of solution, all results of different references have been normalized to 1 m$^2$ of iron surface per milliliter of solution (1 m$^2$/mL). In some cases, the information for normalization is not provided and thus estimates were made by Gillham (1996a).

Table 6-1, extracted from Gillham (1996a), shows half-lives of the contaminants of concern at CS-4. The results are grouped between iron powder of high purity and commercial, granular iron.

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>Pure iron $t_{1/2}$ (hr)</th>
<th>Commercial iron $t_{1/2}$ (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>0.28$^a$; 5.2$^n$</td>
<td>2.1-10.8$^b$; 3.2$^c$</td>
</tr>
<tr>
<td>TCE</td>
<td>0.67$^m$; 7.3-9.7$^d$; 0.68$^e$</td>
<td>1.1-4.6$^b$; 2.4$^c$; 2.8$^f$</td>
</tr>
<tr>
<td>cis 1,2 DCE</td>
<td>19.7$^a$</td>
<td>10.8-33.9$^b$; 47.6$^c$</td>
</tr>
<tr>
<td>trans 1,2 DCE</td>
<td>6.4$^a$</td>
<td>4.9$^b$; 6.9$^c$; 7.6$^f$</td>
</tr>
<tr>
<td>VC</td>
<td>12.6$^a$</td>
<td>10.8-12.3$^b$; 4.7$^c$</td>
</tr>
<tr>
<td>1,1,2,2 TeCA</td>
<td>0.053$^a$</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Gillham and O'Hannesin, 1994  $^b$ Matheson and Tratnyek, 1994
$^m$ Unpublished Waterloo data  $^c$ Orth and Gillham, 1995
$^n$ Sivavec and Horney, 1995  $^f$ Mackenzie et al., 1995

Though there is considerable variation in the reported half-lives for a particular compound, there is a trend towards increasing half-life with decreasing degree of chlorination. PCE degrades a little faster than TCE, the rate for the DCE isomers is lower the one for TCE, and lower yet for vinyl chloride (compared to trans DCE). This trend is consistent with reductive dehalogenation, since the most highly chlorinated compounds are the most oxidized and would therefore be expected to be the least stable under reducing conditions (Gillham, 1996a).

Field measurements from six industrial sites show consistent half-lives for TCE. Data from Gillham (1996a) are depicted in Table 6-2.
Furthermore, Table 6-3 shows the measured half-lives of several column tests, which were conducted for several sites. The values indicate that the half-lives of PCE are slightly smaller than the ones for TCE. The half-lives of PCE and TCE average at about 0.4 and 0.5 hr, respectively.

**Table 6-3: Half-lives from column tests**

<table>
<thead>
<tr>
<th>Study area</th>
<th>PCE (hr)</th>
<th>TCE (hr)</th>
<th>cDCE (hr)</th>
<th>VC (hr)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aboveground treatment system of industrial facility, New Jersey</td>
<td>0.4</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>a</td>
</tr>
<tr>
<td>DOE facility, Hanford, Washington</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>b</td>
</tr>
<tr>
<td>DOE Kansas City Plant</td>
<td>-</td>
<td>0.98</td>
<td>3.5</td>
<td>6.0</td>
<td>c</td>
</tr>
<tr>
<td>Industrial facility, New Jersey</td>
<td>0.5</td>
<td>0.6</td>
<td>1.5/3.7</td>
<td>1.2/0.9</td>
<td>b</td>
</tr>
</tbody>
</table>

a  Chen 1996, EPA (unpublished draft)
b  EnviroMetal Technologies Inc., 1995a
c  EnviroMetal Technologies Inc., 1995b

There are reasons to believe that lower half-life values than the ones used for the calculations and in Table 6-1 could be achieved. For practical applications, Gillham (1996a) concludes the following. If one considers a reactive bed (vessel or wall) containing only granular iron, and the porosity of the bed would be around 40%, then the ratio of iron mass to volume of solution would be about 12 g/mL. The specific surface area of the iron is highly variable, depending upon grain size, shape, surface morphology and the presence of microstructuring or fracturing. Values of 0.29 m²/g (electrolytically produced iron powder), 1.1 m²/g (commercial iron with 0.57 to 2.0 mm grain size) and

---

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0.7 m²/g (acid pretreatment) are reported from Gillham and O'Hannesin (1994) and Matheson and Tratnyek (1994), respectively. Using a conservative estimate of specific surface area of 0.5 m²/g, the iron density of 8 g/mL and the mass-to-volume ratio given above (12 g/mL), the surface area to volume ratio in a packed bed of iron would be about 6 m²/mL. Consequently, an approximately six times faster degradation rate can be expected.

Recently, chemical enhancement of the reaction rate has been reported. Several researchers (Cipollene et al., 1993; Lipczynska-Kochany et al., 1994) have reported enhanced degradation with granular iron in the presence of compounds containing sulfur. Other studies, for which metals such as nickel or platinum are plated onto the iron show enhanced degradation of the contaminants as well (Gillham, 1996b). This summer, some forms of iron enhancements, for which half-lives are expected to be 5 - 20 times faster, will be pilot-tested (EnviroMetal Technology, 1996).

It is highly probably that with greater experience and with a fuller understanding of the mechanisms, the metal-enhanced degradation process will may be optimized, resulting in lower half-lives than the ones shown in Table 6-1 to 6-3.

6.3 Design Parameters

6.3.1 Required Degradation Time

Not taking these prospective improvements of the degradation rate into account, the chosen half-lives in order to calculate the required volume of iron to degrade the extracted CS-4 contaminants, are based on the following reflections. The field measurements and the column tests indicate that, for a surface area to volume of solution ratio of 1 m²/mL, TCE-half-life of 0.5 is a reasonable assumption. For PCE, only a few field half-life numbers are available. Assuming that PCE degrades a little faster than TCE and based on the values from the column tests, a value of 0.4 was chosen as the design half-life (for ratio 1 m²/mL). Since the use the iron technology at the CS-4 site will be in combination with the GAC, no engineering safety factors have to be added.
As shown above, a surface area-to-volume of solution ratio of 6 m²/mL can be expected. Therefore, the half-lives need to be adapted to this ratio. First, the intrinsic rate constant was calculated, which is independent of this ratio. The following calculations are shown for PCE.

\[
\frac{d(PCE)}{dt} = k_{\text{int}} \cdot (F_{\text{surface}}) \cdot (PCE)
\]
\[(16)\]

where \( k = k_{\text{int}} \cdot (F_{\text{surface}}) \)
\[(17)\]

for a ratio of 1 m²/mL:

\[
k_{\text{int}} = \frac{\ln 2}{t_{1/2} \cdot (F_{\text{surface}})} = \frac{0.69}{0.4 \cdot 1} = 1.73 \frac{mL}{m^2 \cdot hr}
\]
\[(18)\]

for 6 m²/mL:

\[
t_{1/2} = \frac{\ln 2}{k_{\text{int}} \cdot (F_{\text{surface}})} = \frac{0.69}{1.73 \cdot 6} = 0.066 \cdot hr
\]
\[(19)\]

\[
k = \frac{\ln 2}{t_{1/2}} = \frac{0.69}{0.066} = 10.4 \cdot hr^{-1}
\]
\[(20)\]

The half-lives were calculated using the above equations for the whole degradation sequence (PCE to ethene). Since TeCA degrades much faster than the ethenes, (Table 6-1), it was assumed that it degrades "parallel" to the ethenes without influencing the required time for the overall degradation process. Table 6-4 lists the reaction rates, which are adapted to surface area to volume of solution ratio of 6 m²/mL. The results show that the reaction rates decrease with decreasing degree of chlorination. While the rates for PCE and TCE are based on several field measurements and are therefore fairly good estimates, the rates for DCE and VC are conservative assumptions (the reactions are fast).
Table 6-4: Design reaction rates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Approximate half-lives for ratio of 1 m²/mL (hr)</th>
<th>Half-lives adapted to 6 m²/mL (hr)</th>
<th>Reaction rates for 6 m²/mL (hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>0.4</td>
<td>0.066</td>
<td>10.4 (=k₁)</td>
</tr>
<tr>
<td>TCE</td>
<td>0.5</td>
<td>0.083</td>
<td>8.3 (=k₂)</td>
</tr>
<tr>
<td>DCE</td>
<td>6</td>
<td>1</td>
<td>0.69 (=k₃)</td>
</tr>
<tr>
<td>VC</td>
<td>12</td>
<td>2</td>
<td>0.35 (=k₄)</td>
</tr>
</tbody>
</table>

Since the rates of DCE and VC are slower than the ones of PCE and TCE, it must be assumed that DCE and VC will temporarily build up as a result of the degradation of PCE and TCE.

The build up of the byproducts DCE and VC through the degradation of PCE and TCE was described mathematically, using the equations 12 - 15 and the rate constants derived in Table 6-4. The solutions of the equations are:

\[
(PCE)_t = (PCE)_{t-1} \cdot e^{-k_1 \cdot \Delta t} \tag{21}
\]

\[
(TCE)_t = (TCE)_{t-1} \cdot e^{-k_2 \cdot \Delta t} + (PCE)_{t-1} \cdot \frac{k_1}{k_2 - k_1} \left( e^{-k_1 \cdot \Delta t} - e^{-k_2 \cdot \Delta t} \right) \tag{22}
\]

\[
(DCE)_t = (DCE)_{t-1} \cdot e^{-k_3 \cdot \Delta t} + (TCE)_{t-1} \cdot \frac{k_2}{k_3 - k_2} \left( e^{-k_2 \cdot \Delta t} - e^{-k_3 \cdot \Delta t} \right) \tag{23}
\]

\[
(VC)_t = (VC)_{t-1} \cdot e^{-k_4 \cdot \Delta t} + (DCE)_{t-1} \cdot \frac{k_3}{k_4 - k_3} \left( e^{-k_3 \cdot \Delta t} - e^{-k_4 \cdot \Delta t} \right) \tag{24}
\]

a) Scenario 1

For scenario 1 (see Table 4-3), Figure 6-1 presents the modeled concentrations versus time. In this graph, TeCA was neglected. As shown before, its degradation is faster than the degradation for the graphed contaminants.
Figure 6-1: Expected concentrations versus time for scenario 1.

Figure 6-1 shows the importance of the build up of TCE, DCE, and VC as a result of the degradation of the PCE and TCE, respectively. The initial concentrations (time 0) are given as scenario 1. As PCE has a fast reaction rate, it degrades rapidly. TCE builds up initially and degrades to a level of 5 ppb (equals MCL) after about 0.34 hours. The increase of DCE up to 40 ppb is not of direct concern since the MCL for DCE is 70 ppb. A main concern though is the concentration curve of VC. After 0.17 hours, the concentration has increased up to the MCL of 2 ppb, and continues to increase up to about 25 ppb. After 2 hours, the concentration decreases very slowly, reaching 2 ppb again after more than about 10 hours (not shown on graph). As VC is a highly toxic carcinogen, the initial build up over 2 ppb must be avoided, especially as the degradation proceeds very slowly.
In order to determine the sensitivity of the increase and degradation of DCE and VC with respect to their degradation rates, a brief sensitivity analysis was conducted. Figure 6-2 shows the concentration curve for DCE, calculated for a range of its degradation half-lives of 0.7 to 80 hrs for the degradation of DCE to VC and for a fixed half-life of 0.083 hr (see Table 6-4) for TCE to DCE degradation. Even for very slow degradation rates (DCE to VC), DCE will not build up to more than 52 ppb, which is still below MCLs (70 ppb). This indicates that DCE concentrations will not approach critical values. The maximum build up for DCE to 52 ppb for very slow degradation rates from DCE to VC (half-life of 80 hrs, Figure 6-2) is the sum of the initial values of PCE, TCE and DCE, which is 27, 14, and 11 ppb, respectively.

For VC, Figure 6-3 shows that VC may increase to a maximum of about 50 ppb, depending on its half-life of degradation (VC to Ethylene, range from 1.5 to 80 hrs). The
half-life of DCE to VC degradation was assumed to be 1 hr, which is a reasonable value taken from Table 6-4. The analysis indicates that the potential build up of VC up to 52 ppb (again equals sum of initial concentrations) for very slow VC degradation rates (> 80 hrs) may be considerable and a great potential in exceeding MCLs by a factor of 25.

![Graph showing VC concentration over time with different half-lives](image)

*Figure 6-3: Sensitivity analysis of VC with respect to half-life of VC degradation.*

In order to impede the build up of VC to more than 2 ppb (MCL), the contact time of the water with the granular iron has to be less than 0.17 hours (Figure 6-1). As a design residence time, a value of 0.17 hours was therefore chosen. This requirement is necessary despite the fact that the water will flow through the GAC after the iron treatment step, because the adsorption capacity of the GAC for VC is expected to be low (low mg/g value). Therefore a rapid breakthrough would occur.
b) Scenario 2

Figure 6-4 shows the concentration versus time plot for scenario 2. For this case, the initial concentrations for PCE, TCE and DCE were 8 ppb, 4 ppb and 0 ppb, respectively.

![Figure 6-4: Expected concentrations versus time for scenario 2.](image)

As seen in Figure 6-4, VC is not expected to build up over a value of 6 ppb and its MCL is reached only after 0.5 hours. This is mainly due to the initial DCE concentration of zero. For this scenario, VC is not expected to build up over 12 ppb for even very slow degradation rates of VC to ethylene, since the sensitivity analysis (Figure 6-3) shows that the range of maximum build up reaches the sum of the initial PCE, TCE, DCE and VC concentration. DCE grows to a maximum of 9 ppb (Figure 6-4).
The residence time for design purposes was also chosen to be 0.17 hr, which is the same as for scenario 1. This has the advantage that the size of the to be installed zero-valent iron system is independent of the scenario.

Table 6-5 summarizes the design contact time for the two scenarios of influent concentrations:

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Design contact time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>0.17</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>0.17</td>
</tr>
</tbody>
</table>

In contrast of the expectations regarding the build up of DCE and VC as shown in Figure 6-1 to 6-4, Thomas et al. (1995), EnviroMetal Technologies Inc. (1995a), and Gillham (1996a) reported that both column tests and field measurements have shown that the total measured DCE yielding from the breakdown of PCE and TCE amounted to less than 10% of the original PCE and TCE concentrations. Measured VC concentrations were less than 0.1%-3% of the original concentrations. Despite these reported findings, the design contact time of Table 6-5 will be used to design the size of the iron vessel.

6.3.2 Required Volume of Iron

The volume of iron needed to degrade the contaminants during the required contact time $t_{\text{contact}}$ can be calculated as follows:
\[ \nu = \frac{Q \cdot t_{\text{contact}}}{n} \]  \hspace{1cm} (25)

where

- \( Q = \) Flowrate (140 gpm)
- \( n = \) Porosity of iron = 0.40 (Gillham, 1996a)
- \( t_{\text{contact}} = 0.17 \) hr (see Table 6-5)

Using equation 25, the volume was calculated to be 480 ft\(^3\), for both scenarios. This volume was compared with the volume of a carbon adsorption vessel. The existing carbon vessels are 7.5 ft in diameter, with a carbon bed depth of 10 ft. However, the vessel supplier now sells models with 8 ft diameter (Calgon Carbon Corporation, 1996). The volume of the 8 ft diameter model approximates 510 ft\(^3\). The required 480 ft\(^3\) of iron could thus be filled in a vessel which originally was designed for the containment of carbon.

### 6.3.3 Flowrate Through Iron

If the vessel filled with iron is installed in series to the two vessels filled with carbon, the flowrate is determined by the limiting vessel with respect to the seepage velocity. Since it can be assumed that the flow through granular iron is faster than the flow through granular activated carbon, the flowrate is not limited by the iron vessel (same diameter as carbon vessel). The existing GAC vessels are able to handle a flowrate of 140 gpm.

### 6.3.4 Effluent Concentrations

The chosen contact time of 0.17 hours will not degrade the contaminants, PCE and TCE, down to MCLs. The resulting concentrations in the water after flowing through the iron vessel were calculated from equations 21 - 24 (\( t = 0.17 \) hours). They can also be seen in Figures 6-1 and 6-4. Table 6-6 summarizes the values:
Table 6-6: Influent and effluent concentrations of iron vessel.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Scenario 1</th>
<th>Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>influent concentration (ppb)</td>
<td>effluent concentration (ppb)</td>
</tr>
<tr>
<td>PCE</td>
<td>27</td>
<td>4</td>
</tr>
<tr>
<td>TCE</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>DCE</td>
<td>11</td>
<td>27</td>
</tr>
<tr>
<td>VC</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>TeCA</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

6.4 Cost

As a preliminary estimate, the capital cost of the installment of the vessel filled with granular iron can be divided into the six categories. To estimate the cost, the following assumptions were made:

- Cost of iron: $23,000 ($450/ton, density 0.09 tons/ft$^3$ (EnviroMetal Technologies Inc., 1996))
- Cost of vessels: $80,000 (Calgon Carbon Corporation, 1996)
- Building change: $30,000 (10% of capital cost of building ($300,000))
- Installation vessel: $20,000 (20% of vessel/building)
- Indirect cost: $26,000 (20% of vessel, building, and installation, for engineering, health/safety, permitting, services)
- Monitoring: $30,000 (Start up and intensive monitoring in start up period)

Total: $200,000

These installation costs are valid for both scenarios. The purchase and installation of the vessel amounts to about half of the cost. Monitoring cost must be included since
especially the build up of byproducts (VC) needs to be monitored during the first weeks of operation.

Not taken into account was the possibility that the iron gets degraded (rusting), resulting in plugging and a decrease in reaction rates. This would probably require to exchange the top layer (1 cm approximately) periodically (maybe every 5 years). No data on this issue is available yet.
7. Combination of Zero-Valent Iron and GAC

The vessel filled with zero-valent iron is placed before the GAC (Figure 7-1).

![Diagram](image)

*Figure 7-1: Conceptual model of zero-valent iron and GAC combination.*

The extracted water, coming from the pumping wells, will first flow through the vessel filled with zero-valent iron. Since the zero-valent iron will degrade the contaminants only to a certain extent, the residual contaminants will sorb to the activated carbon. The calculation of the carbon usage was done similar to the one in chapter 4.3.3 and are presented in Appendix E. Table 7-1 shows the results. As the iron vessel is sized so that VC will not build up to 2 ppb (MCL), VC does not need to be considered for the overall loading rate estimation.
For scenario 2, the concentrations leaving the iron treatment are less than MCLs for all the contaminants. Although the water flows through the carbon vessels thereafter, the carbon will not get exhausted with respect to MCLs and therefore does not need to be exchanged (the influence of other organic material present in the water, e.g. dissolved organic carbon, is not taken into account). For scenario 1, the carbon exchange cost are $500,000, similar to the ones calculated in chapter 4, where no iron pretreatment is assumed. The reason why the carbon exchange cost did not decrease with the iron precursor is because the TCE concentration remains at 15 ppb (after 0.17 hr residence time in the iron pores) due to the dechlorination of PCE as seen in Figure 6-1.

In order to determine whether combining the metal technology with the existing GAC is economical favorable, it was assumed that the operation and maintenance cost without counting the carbon exchange cost, would not differ much for either only a stand-alone GAC system or the GAC combined with the zero-valent iron vessel. This is a reasonable assumption especially as initial monitoring costs are included in the capital iron-technology cost.
A comparison between expected cost with and without iron pretreatment (Table 7-2) shows that no savings can be achieved due to the iron pretreatment at the CS-4 site. For scenario 1, a loss of $200,000 would have to be expected. The main reason for this is the build up of vinyl chloride, which impedes longer residence times of the water in the iron pores. Therefore, the TCE concentration is not decreasing enough to reduce carbon exchange cost. In scenario 2, the iron vessel is able to reduce contaminants below MCLs for all the contaminants. While carbon exchange cost can be reduced to approximately zero, the capital cost of installing the iron vessel balance the savings in carbon cost.

Table 7-2: Net savings yielding in combination of GAC with zero-valent iron.

<table>
<thead>
<tr>
<th></th>
<th>Scenario 1</th>
<th>Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Savings:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present worth of carbon exchange cost ($)</td>
<td>500,000</td>
<td>200,000</td>
</tr>
<tr>
<td><strong>Investment:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Installation of zero-valent iron system ($)</td>
<td>200,000</td>
<td>200,000</td>
</tr>
<tr>
<td>• Carbon exchange for combination ($)</td>
<td>500,000</td>
<td>0</td>
</tr>
<tr>
<td><strong>Total savings ($)</strong></td>
<td>-200,000</td>
<td>0</td>
</tr>
</tbody>
</table>

Despite the uncertainty of some design parameters, the results indicates that for both conservative (scenario 1) and optimistic (scenario 2) concentration assumptions, no net savings can be expected.
8. Conclusions

The objective of this thesis was to evaluate the economic consequences of combining the existing GAC at the CS-4 site with an alternative treatment technology, which turned out to be the emerging zero-valent iron technology.

The results indicate that the combination of granular activated carbon with zero-valent iron could be feasible, but would not result in a more economic aboveground treatment than the existing one. Although there is a certain range of optimization regarding the residence time of the fluid in the iron pores for scenario 2 left, no significant changes in the result (savings) could be expected. However, especially as in the near future the iron process is expected to progress, and since the combined system could be tested easily without major construction, it would be interesting to conduct a bench scale or a pilot test in order to verify the results.

The build up of VC due to reductive dehalogenation of PCE, TCE and DCE seems to be a major concern and must be taken into account if designing a zero-valent iron treatment system. This contrasts with the conclusions made in the literature (Gillham, 1995a) for other sites, where zero-valent iron was implemented.
References

ABB Environmental Services Inc., 1992a (February). *Groundwater Focused Feasibility Study, West Truck Road Motor Pool (AOC CS-4)*, Installation Restoration Program, Massachusetts Military Reservation, prepared for HAZWRAP, Portland ME.

ABB Environmental Services Inc., 1992b (May). *Record of Decision, Interim Remedial Action West Truck Road Motor Pool (AOC CS-4) Groundwater Operable Unit*, Installation Restoration Program, Massachusetts Military Reservation, prepared for HAZWRAP; Portland ME.


ABB Environmental Services Inc., 1996. *Personal communication*.


Gelhar, L.W., 1996 (April). *Personal communication*.


Appendices

Appendix A  Chemistry of Plumewater and Soil at Source
Appendix B  Literature Values for Freundlich Constants
Appendix C  Isotherms of Calgon Carbon Corporation
Appendix D  Empty Bed Contact Time (Calgon Carbon Corporation)
Appendix E  Spreadsheet Calculations for Carbon Exchange and Zero-Valent Iron Cost
Appendix F  Executive Summary and Results of Team-Project
Appendix A: Chemistry of Plumewater and Soil at Source

Detected chemicals in the groundwater in the CS-4 plume area and the soil at the source area (extracted from E.C. Jordan Co., 1990; ABB ES, 1992a; ABB ES, 1992b; ABB ES, 1992c).

**Table A-1: Chemistry of plumewater and soil at source.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Soil max conc. [ug/kg] (ppb)</th>
<th>Groundwater max conc. [ug/L] (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inorganic compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>88,500,000</td>
<td>ND</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>4,400</td>
<td>31</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>-</td>
<td>29</td>
</tr>
<tr>
<td>Boron</td>
<td>Bo</td>
<td>-</td>
<td>112</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>3,000</td>
<td>8,000</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>25,000</td>
<td>ND</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>34,000</td>
<td>ND</td>
</tr>
<tr>
<td>Cyanide</td>
<td></td>
<td>870</td>
<td>ND</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>18,300,000</td>
<td>3,500</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
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<td>Magnesium</td>
<td>Mg</td>
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<td>3,120</td>
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<tr>
<td>Manganese</td>
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<td>Mercury</td>
<td>Hg</td>
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<tr>
<td>Nickel</td>
<td>Ni</td>
<td>35</td>
<td>86</td>
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<tr>
<td>Nitrite/Nitrate</td>
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<td>-</td>
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<td>Potassium</td>
<td>K</td>
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<td>Silver</td>
<td>Ag</td>
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<td>Sodium</td>
<td>Na</td>
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<td>V</td>
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<td>Zn</td>
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<td><strong>Volatile Organic Compounds</strong></td>
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<td>2-Butanone</td>
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<td>Ethylbenzene</td>
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<tr>
<td>Tetrachloroethene</td>
<td>PCE</td>
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<td>Toluene</td>
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</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
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<td>ND</td>
</tr>
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<td>1,1,2,2-Tetrachloroethane</td>
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<td>-</td>
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<tr>
<td>Trichloroethene</td>
<td>TCE</td>
<td>100,000</td>
<td>32</td>
</tr>
<tr>
<td>Xylene (total)</td>
<td></td>
<td>3,300</td>
<td>7</td>
</tr>
<tr>
<td>1,2-Dichloroethene (total)</td>
<td>1,2-DCE</td>
<td>32000</td>
<td>26</td>
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</tbody>
</table>
### Table A-I: Chemistry of plumewater and soil at source (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abreviation</th>
<th>Soil max conc. [µg/kg (ppb)]</th>
<th>Groundwater max conc. [µg/L (ppb)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi volatile organic compounds</td>
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<tr>
<td>Benz(a)Anthracene</td>
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<td>-</td>
</tr>
<tr>
<td>Benzo(a)Pyrene</td>
<td></td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td>Benzo(b)Fluoranthene</td>
<td></td>
<td>350</td>
<td>-</td>
</tr>
<tr>
<td>Benzo(g,h,i)Perylene</td>
<td></td>
<td>470</td>
<td>-</td>
</tr>
<tr>
<td>Benzo(k)Fluoranthene</td>
<td></td>
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<td>Chrysene</td>
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<td>-</td>
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<td>Fluoranthene</td>
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<td>2,400</td>
<td>-</td>
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<td>Naphthalene</td>
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<td>1,800</td>
<td>-</td>
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<tr>
<td>Phenanthrene</td>
<td></td>
<td>2,800</td>
<td>-</td>
</tr>
<tr>
<td>Pyrene</td>
<td></td>
<td>2,300</td>
<td>-</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td></td>
<td>6,600</td>
<td>-</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl)phthalate</td>
<td></td>
<td>-</td>
<td>15</td>
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<tr>
<td>Pesticides/PCB</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>4,4’-DDT</td>
<td>4,4’-DDT</td>
<td>41</td>
<td>-</td>
</tr>
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<td>4,4’-DDE</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>4,4’-DDD</td>
<td>4,4’-DDD</td>
<td>110</td>
<td>-</td>
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<tr>
<td>Dieldrin</td>
<td></td>
<td>67</td>
<td>-</td>
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<tr>
<td>PCB-1260</td>
<td>PCB-1260</td>
<td>670</td>
<td>-</td>
</tr>
</tbody>
</table>
Appendix

Appendix B: Literature Values for Freundlich Constants

### Tetrachloroethylene:

<table>
<thead>
<tr>
<th>Reference</th>
<th>$K_f$ (L/g)</th>
<th>1/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montgomery Consulting Eng., 1985</td>
<td>50.8</td>
<td>0.56</td>
</tr>
<tr>
<td>Benedict, A.L., 1982 (GAC)</td>
<td>57.7</td>
<td>0.48</td>
</tr>
<tr>
<td>Love and Eilers, 1982 (GAC)</td>
<td>84.1</td>
<td>0.41</td>
</tr>
<tr>
<td>Dobbs and Cohen, 1980 (PAC)</td>
<td>50.8</td>
<td>0.56</td>
</tr>
<tr>
<td>Crittenden et al., 1985</td>
<td>7.52</td>
<td>0.5</td>
</tr>
<tr>
<td>Values chosen by ABB ES for design</td>
<td>51</td>
<td>0.56</td>
</tr>
</tbody>
</table>

### Trichloroethylene:

<table>
<thead>
<tr>
<th>Reference</th>
<th>$K_f$ (L/g)</th>
<th>1/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weber, W.J. Jr, 1981 (GAC-C)</td>
<td>32</td>
<td>0.45</td>
</tr>
<tr>
<td>Weber, W.J., Jr, 1981 (GAC)</td>
<td>26.2</td>
<td>0.50</td>
</tr>
<tr>
<td>Dobbs and Cohen, 1980 (PAC)</td>
<td>28.0</td>
<td>0.62</td>
</tr>
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<td>Weber, W.J. Jr, 1980 (PAC-A)</td>
<td>16.5</td>
<td>0.54</td>
</tr>
<tr>
<td>Weber, W.J. Jr, 1980 (PAC-B)</td>
<td>28.0</td>
<td>0.52</td>
</tr>
<tr>
<td>Weber, W.J. Jr, 1980 (PAC-C)</td>
<td>11.0</td>
<td>0.67</td>
</tr>
<tr>
<td>Crittenden et al., 1985</td>
<td>3.26</td>
<td>0.41</td>
</tr>
<tr>
<td>Values chosen by ABB ES for design</td>
<td>28</td>
<td>0.62</td>
</tr>
</tbody>
</table>

### Total-1,2-Dichloroethylene:

<table>
<thead>
<tr>
<th>Reference</th>
<th>$K_f$ (L/g)</th>
<th>1/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dobbs and Cohen (Faust and Aly) (PAC, trans)</td>
<td>3.05</td>
<td>0.51</td>
</tr>
<tr>
<td>Crittenden et al. 1985 (cis)</td>
<td>0.18</td>
<td>0.64</td>
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<tr>
<td>Values chosen by ABB ES for design</td>
<td>3.1</td>
<td>0.51</td>
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</tbody>
</table>

### Tetrachloroethane:

<table>
<thead>
<tr>
<th>Reference</th>
<th>$K_f$ (L/g)</th>
<th>1/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dobbs and Cohen, 1980 (PAC)</td>
<td>10.6</td>
<td>0.37</td>
</tr>
<tr>
<td>Values chosen by ABB ES for design</td>
<td>10.6</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Appendix

Appendix C: Isotherms of Calgon Carbon Corporation

Calgon Carbon Corporation Isotherms

Adsoption Capacity & Equilibrium (mg/g)

1000

100

10

1

0.1

0.01 0.1 1 10 100

Inflow Concentration (mg/L)

y = 134.71x^{0.4278}

y = 50.173x^{0.4745}

y = 13.187x^{0.866}

y = 11.176x^{0.5994}

PCE

TCE

cis DCE

trans DCE

PCA

Power (PCE)

Power (TCE)

Power (cis DCE)

Power (PCA)
Appendix

Appendix D: Empty Bed Contact Time (Calgon Carbon Corporation)
(together with Multicomponent Adsorption Estimation)

WATERADS RELEASE 4
EQUILIBRIUM MODEL OF FORMATION OF ADSORPTION BANDS IN COLUMNS 
BASED ON MULTICOMPONENT ADSORPTION CALCULATIONS USING 

ACTUAL CARBON NAME IS FILTRASORB 300 (1991 PRODUCTION)

10-Apr-96
11:41 AM

Stream Description :WT
Customer Name : 
Customer Location : 
Program Run By :MJP

RESULTS FOR ADSORPTION OF THE LIQUID PHASE MIXTURE ON THE COLUMN 
OF FILTRASORB 300 (1991 PRODUCTION) CARBON

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>112TCA</td>
<td>0.0150</td>
</tr>
<tr>
<td>11DCE</td>
<td>0.0260</td>
</tr>
<tr>
<td>TCE</td>
<td>0.0320</td>
</tr>
<tr>
<td>PERC</td>
<td>0.0620</td>
</tr>
</tbody>
</table>

THE ADSORBATE DESIGNATIONS ARE AS FOLLOWS;
THE SOURCE OF V*/V AND 1/GAMMA FOR 112TCA 
S 
ESTIMATED FROM 111-TCA - REVISED 7/3/91

THE SOURCE OF V*/V AND 1/GAMMA FOR 11DCE 
IS 
BELLISSIMO 6/15/84 6-PT. ISOTHERM - REVISED 7/3/91

THE SOURCE OF V*/V AND 1/GAMMA FOR TCE 
IS 
MCNAMARA ISOTHERM & 9/7/89 ISOTHERM (8-PTS. TOTAL) - REVISED 2/22/91

THE SOURCE OF V*/V AND 1/GAMMA FOR PERC 
IS 
BELLISSIMO 5/1/84 5-PT. ISOTHERM - REVISED 7/3/91

THE MISCIBLE MODEL WAS USED-ASSUMES NO BULK MISCIBILITY
LIMITS IN PORE SPACE
V* - TYPE COMPETITION WAS USED IN THE CALCULATION
Appendix D: Empty Bed Contact Time (Calgon Carbon Corporation) (together with Multicomponent Adsorption Estimation) (continued/2)

The following tables are only valid for a gpm flow rate of 140 USE RATE (LB./1000 GAL.) SERIES

<table>
<thead>
<tr>
<th>LIQUID COMPONENT</th>
<th>MODEL 10 &amp; DUAL</th>
<th>MOBILE</th>
<th>MODEL 7.5 &amp; CYCLESORB</th>
<th>350 GAL</th>
<th>55 GAL</th>
<th>DISPOSORB</th>
</tr>
</thead>
<tbody>
<tr>
<td>112TCA</td>
<td>0.491</td>
<td>0.491</td>
<td>0.556</td>
<td>0.589</td>
<td>0.589</td>
<td>0.589</td>
</tr>
<tr>
<td>11DCE</td>
<td>0.133</td>
<td>0.133</td>
<td>0.150</td>
<td>0.159</td>
<td>0.159</td>
<td>0.159</td>
</tr>
<tr>
<td>TCE</td>
<td>0.071</td>
<td>0.071</td>
<td>0.080</td>
<td>0.085</td>
<td>0.085</td>
<td>0.085</td>
</tr>
<tr>
<td>PERC</td>
<td>0.020</td>
<td>0.020</td>
<td>0.023</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
</tbody>
</table>

USE RATE (LB./1000 GAL.) PARALLEL

<table>
<thead>
<tr>
<th>LIQUID COMPONENT</th>
<th>MODEL 10 &amp; DUAL</th>
<th>MOBILE</th>
<th>MODEL 7.5 &amp; CYCLESORB</th>
<th>350 GAL</th>
<th>55 GAL</th>
<th>DISPOSORB</th>
</tr>
</thead>
<tbody>
<tr>
<td>112TCA</td>
<td>0.654</td>
<td>0.654</td>
<td>0.720</td>
<td>0.818</td>
<td>0.818</td>
<td>0.818</td>
</tr>
<tr>
<td>11DCE</td>
<td>0.177</td>
<td>0.177</td>
<td>0.195</td>
<td>0.221</td>
<td>0.221</td>
<td>0.221</td>
</tr>
<tr>
<td>TCE</td>
<td>0.095</td>
<td>0.095</td>
<td>0.104</td>
<td>0.118</td>
<td>0.118</td>
<td>0.118</td>
</tr>
<tr>
<td>PERC</td>
<td>0.027</td>
<td>0.027</td>
<td>0.030</td>
<td>0.034</td>
<td>0.034</td>
<td>0.034</td>
</tr>
</tbody>
</table>

TABLE OF EMPTY BED CONTACT TIMES

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Series</th>
<th>Empty Bed Contact time (minutes/bed)</th>
<th>Parallel</th>
<th>Empty Bed Contact time (minutes/bed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MODEL 10</td>
<td>37.5</td>
<td>75.0</td>
<td>18.7</td>
<td>37.5</td>
</tr>
<tr>
<td>MOBILE</td>
<td>30.0</td>
<td>60.0</td>
<td>3.8</td>
<td>7.5</td>
</tr>
<tr>
<td>MODEL 7.5</td>
<td>3.8</td>
<td>7.5</td>
<td>3.8</td>
<td>7.5</td>
</tr>
<tr>
<td>MODEL 4</td>
<td>3.8</td>
<td>7.5</td>
<td>2.5</td>
<td>5.0</td>
</tr>
<tr>
<td>CYCLESORB</td>
<td>2.5</td>
<td>5.0</td>
<td>0.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

For estimates only no guarantees. Source WGS memo 3/13/88

THIS PROGRAM IS THEORETICAL AND IS FROM DR. GREENBANKS THESIS

THIS PROGRAM HAS NOT BEEN APPROVED BY RESEARCH AND HAS NOT BEEN
FORMALLY RELEASED OR DOCUMENTED. USE THIS PROGRAM AT YOUR OWN
RISK.
Appendix

Appendix E: Spreadsheet Calculations for Carbon Exchange and Zero-Valent Iron Cost

Given / Assumed

<table>
<thead>
<tr>
<th>Scenario 1: max measured</th>
<th>PCE (mg/L)</th>
<th>TCE (mg/L)</th>
<th>DCE (mg/L)</th>
<th>PCA (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>inflow to treatment</td>
<td>0.062</td>
<td>0.032</td>
<td>0.026</td>
<td>0.024</td>
</tr>
<tr>
<td>Scenario 2: average measured</td>
<td>0.027</td>
<td>0.014</td>
<td>0.011</td>
<td>0.010</td>
</tr>
<tr>
<td>inflow to treatment</td>
<td>0.018</td>
<td>0.009</td>
<td>0.001</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Freundlich Kf, Calgon graph | 134.0 L/g | 50.0 L/g | 13.0 L/g | 11.2 L/g |
Freundlich 1/n, Calgon graph | 0.40 | 0.47 | 0.52 | 0.60 |
Freundlich Kf, literature | 51.00 L/g | 28.00 L/g | 3.10 L/g | 10.60 L/g |
Freundlich 1/n, literature | 0.56 | 0.62 | 0.51 | 0.37 |

Field scale efficiency | 40% | (Metcal & Eddy, 1991) |
Flowrate | 140 gpm | (Lopez-Calva, 1996) |
Cost of reactivation of carbon | 1.13 $/lb | (Calgon Carbon Corporation, 1996) |
Cost of transport (roundtrip) | 2,000 $ | (Calgon Carbon Corporation, 1996) |
Interest rate | 0.05 | | |
Required pumping years | 90 years | (including retardation, Khachikian, 1996; Lazaro, 1996) |
Ratio dirty water of total | 0.43 | (Lopez-Calva, 1996, Influence on concentration) |

Porosity of iron | 0.40 | (Gillham, 1996a) |
Density of iron (incl. porosity) | 0.09 ton/ft³ | (EnviroMetal Technologies Inc., 1996) |
Cost of iron | 450 $/ton | ($400 minimum, EnviroMetal Tech. Inc., 1996) |
Cost of vessels, pipes | 80,000 $/vessel | (Calgon Carbon Corporation, 1996) |
Cost of building adaption | 30,000 $ | (10% of capital cost of building (300,000)) |
Installation per vessel | 20,000 $/vessel | (20% of vessel, building cost) |
Indirect cost | 26,000 $ | (20% of vessel, building, installation, for engineering, health/safety, permitting, services) |
Appendix E: Spreadsheet Calculations for Carbon Exchange and Zero-Valent Iron Cost (Continued/2)

Carbon only

### Scenario 1

<table>
<thead>
<tr>
<th></th>
<th>PCE</th>
<th>TCE</th>
<th>DCE</th>
<th>TeCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>for influent concentration</td>
<td>0.027 mg/L</td>
<td>0.014 mg/L</td>
<td>0.011 mg/L</td>
<td>0.010 mg/L</td>
</tr>
<tr>
<td>single component, literature</td>
<td>6.747 mg/g</td>
<td>1.985 mg/g</td>
<td>0.311 mg/g</td>
<td>1.929 mg/g</td>
</tr>
<tr>
<td>C effluent, target level</td>
<td>0.005 mg/L</td>
<td>0.005 mg/L</td>
<td>0.070 mg/L</td>
<td>0.002 mg/L</td>
</tr>
<tr>
<td></td>
<td>0.033 lb/1000 gal</td>
<td>0.049 lb/1000 gal</td>
<td>0.000 lb/1000 gal</td>
<td>0.039 lb/1000 gal</td>
</tr>
<tr>
<td>overall loading rate</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>multicomponent equ., literature</td>
<td>6.218 mg/g</td>
<td>0.578 mg/g</td>
<td>0.016 mg/g</td>
<td>0.547 mg/g</td>
</tr>
<tr>
<td>C effluent</td>
<td>0.005 mg/L</td>
<td>0.005 mg/L</td>
<td>0.070 mg/L</td>
<td>0.002 mg/L</td>
</tr>
<tr>
<td></td>
<td>0.033 lb/1000 gal</td>
<td>0.167 lb/1000 gal</td>
<td>0.000 lb/1000 gal</td>
<td>0.139 lb/1000 gal</td>
</tr>
<tr>
<td>overall loading rate</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calgon isotherms, single</td>
<td>31.597 mg/g</td>
<td>6.724 mg/g</td>
<td>1.246 mg/g</td>
<td>0.705 mg/g</td>
</tr>
<tr>
<td>C effluent</td>
<td>0.005 mg/L</td>
<td>0.005 mg/L</td>
<td>0.070 mg/L</td>
<td>0.002 mg/L</td>
</tr>
<tr>
<td></td>
<td>0.007 lb/1000 gal</td>
<td>0.014 lb/1000 gal</td>
<td>0.000 lb/1000 gal</td>
<td>0.107 lb/1000 gal</td>
</tr>
<tr>
<td>overall loading rate</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>multicomponent equ., Calgon</td>
<td>124.64 mg/g</td>
<td>6.177 mg/g</td>
<td>0.234 mg/g</td>
<td>0.078 mg/g</td>
</tr>
<tr>
<td>C effluent</td>
<td>0.005 mg/L</td>
<td>0.005 mg/L</td>
<td>0.070 mg/L</td>
<td>0.002 mg/L</td>
</tr>
<tr>
<td></td>
<td>0.002 lb/1000 gal</td>
<td>0.016 lb/1000 gal</td>
<td>0.000 lb/1000 gal</td>
<td>0.865 lb/1000 gal</td>
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<td>overall loading rate</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
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</table>

### Scenario 2

<table>
<thead>
<tr>
<th></th>
<th>PCE</th>
<th>TCE</th>
<th>DCE</th>
<th>TeCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>for influent concentration</td>
<td>0.008 mg/L</td>
<td>0.004 mg/L</td>
<td>0.000 mg/L</td>
<td>0.003 mg/L</td>
</tr>
<tr>
<td>single component, literature</td>
<td>3.414 mg/g</td>
<td>0.913 mg/g</td>
<td>0.000 mg/g</td>
<td>1.235 mg/g</td>
</tr>
<tr>
<td>C effluent, target level</td>
<td>0.005 mg/L</td>
<td>0.005 mg/L</td>
<td>0.070 mg/L</td>
<td>0.002 mg/L</td>
</tr>
<tr>
<td></td>
<td>0.014 lb/1000 gal</td>
<td>0.014 lb/1000 gal</td>
<td>0.000 lb/1000 gal</td>
<td>0.014 lb/1000 gal</td>
</tr>
<tr>
<td>overall loading rate</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>multicomponent equ., literature</td>
<td>1.657 mg/g</td>
<td>0.128 mg/g</td>
<td>0.000 mg/g</td>
<td>0.230 mg/g</td>
</tr>
<tr>
<td>C effluent</td>
<td>0.005 mg/L</td>
<td>0.005 mg/L</td>
<td>0.070 mg/L</td>
<td>0.002 mg/L</td>
</tr>
<tr>
<td></td>
<td>0.028 lb/1000 gal</td>
<td>0.099 lb/1000 gal</td>
<td>0.000 lb/1000 gal</td>
<td>0.073 lb/1000 gal</td>
</tr>
<tr>
<td>overall loading rate</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calgon isotherms, single</td>
<td>19.424 mg/g</td>
<td>3.732 mg/g</td>
<td>0.000 mg/g</td>
<td>0.342 mg/g</td>
</tr>
<tr>
<td>C effluent</td>
<td>0.005 mg/L</td>
<td>0.005 mg/L</td>
<td>0.070 mg/L</td>
<td>0.002 mg/L</td>
</tr>
<tr>
<td></td>
<td>0.002 lb/1000 gal</td>
<td>0.003 lb/1000 gal</td>
<td>0.000 lb/1000 gal</td>
<td>0.049 lb/1000 gal</td>
</tr>
<tr>
<td>overall loading rate</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Carbon usage rate**

- **Scenario 1**: 0.250 lb/1000 gal, 0.125 lb/1000 gal
- **Scenario 2**: 0.250 lb/1000 gal, 0.125 lb/1000 gal

**Carbon exchange cost**

- **Scenario 1**: 1.8 times/year, 0.9 times/year
- **Scenario 2**: 24'467 $, 12'233 $

**Required pumping years**

- **Scenario 1**: 90 years
- **Scenario 2**: 90 years

**Present worth factor**

- **Scenario 1**: 19.8
- **Scenario 2**: 19.8

**Cost over required years**

- **Scenario 1**: 0.5 million $, 0.2 million $
Appendix

Appendix E: Spreadsheet Calculations for Carbon Exchange and Zero-Valent Iron Cost (Continued/3)

Combination of GAC with Iron

<table>
<thead>
<tr>
<th>Time needed</th>
<th>PCE and TCE together</th>
<th>Scenario 1</th>
<th>Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>0.17 hr</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>0.17 hr</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Volume needed   | 477 ft³               | 477 ft³    |
| Number of vessels | 1                    | 1          |

<table>
<thead>
<tr>
<th>Scenario</th>
<th>PCE</th>
<th>TCE</th>
<th>DCE</th>
<th>TeCA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scenario 1</td>
<td>0.004</td>
<td>0.015</td>
<td>0.027</td>
<td>0.000</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>0.004</td>
<td>0.015</td>
<td>0.027</td>
<td>0.000</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>C effluent, target level</th>
<th>PCE</th>
<th>TCE</th>
<th>DCE</th>
<th>TeCA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scenario 1</td>
<td>0.005</td>
<td>0.005</td>
<td>0.070</td>
<td>0.002</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>0.005</td>
<td>0.005</td>
<td>0.070</td>
<td>0.002</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Overall loading rate</th>
<th>0.05</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Multicomponent equ., literature C effluent</th>
<th>PCE</th>
<th>TCE</th>
<th>DCE</th>
<th>TeCA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scenario 1</td>
<td>0.005</td>
<td>0.005</td>
<td>0.070</td>
<td>0.002</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>0.005</td>
<td>0.005</td>
<td>0.070</td>
<td>0.002</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Overall loading rate</th>
<th>0.2</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Design loading rate</th>
<th>0.250 lb/1000 gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily carbon usage rate</td>
<td>0 lb/1000 gal</td>
</tr>
<tr>
<td>Change of vessels after</td>
<td>0 d</td>
</tr>
<tr>
<td>Changes of vessel per year</td>
<td>1.8 times/year</td>
</tr>
<tr>
<td>Carbon exchange cost per year</td>
<td>24,467 $</td>
</tr>
<tr>
<td>Required pumping years</td>
<td>90 years</td>
</tr>
<tr>
<td>Present worth factor</td>
<td>19.8</td>
</tr>
<tr>
<td>Cost over required years</td>
<td>0.5 million $</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Capiital cost</th>
<th>Iron</th>
<th>19'330 $</th>
<th>19'330 $</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cost of vessels, pipes</td>
<td>80'000 $</td>
<td>80'000 $</td>
</tr>
<tr>
<td></td>
<td>Cost of building adaption</td>
<td>30'000 $</td>
<td>30'000 $</td>
</tr>
<tr>
<td></td>
<td>Installation of vessel</td>
<td>20'000 $</td>
<td>20'000 $</td>
</tr>
<tr>
<td></td>
<td>Indirect cost</td>
<td>26'000 $</td>
<td>26'000 $</td>
</tr>
<tr>
<td></td>
<td>Monitoring after startup</td>
<td>30'000 $</td>
<td>30'000 $</td>
</tr>
<tr>
<td></td>
<td>Total capital cost</td>
<td>0.2 million $</td>
<td>0.2 million $</td>
</tr>
</tbody>
</table>

| Sum                   | 0.7 million $ | 0.2 million $ |

| Net savings | -0.2 million $ | 0.0 million $ |

82
Appendix F: Executive Summary and Results of Team-Project

(The results regarding the aboveground treatment are not included, since they are described in the thesis report).

1. Executive Summary (of Team-Project)

This report covers the technical aspects of the current situation of the Chemical Spill 4 (CS-4) groundwater plume at the Massachusetts Military Reservation (MMR), and proposes a final remedial design.

The aquifer underlying the MMR is contaminated by various pollutants forming a plume. The CS-4 plume is currently contained using a pump and treat system. The contaminants of concern detected in CS-4 are perchloroethylene (PCE), trichloroethylene (TCE), 1,2-dichloroethylene (DCE), and 1,1,2,2-tetrachloroethane (TeCA). Granular activated carbon (GAC) is used to treat the extracted groundwater which is reinjected to the aquifer after treatment. This system was designed as an interim remedial action to quickly respond to the plume migrating off site. A final remedial design must be formulated.

In order to propose a final remedial system for CS-4, the following aspects are examined in depth: (1) an extensive site characterization, (2) the development of a computer model to simulate flow and contaminant transport, (3) the evaluation of the feasibility of bioremediation and its design, (4) the examination of the current aboveground treatment system and possibilities of its enhancing it; and (5) an evaluation of the risk associated with these remedial strategies.

Site characterization was based on previous studies of the area. Equilibrium sorption, however, was tested in the laboratory since this factor may affect the fate and transport of the contaminants. A three-dimensional model was constructed from the results of the site characterization. The model was used to simulate flow and transport under natural conditions, and to predict effective capture curves for the extraction of the contaminated
Appendix

water. An innovative in situ bioremediation system consisted of an anaerobic zone sequenced by an aerobic zone was designed. The removal due to biodegradation was calculated. Optimization of the currently operating treatment system was conducted by evaluating economic benefits of combining the existing GAC system with zero-valent iron technology. Risk assessment was performed considering EPA acceptable range of carcinogenic and non-carcinogenic risk.

*The results are as follows:*

**a) Site Characterization**

On a regional scale, the geology of western Cape Cod is composed of two glacial moraines deposited along the western and northern edges and a broad outwash plain between the two moraines. The outwash is composed of poorly sorted fine to coarse grained sands, and its thickness varies from approximately 175 feet to 325 feet. Precipitation is the sole source of recharge to the aquifer. Values of recharge are between 18 in/yr and 23 in/yr. A value of 380 ft/day has been accepted as a representative value of average horizontal hydraulic conductivity of the outwash sands. Effective porosity is estimated to be about 0.39 and the average hydraulic gradient is 0.0014.

The groundwater contains high values of dissolved oxygen (5-10 mg/L), and has a pH between 5 and 7. The average temperature is about 10°C. The average concentrations of the main contaminants in CS-4 are 18 ppb, 9.1 ppb, 1.1 ppb and 6.8 ppb for PCE, TCE, DCE and TECA respectively. Previous field observations suggested that the plume is 11,000 ft long, 800 ft wide and 50 ft thick.

*Equilibrium Sorption:*

The organic carbon content in the sediments is very low (in general, less than 0.01 %). For this low organic content, the degree of sorption of the contaminants is relatively small. The depth-averaged retardation coefficients are 1.04, 1.1 and 1.25 for DCE, TCE
Appendix

and PCE, respectively. For the more strongly sorbing PCE, the retarded longitudinal macrodispersivity increases by a factor of 2.1 relative to a non-sorbing solute. For the least sorptive compound (DCE), the velocity variances introduced by sorption are small as reflected by a small increase in the longitudinal macrodispersivity (factor of 1.2).

b) Groundwater Model

The groundwater flow model showed great sensitivity to the properties of the glacial moraine. The calibrated model (based on head distributions and particle tracking) has an average hydraulic conductivity of 221.6 ft/day, a hydraulic gradient of 0.0014, a seepage velocity of 0.8 ft/day, and a recharge of 19 in/yr.

Contaminant Transport Model:

Simulating a continuous input of the contaminants, the plume resulting from the simulations had greater dimensions than the plume defined by field observations. Average dimensions were 1,180 ft for the width, 40 ft for the height, and 12,660 ft for the length.

The no action alternative for remediation was simulated. According to the model, the total time it took for all the contaminants to enter the nearest pond was between 80 to 85 years. On the other hand, the total time for clean-up using the existing system was approximately 70 years.

Simulation of Pumping Schemes:

Simulations using the current 13-well fence indicated that for a plume defined according to the existing field observations the currently operating pumping scheme is appropriate.
Appendix

The flexibility of the current well fence was tested using a plume 50% larger (in cross-sectional area) that was captured by increasing the overall pumping rate by 78%. Results of different pumping schemes showed that similar capture curves can be obtained with the existing pumping scenario, and with a pumping system of seven wells located 120 ft apart and extracting water at an overall rate of 140 gpm. This seven-well option may be a better option, since presumably, operation and maintenance cost would be reduced.

c) Bioremediation

The in situ bioremediation system consists of three phases. Phase 1 has the objective to create the necessary conditions for reductive dechlorination (phase 2) to take place. Reductive dechlorination is an anaerobic process in which 99% of PCE was estimated to be transformed to TCE and other less chlorinated ethylenes if given sufficient residence time. In the third phase, TCE, and DCE (and vinyl chloride if produced in phase 2) are degraded by cometabolic oxidation. The degradation of TCE, DCE, and VC were calculated to be 97% for TCE and 100% for DCE and VC.

d) Aboveground Treatment Alternative

Adding aboveground vessels, filled with zero-valent iron, to the currently operating granular activated carbon (GAC) system to pretreat the extracted water is probably not an effective means to reduce long-term treatment costs. The investments of adding zero-valent iron do not balance the overall savings. The build up of vinyl chloride (VC) as a result of the degradation of the chlorinated hydrocarbons by the iron was a major concern and was modeled using kinetic expressions. It was shown that an increase of VC over regulatory limits must be expected if contact time of the contaminated water with the iron is more than 0.17 hr.
Appendix

e) Risk Assessment

Worst case scenarios using pump and treat resulted in a carcinogenic risk of $1.4 \times 10^{-6}$. Using bioremediation resulted in a carcinogenic risk of $2.6 \times 10^{-6}$. The no action alternative resulted in a carcinogenic risk of $10^{-4}$.

Conclusion

This project was undertaken to fully understand the transport mechanisms of groundwater and contaminants in the western Cape Cod aquifer, and to develop a final remediation scheme for the CS-4 plume. The following conclusions are drawn:

- Site characterization must be improved in order to provide a clearer understanding of the contamination problem. The representation of the aquifer conditions with the computer model was limited because of insufficient data.

- Total clean-up times using the current interim remedial scheme are very long and cost intensive. Development of a final remediation method which decreases clean-up times and decreases costs is necessary.

- Using only seven of the 13 existing wells produces the same results as the current operation. Reexamination of the current pumping scheme would reduce operation and maintenance costs. It is recommended that this new scheme be examined as an alternative to the existing operation.

- The anaerobic/aerobic in situ bioremediation scheme proposed demonstrates that it has the potential to completely degrade PCE, TCE, and DCE. A pilot test is needed to demonstrate the efficacy of this technology and determine the final design parameters.
Appendix

- By combining the existing GAC with the emerging zero-valent iron technology will not result in a reduction of overall treatment costs. A bench-scale study should be conducted to verify the results.

- Risk calculations indicate that the CS-4 plume must be remediated to comply with regulations. The remediation strategies reduce the risks to acceptable levels.
Appendix

2. Results of Team-Project

2.1 Site Characterization

2.1.1 Geology

The geology of western Cape Cod is composed predominantly of glacial sediments deposited during the Wisconsin Period (7,000 to 85,000 years ago) (E.C. Jordan, 1989b). The three predominant geologic formations of the western Cape are: the Sandwich Moraine (SM), the Buzzards Bay Moraine (BBM), and the Mashpee Pitted Plain (MPP) (E.C. Jordan, 1989b). The two moraines were deposited by the glacier along the northern and western edges of western Cape Cod. Between the two moraines lies a broad outwash plain (the MPP) which is composed of well sorted, fine to coarse-grained sands. At the base of the unconsolidated sediments (below the MPP), fine grained, glaciolacustrine sediment and basal till are present.

Both the outwash and moraines have relatively uniform characteristics at the regional scale, even though they contain some local variability. The sediments are stratified and thus the hydraulic conductivities are anisotropic. The MPP is more permeable and has a more uniform grain size distribution than the moraines (E.C. Jordan, 1989b).

The total thickness of the unconsolidated sediments (i.e., moraine, outwash, lacustrine, and basal till) is estimated to increase from approximately 175 feet near the Cape Cod Canal in the northwest to approximately 325 feet in its thickest portion in the BBM; it then decreases to 250 feet near Nantucket Sound in south. The thickness of the MPP outwash sediments ranges from approximately 225 feet near the moraines, to approximately 100 feet near shore of Nantucket Sound (E.C. Jordan, 1989a).

2.1.2 Hydrology

Cape Cod's temperate climate produces an average annual precipitation of about 48 inches, widely distributed throughout the year (Masterson and Barlow, 1994). High permeability sands and low topographic gradient, minimize the potential for runoff and
erosion, and thus recharge values have been reported in the range of 17 to 23 inches/year (LeBlanc, 1986). Consequently, about one half of the water that precipitates recharges the aquifer. This creates a high probability of contaminant transport from the surface to the groundwater.

Beneath western Cape Cod lies a single groundwater system (from the Cape Cod Canal to Barnstable and Hyannis) which the U.S. Environmental Protection Agency (EPA) has designated as a sole source aquifer (E.C. Jordan, 1990). This aquifer is unconfined and its only form of natural recharge is by infiltration from precipitation. The highest point of the water table (the top of the groundwater mound) is located beneath the northern portion of the MMR. In general, groundwater flows radially outward from this mound and ultimately discharges to the ocean.

Kettle hole ponds, depressions of the land surface below the water table, are common on the MPP. These ponds influence the groundwater flow on a local scale. Streams, wetlands and cranberry bogs serve as drainage for some of these ponds and as areas of groundwater discharge, and thus comprise the rest of the hydrology of the western Cape.

2.1.3 Hydrogeology

The geology and hydrology of western Cape Cod define the hydrogeologic characteristics of the aquifer. General information on the geology and hydrology of Cape Cod can be found in the works by Oldale (1982), Guswa and LeBlanc (1985), LeBlanc et al. (1986), and Oldale and Barlow (1987). This section summarizes the data on the major aquifer properties measured throughout the area. Variability of these values may be due not only to natural heterogeneities of the soil, but also to differences in measuring techniques and data analysis (E.C. Jordan, 1989a).

a) Hydraulic Conductivity

Throughout the western Cape, there appears to be a general trend of decreasing conductivity from north to south and from the surface to the bedrock. The conductivity of the western Cape has been studied extensively. Geologic variability within the
Appendix

outwash suggests that some variability in hydraulic conductivity is likely. Nonetheless, the maximum and minimum values reported are probably biased by the analytical method or exhibit a small-scale geologic heterogeneity. A value of 380 ft/d (obtained from the Ashumet Valley pump tests and corroborated by the tracer test south of the MMR) has been accepted as a representative value of the average hydraulic conductivity of the MPP outwash sands (E.C. Jordan, 1989a).

b) Anisotropy Ratio

The anisotropy ratio (ratio of horizontal to vertical hydraulic conductivities, $K_h/K_v$) has been studied along with some of the hydraulic conductivity tests. Typical anisotropy values range from 10:1 to 3:1.

c) Porosity

Measured values of porosity range from 0.20 to 0.42. Effective porosity of the outwash is estimated from a tracer test (Garabedian et al., 1988; LeBlanc et al., 1991) to be about 0.39.

d) Hydraulic Gradient

The hydraulic gradient will be affected by the variations in water table elevations. These typically fluctuate about three feet because of seasonal variations in precipitation and recharge. During the period of a tracer test (22 months), the hydraulic gradient in the study area (Ashumet Valley) varied in magnitude from 0.0014 to 0.0020. Vertical hydraulic gradients measured during this test were negligible except near the ponds (LeBlanc et al., 1991).

2.1.4 Chemistry of the Water

The properties of the chemicals of particular interest to the bioremediation design are shown in Table F-1 (E.C. Jordan, 1990). The dissolved oxygen (DO) values vary with depth. The values reported are for the depths of interest (depth < 100 ft below water table). The concentration of metals is also of particular interest since high concentrations
Appendix

can have a detrimental effect to microbial growth. The concentration of metals tested for at CS-4 are negligible.

**Table F-1: Groundwater properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved oxygen</td>
<td>5.0-10.0</td>
</tr>
<tr>
<td>Nitrate (mg/L)</td>
<td>0-1.8</td>
</tr>
<tr>
<td>pH</td>
<td>5-7</td>
</tr>
<tr>
<td>Temperature</td>
<td>10° C</td>
</tr>
</tbody>
</table>

* Obtained from E.C. Jordan (1990)

2.1.5 Equilibrium Sorption

Sorption of contaminants by aquifer solid matrices significantly affects their fate and transport. The bioavailability of contaminants can be reduced considerably because of sorptive uptake. Also, remediation times can be prolonged substantially because of a continuous feeding of contaminants to the aquifer by the sorbed species. Another effect of sorption is that it may alter the dispersive behavior of contaminants (i.e., enhancement of longitudinal dispersivity).

One way to quantify all of these effects is to use equilibrium sorption distribution coefficients to calculated retardation factors. Laboratory batch tests are setup to determine distribution coefficients. These are used to validate the use of equilibrium relationships to extract retardation factors. Once this relationship is shown, retardation factors were calculated which were then used to assess the behavior of the contaminants.

*a) Equilibrium Sorption Results*

The sand samples used in this study were obtained from the Well S315 (Figure F-1).
The organic carbon content ($f_{oc}$) of the sands used in this study are listed in Table F-2. The $f_{oc}$ is the part of the solid matrix primarily responsible for sorption.

**Table F-2: Sand Identification including laboratory measured $f_{oc}$ and hydraulic conductivities, $K$.
Samples were obtained from Well S315.**

<table>
<thead>
<tr>
<th>Sand ID</th>
<th>Sand Depth (feet)</th>
<th>$f_{oc}$ ($\pm\sigma$), (%)</th>
<th>$K$, cm/s*</th>
</tr>
</thead>
<tbody>
<tr>
<td>S315-5</td>
<td>18-20</td>
<td>0.0433 (0.0015)</td>
<td>0.012</td>
</tr>
<tr>
<td>S315-13</td>
<td>58-60</td>
<td>0.0098 (0.0005)</td>
<td>0.041</td>
</tr>
<tr>
<td>S315-2</td>
<td>73-75</td>
<td>0.0058 (0.0013)</td>
<td>0.100</td>
</tr>
<tr>
<td>S315-14</td>
<td>78-80</td>
<td>0.0048 (0.0008)</td>
<td>0.060</td>
</tr>
<tr>
<td>S315-9</td>
<td>88-90</td>
<td>0.0076 (0.0011)</td>
<td>0.037</td>
</tr>
</tbody>
</table>

*The K values approximated from Figure 4.8.5 of Thompson (1994).

Using these $f_{oc}$ values, equilibrium distribution coefficients are calculated (Table F-3). The $f_{om}$ values listed in Table F-3 are assumed to be twice the measured $f_{oc}$ values (Schwarzenbach et al., 1993). Phase partitioning is assumed as the predominant mechanism controlling sorption.
Appendix

Table F-3: \( K_d' \) values calculated from the linear equilibrium sorption equation \( K_d' = K_d f_{om} \)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( f_{om}, % )</th>
<th>DCE (L/kg)</th>
<th>TCE (L/kg)</th>
<th>PCE (L/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S315-5</td>
<td>0.0866</td>
<td>0.026</td>
<td>0.063</td>
<td>0.158</td>
</tr>
<tr>
<td>S315-13</td>
<td>0.0196</td>
<td>0.006</td>
<td>0.014</td>
<td>0.036</td>
</tr>
<tr>
<td>S315-2</td>
<td>0.0116</td>
<td>0.004</td>
<td>0.008</td>
<td>0.021</td>
</tr>
<tr>
<td>S315-14</td>
<td>0.0096</td>
<td>0.003</td>
<td>0.007</td>
<td>0.017</td>
</tr>
<tr>
<td>S315-9</td>
<td>0.0152</td>
<td>0.005</td>
<td>0.011</td>
<td>0.028</td>
</tr>
</tbody>
</table>

b) Implications of Distribution Coefficients

In this section, the implications of sorption on field-scale contaminant transport is discussed.

Effects of Sorption on Contaminant Transport

The depth-averaged retardation factors calculated for the contaminants of interest were calculated (Table F-4).

Table F-4: Effective retardation factors.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( R_{eff} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCE</td>
<td>1.04</td>
</tr>
<tr>
<td>TCE</td>
<td>1.10</td>
</tr>
<tr>
<td>PCE</td>
<td>1.25</td>
</tr>
</tbody>
</table>
The longitudinal macrodispersivity is a key factor in the modeling and understanding of plume transport. The value for the longitudinal macrodispersivity for a conservative substance at Cape Cod is estimated to be 66 ft. However, for sorbing solutes, an adjustment to this value has to be made. The net effect of sorption is to retard the transport (i.e. the velocity) of the contaminants in the aquifer. Variability of sorption can produce an enhanced longitudinal macrodispersivity (Garabedian et al., 1988); this effect is more important when the sorption coefficient and hydraulic conductivity are negatively correlated (Figure F-2).

Figure F-2: The relationship between $f_{om}$ and $K$ with depth is shown in figure a. The experimentally determined retardation factors are shown in figure b. As expected, the $f_{om}$ and $K$ and the $R$ and $K$ are inversely related.
Appendix

The values of the retarded longitudinal macrodispersivity, $A_{11}$, are included in Table F-5. For the more strongly sorbing PCE, the retarded longitudinal macrodispersivity, $A_{11}$, increases by a factor of 2.1 relative to the non-retarded value. This is an important consideration in the modeling or understanding of the transport of this compound. For the least sorptive compound (DCE), the velocity variances introduced by sorption are small as reflected by a small increase in the longitudinal macrodispersivity (factor of 1.2).

Table F-5: Values of the retarded longitudinal macrodispersivity, $A_{11}$, from Khachikian (1996).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A_{11}$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCE</td>
<td>23.5</td>
</tr>
<tr>
<td>TCE</td>
<td>28.7</td>
</tr>
<tr>
<td>PCE</td>
<td>41.3</td>
</tr>
</tbody>
</table>

The retarded longitudinal macrodispersivity, in effect, quantifies the extent of a mixing zone in front of the leading edge of a contaminant plume. While the bulk of the mass of the contamination may be held back (i.e., retarded), some will disperse ahead of the conceived contaminant plume, resulting in early breakthrough times.

Macrodispersivity is a phenomenon that is currently under research. The effects are scale dependent and, thus, presents a certain challenge to the investigator. More research is needed to fully understand this phenomenon and to be able to quantify it.
2.2 Modeling Under Natural Conditions

2.2.1 Description of the Model

A three-dimensional model was constructed using the finite-element modeling code DynSystem (Camp Dresser & McKee, Inc, 1992). More than 100 wells are located in the area of concern. Data of hydraulic head and contaminant concentrations from the wells were used to construct input files to the model.

The model includes an area of approximately 50 mi² on the western. The thickness of the modeled region was non-uniform, defined by ground surface and bedrock elevations. The horizontal boundaries were defined by two no-flow boundaries and the ocean. Johns Pond, Ashumet Pond and Childs River were included in the model as fixed head boundary conditions. Coonamessett Pond is the most important surface water body within the modeled area because of its vicinity to the end of the CS-4 plume region.

2.2.2 Model Recalibration Using Particle Tracking

The calibrated hydrologic flow model was used as the basis for the simulation of contaminant transport in the aquifer. After the first particle run, however, it was evident that the model was not fully calibrated. Even though the heads agreed with the observations, particles went too deep into the aquifer and did not match the field observations. Thus, the model was recalibrated paying special attention to anisotropy ratios, recharge, and the Buzzards Bay Moraine conductivity; (i.e. factors which considerably affected the transport of particles). Table F-6 summarizes the hydraulic parameters in the final calibrated model.
Table F-6: Hydrologic parameters of flow model resulting from the final particle tracking calibration.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Hydraulic Conductivity</td>
<td>221.6 ft/day</td>
</tr>
<tr>
<td>Hydraulic Gradient</td>
<td>0.0014</td>
</tr>
<tr>
<td>Seepage Velocity</td>
<td>0.8 ft/day</td>
</tr>
<tr>
<td>Anisotropy Ratio</td>
<td>10:1 and 12.5:1</td>
</tr>
<tr>
<td>Recharge</td>
<td>19 in/yr</td>
</tr>
<tr>
<td>Head Mean Difference (calc. - obs.)</td>
<td>0.24 ft</td>
</tr>
<tr>
<td>Head Standard Deviation</td>
<td>1.61 ft</td>
</tr>
</tbody>
</table>

2.3 Contaminant Transport Modeling

2.3.1 Description

A particle tracking code was used to simulate the movement of particles from the source for a specified amount of time. Particle locations were recorded at the end of each simulation and concentrations were calculated based on particle weight and number of particles per unit volume. A more detailed description of some aspects and outcomes of the transport model is discussed next.

a) Source

A thorough description of the source, its location, dimensions, and input loadings are essential for a reliable model. E.C. Jordan (1989b) provides a thorough description of what is believed to be the CS-4 plume source.

The transport model focuses on the solvents PCE, TCE and DCE. Due to limitations in the program code, they were modeled as one contaminant. Thus, concentration outputs files included the sum of PCE, TCE, and DCE concentrations. The source loading was calibrated to match the field values. Consequently, the calculated concentrations are compared to the observed values at different well locations.
Appendix

The source was modeled as a continuous source input. From groundwater velocity data, it was determined that the contamination must have started at least 15 years ago. The source loading was modeled as seven 5 year intervals, from 1960 to 1993 (Figure F-3).

![Figure F-3: Source Loadings for the CS-4 Model](image)

**b) Dispersivity**

Garabedian et al. (1988) calculated dispersivities using the data obtained during the Ashumet Valley tracer test. The method of spatial moments was used to interpret the data; which was regarded by Gelhar et al. (1992) as having a high degree of reliability. Values of dispersivity obtained by Garabedian et al. (1988) are summarized in Table F-7 below.

<table>
<thead>
<tr>
<th>Dispersivity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal ($A_0$)</td>
<td>3.15 ft</td>
</tr>
<tr>
<td>Transverse, horizontal ($A_{22}$)</td>
<td>0.59 ft</td>
</tr>
<tr>
<td>Transverse, vertical ($A_{33}$)</td>
<td>0.005 ft</td>
</tr>
</tbody>
</table>
Appendix

It must be noted that these values, which are generally well accepted in the literature for the site, were obtained for a source with different dimensions as the CS-4 site. The displacement of the CS-4 plume is larger than that of bromide used in the tracer test experiment. Consequently, the overall test scale of the CS-4 site is larger, and the macrodispersivity should be modified (Gelhar, 1993). In addition, Rajaram and Gelhar (1995) conclude that dispersivities for transport over large scales are significantly influenced by the source dimensions. The authors define a relative dispersivity which are is appropriate for characterizing the dilution and spreading at individual heterogeneous aquifers. Using their two scale exponential model, the relative longitudinal dispersivity ($A_0^l$) is estimated to be 66 ft (Gelhar, 1996).

Transverse dispersivities are not affected, since their variability is not due to this phenomenon but to temporal variations of the hydraulic gradient’s direction. This is a topic that is undergoing current research, and thus is beyond the scope of this work.

2.3.2 Transport Model Results

The code’s capabilities allow concentration contours to be delineated. From this information the general size and shape of the contaminant plume was evaluated. The figures below (Figures F-4 to F-6) show the graphical output of the model.
Appendix

Figure F-4: Distribution of Particles in the CS-4 Plume Simulation.
Figure F-5: Plan View of Maximum Concentration Contours.
Appendix

Figure F-6: North-South Cross Section of CS-4 Plume Showing Particle Distribution (top), Concentration Contours (bottom).
Appendix

Table F-8: Dimension of Modeled Plume.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>3,840 m (12,600 ft)</td>
</tr>
<tr>
<td>Maximum Width</td>
<td>640 m (2,100 ft)*</td>
</tr>
<tr>
<td>Average Width</td>
<td>360 m (1,180 ft)</td>
</tr>
<tr>
<td>Maximum Height</td>
<td>17 m (55 ft)</td>
</tr>
<tr>
<td>Average Height</td>
<td>12 m (40 ft)</td>
</tr>
</tbody>
</table>

*Maximum width is probably overestimated due to grid resolution

In general, the dimensions of the modeled plume are greater than the ones reported by ABB Environmental Services Inc. (1992b) (Table F-8). This result does not necessarily invalidate either plume interpretation. The plume defined by ABB Environmental Services Inc. (1992a) was developed from interpretation of the field observations. This simulation used field observations and site characterization data, applied to a calibrated natural conditions model of the Cape Cod aquifer, and thus probably produces a more appropriate representation of the real plume. Nevertheless, there are many assumptions that are made and factors that come in when a computer model is constructed. Some of these, such as source dimensions and location, recharge, hydraulic conductivity distribution, amount of data available; may ultimately be the sources of discrepancy between the modeled solution and the real plume. This suggests that site characterization should be improved in order to obtain a clearer understanding of the subsurface conditions.

2.3.3 Transport Simulations

The CS-4 plume model described above was used to simulate two different remediation alternatives. Both simulations were started with the plume as shown in Figure F-5 (in the
These simulations attempted to forecast the clean-up times for the alternatives examined.

The first simulation was the no option alternative and therefore modeled the natural flushing of contaminants. The total time it took for all the particles to enter Coonamesett Pond was between 80 to 85 years. Thus, the model suggests that if the well fence had not been operating, the aquifer under the MMR would be “clean” approximately by the year 2075. Once the particles reached the pond, concentrations dropped notably, possibly due to dilution effects. This model could be used as the basis for further studies on surface water impacts.

The second simulation attempted to replicate the current pump and treat scheme used at the MMR. Thirteen extraction wells at the toe of the plume pump at a total rate of 140 gpm. The purpose of the simulation was to predict the time it would take to operate the pump and treat system continuously until concentrations reach acceptable levels. This occurred approximately 70 years after the simulation run started. This strongly suggests that a more economically efficient final remediation scheme should be put in place. It is interesting to note however, that some particles escaped the well fence and ultimately ended up in Coonamesett Pond. This is most probably be due to the fact the well fence is designed for an 800 ft (244 m) wide plume. López-Calva (1996) presents pumping schemes for the well fence in question.
2.4 *Modeling Pumping Schemes for Remediation*

An aquifer test was carried out by E. C. Jordan (1990) and results are reported in the feasibility study for CS-4 area. This aquifer test was simulated using the model, in order to calibrate it under pumping conditions.

The first step in the design of a pump-and-treat system is to determine the quantity of groundwater that will need to be pumped from the aquifer. The minimum overall pumping rate of any remedial system needs to be 60 gpm.

2.4.1 *Analysis of the Capture Zones Under Different Pumping Schemes*

The particles which reach the well fence in the middle between pumping wells may or may not be captured, depending on the distribution of hydraulic head. Points of greater head value are formed at the midpoint between the pumping wells. This factor was important in the geometry for the capture zones as described below.

The results from the simulation of six wells non-uniformly spaced indicate that this option was less effective than the equally-spaced option. However, an efficient capture curve can be achieved with a proper combination of pumping.

2.4.2 *Flexibility of the current well fence*

The existing well fence was simulated first. A particle tracking simulation using 13 wells, pumping a total flow rate of 140 gpm, located 60 feet apart, as in the existing well fence, was run.
The pumping rate and the number and spacing of wells in the existing well fence can be considered adequate (Figure F-7). In the horizontal view, a capture curve about 1,100 feet wide is observed. However, this horizontal view of the capture zone does not give information about the three-dimensional geometry. In order to obtain this information, a cross-sectional particle tracking was run. The particles were introduced into the modeled aquifer 1,500 feet upgradient of the well fence. The simulation was run and the starting points of the particles were plotted. The plot of the starting points is only a cross-section of the aquifer showing where the particles were at the beginning of a simulation. A second plot was made on top of the first one, showing only the starting points of the particles that, as a result of the pumping, were removed from the aquifer. In Figure F-8 a cross-sectional particle tracking for the simulation of the IRP well fence is shown. The larger dots can be interpreted as the cross-sectional area of the capture zone, 1,500 feet upgradient of the well fence.

*Figure F-7: Capture curve simulation of the IRP well fence.*
Figure F-8: Cross-sectional areas of the capture curve 1,500 feet upgradient of the 13-well system (IRP well fence). The capture curve is represented by the larger dots.

From the analysis of the cross-sectional area of the capture zone (Figure F-8), the vertical and horizontal effects of the pumping scheme were sufficient for the capture of the plume. The capture zone was calculated to be approximately 250 feet wider and 25 feet thicker than the CS-4 plume. The area of the ellipse formed by the plume is $31,400 \text{ ft}^2$. The area of the ellipse formed by the capture zone is about $64,800 \text{ ft}^2$. The cross-section of the capture zone is two times bigger than the cross-section area of the plume. This guarantee the removal of all contaminated water.

The simulated plume is wider than the plume reported by E.C. Jordan (1990). The flexibility of the 13 well containment system, in terms of its response to different field conditions such as a wider plume was tested. In order to do this, simulations using the current well fence but increasing the pumping rate were made and the extent of the resulting capture zones were analyzed. Results indicate that pumping an overall discharge of 220 gpm, 13 wells will capture a plume about 50% bigger (in cross-sectional area) than that reported by E.C. Jordan (1990). However, if the plume is located deeper in the aquifer, the increase in pumping rate will not be effective, since the lower limit of the capture zone does not go deeper even for a pumping rate 75% larger than the original pumping rate. Placing the well screens deeper into the aquifer is a more effective way to
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contain a deeper plume than increasing the pumping rate. The 220 gpm pumping rate, however, would not be enough to capture a plume with the dimensions of that simulated in this study. Higher pumping rates would be needed. A better solution for the containment of a plume with the dimensions of the modeled one, would be the placement of new wells to increase the length of the well fence.

2.4.3 Prediction of an Alternative Pumping Scheme

After the analysis of the current well fence of 13 wells, and the response of the aquifer to different pumping scenarios, the option of an alternative containment system was addressed. The different simulation runs for this purpose are presented in Table F-9.

**Table F-9: Simulations to predict an alternative effective capture zone for CS-4 plume. Simulations were run according to the dimensions of the plume reported by E. C. Jordan (1989).**

<table>
<thead>
<tr>
<th>Number of wells</th>
<th>Wells operating</th>
<th>Pumping rate (gpm)</th>
<th>Individual pumping rate</th>
<th>Distance between wells (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>13, 11, 10, 8, 7, 5, 3, 1</td>
<td>140</td>
<td>20 in the outside wells, and 16.7 at the rest of the wells</td>
<td>102</td>
</tr>
<tr>
<td>8</td>
<td>13, 11, 10, 8, 7, 5, 3, 1</td>
<td>140</td>
<td>17.5</td>
<td>102</td>
</tr>
<tr>
<td>7</td>
<td>13, 11, 9, 7, 5, 3, 1</td>
<td>140</td>
<td>20</td>
<td>120</td>
</tr>
<tr>
<td>5</td>
<td>13, 10, 7, 4, 1</td>
<td>140</td>
<td>28</td>
<td>180</td>
</tr>
</tbody>
</table>

All simulations were run with schemes of equally-spaced wells, since in the six-well simulation it was clear that an option of non-equally spaced wells presents disadvantages compared with the uniformly-spaced options. The results in the cross-section capture zone generated by eight wells were very similar in terms of the shape of the capture zone and almost identical in terms of cross-sectional area, which is of about 64,800 ft².

Since fewer wells for a fixed pumping rate (140 gpm) may imply reduction in the operation and maintenance costs, the simulation of seven wells was performed. The
resulting capture zone cross-section is illustrated in Figure F-9 (while in Figure F-8, the capture zone resulting from the existing well fence is presented).

![Figure F-9: Cross-sectional areas of the capture curve 1,500 feet upgradient of the 7-well system, pumping a total of 140 gpm. The capture curve is represented by the larger dots.](image)

The area of the seven-well pumping strategy was also approximately 64,800 ft², which is the same as the 13 well and the previous eight well simulations. The seven well option is preferred over the eight-well option because both produced the same results, and in the eight-well system the wells had to be relocated. This relocation of wells would imply costs, not needed for the seven-well scheme.

For the simulation of five wells, pumping 140 gpm was not enough to contain the plume. Pumping rate had to be increased to offset the effect of well spacing. An increase of more than 40 % in pumping rate gave a capture zone of approximately 79,000 ft², which was greater than the one obtained from the other schemes. This capture curve, however, was not effective in containing all the contaminants. No further simulations with five
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wells were run, since the greater capture zone from the five-well simulation implies the capture of a larger proportion of clean water, which makes this option less effective.

From the results of this study, no significant changes for the existing well fence and the seven-well alternative were observed. The seven-well alternative consists of wells located 120 feet apart, which is twice the distance between the wells in the current well fence. The pumping rate for each individual well was increased, although the overall pumping rate remained constant. The results show that the negative effect of increasing distance between wells was offset by the positive effect of increasing individual pumping rates.

In conclusion, the seven-well system may be a better option for the containment of CS-4. The operation and maintenance cost would be reduced and the capture of CS-4 plume would still be attained.
2.5 Bioremediation

Bioremediation engineering is the application of biological process principles to the treatment of water or soil contaminated with hazardous substances (Cookson, 1995). In situ bioremediation provides a more effective and inexpensive approach because it has the potential to: (1) completely degrade the contaminants (2) decrease the treatment time (3) use the subsurface as a bioreactor eliminating the need to pump the water to the surface for treatment; and (4) treat the contaminant “in place” causing minimal disturbance to the subsurface.

2.5.1 General Considerations

Several requirements are necessary for the biochemical reactions to take place. In order to optimize biodegradation, it is important to create an environment where all these factors are conducive to biodegradation and the limiting factor(s) are the contaminants. This generally requires the addition of a substrate, oxygen, and nutrients.

The engineering of the delivery systems and their control present the engineer more challenge than understanding the biochemical process. The main problem with traditional applications of in situ bioremediation is that the delivery of the added agents is in the liquid form resulting in displacement of the contaminated water and therefore inadequate mixing. This results to minimal biodegradation.

To overcome this problem, all agents of choice are added in the gaseous form. The injected gases move through the aquifer in discrete channels (Hayes, 1996) diffusing into the water on their way to the surface (carried by buoyancy). This creates a continuous source of the injected agent in the water.

2.5.2 Cometabolic Oxidation and Reductive Dechlorination

Xenobiotic compounds (i.e. foreign to natural biota) such as the chlorinated solvents found at the CS-4 site cannot be utilized by microorganisms for growth and energy (Buyer, 1992). The process of aerobic cometabolic oxidation has been proven to
biodegrade TCE and other aliphatic compounds. Methane-oxidizing microorganisms have been found to be capable of cometabolically oxidizing TCE, DCE, and vinyl chloride (VC) in aerobic environments (Semprini and McCarty, 1991).

PCE, however, can only be removed in anaerobic environments in a process termed reductive dechlorination. In this process, PCE loses a chlorine atom (turning into TCE) and achieves a lower oxidation state becoming susceptible to cometabolic oxidation.

2.5.3 Process Design

A successful bioremediation scheme for CS-4 should consist of an aerobic phase (for the treatment of TCE and DCE) and an anaerobic phase (for the treatment of PCE). This design was incorporated in three phases (Figure F-10).

Horizontal wells were utilized to inject the gases. Horizontal wells are advantageous over vertical ones because they can extend along a wide plume replacing up to 10 wells (Parmentier and Klemovich, 1996). The area of influence of the injected gases creates a biozone where the treatment takes place. It was assumed that a methane concentration of 1 mg/L and DO concentration of 10 mg/L can be achieved in the biozone.

A pilot field test conducted at another site consisted the modeling basis of the aerobic cometabolic part of the system design at CS-4 (Semprini and McCarty, 1991; Semprini and McCarty, 1992). The reductive dechlorination estimations were based on lab studies as discussed by Collins (1996).

2.5.4 Phase 1

The objective of phase 1 was to stimulate microbial growth by injecting methane, air, and nutrients so a steady-state methanotrophic biomass (SSMB) concentration was reached. Once SSMB was reached, phase 2 begins. It was calculated that it took about 5 days to create a SSMB of 5 mg/L.
2.5.5 Phase 2

Phase 2 was an anaerobic phase. Its objective was the removal of PCE. The SSMB created in phase 1 was required as the electron donor in phase 2. To create an anaerobic environment, the injection of methane and nutrients was continued while the injection of air was stopped. This exerted a biochemical oxygen demand to the aquifer turning it anaerobic in. The DO carried into the biozone by the water was consumed in just 2 ft. Collins (1996) calculated that under these conditions a 99 % removal of PCE can be achieved if adequate residence time is allowed. The residence time can be increased by the addition of horizontal wells which will extent the biozone by 200 ft per well. This corresponds to a residence time of 250 days per well since the seepage velocity is 0.8 ft/d (Lázaro, 1996).
2.5.6 Phase 3

Biozone II was placed downstream at a distance where no interference with biozone I would be possible (about 300 ft). In phase 3, methane and air were injected into the subsurface to stimulate cometabolic oxidation of TCE, DCE, and VC (VC be a by-product of phase 2). The resulting normalized concentrations of the contaminants are shown in Table F-10.

<table>
<thead>
<tr>
<th></th>
<th>TCE</th>
<th>c-DCE</th>
<th>t-DCE</th>
<th>VC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{oe}$ (d$^{-1}$)</td>
<td>0.014</td>
<td>0.068</td>
<td>1.36</td>
<td>1.36</td>
</tr>
<tr>
<td>$t$ (d)</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$Cc / Cc_o$</td>
<td>0.03</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table F-10: Resulting normalized concentration of TCE, DCE, and VC.

Figure F-11 shows the degradation of the contaminants within the biozone as a function of distance.
2.5.7 Discussion

A 97% removal of TCE, 99% removal of PCE, and complete removal of the rest of the contaminants was achieved by this scheme. The conditions required (1.0 mg/L methane aqueous concentration and 10.0 mg/L) were assumed to be achievable in the field through proper engineering measures.

Field conditions are complex and hard to control. Factors affecting the in situ bioremediation of contaminants vary from site to site and caution must be given in the interpretation of the results obtained in this design. The contaminant removal calculated must serve for estimation purposes only. The mass transfer limitations and the spatial heterogeneity encountered at a site create conditions that cannot be adequately predicted
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by theoretical approaches. A pilot test is necessary to predict the system’s efficacy and
determine final design parameters.
2.6 Risk

2.6.1 Introduction

There are numerous risks involved in any groundwater contamination or cleanup. Risk assessment is the identification and quantification of these risks and it is an objective scientific evaluation of the expected adverse health effects of exposure to potentially hazardous substances. Risk assessment consists of hazard identification, dose-response assessment, exposure assessment, and risk characterization. The data generated by a risk assessment is useful in determining the level of cleanup of a particular site, and in selecting the best remedial strategy for that site.

In the CS-4 plume, four hazardous substances are identified as primary contaminants in the groundwater: PCE, TCE, DCE and TeCA. Both carcinogenic and non-carcinogenic health effects are associated with these chemicals.

Risk calculations for carcinogens yield the probability of excess lifetime cancer from the exposure to the particular chemical. The cancer slope factor is needed for this calculation. This factor can be derived from dose-response relationships of the specific chemical. It represents the carcinogenic potency for the chemical. Carcinogenic risk can be calculated as follows (LaGrega et al., 1994):

\[
Risk = CDI \times SF
\]

where \( CDI \) is the chronic daily intake (mg/kg-day) and \( SF \) is the carcinogen slope factor (kg-day/mg). The acceptable range of carcinogenic risk (as set by EPA) is between \( 10^{-4} \) and \( 10^{-6} \) probability of excess lifetime cancer. However, the EPA uses a risk of \( 10^{-6} \) as a point of departure: risk above this level is acceptable only under extenuating circumstances.

Non-carcinogenic risk is quantified by a hazard index (HI). The hazard index is the ratio of the intake to the reference dose. Unlike carcinogens, non-carcinogens do not produce adverse health effects below a specific dose, or threshold. This dose or threshold is
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referred to as the reference dose. Non-carcinogenic risk is measured relative to this reference dose. A hazard index greater than 1.0 thus indicates that there is a possibility of adverse health effects. The hazard index, quantitatively, is (LaGrega et al., 1994):

\[
HI = \frac{CDI}{RfD}
\]

where \( RfD \) is reference dose (mg/kg-day) and CDI has been defined previously. The major pathways of human exposure to the contaminants are through direct ingestion of contaminated water, and through inhalation of vapors (volatilized during showering, etc.). The chronic daily intake (CDI) of the contaminants may be calculated directly from groundwater concentrations for the ingestion pathway. However, the concentration of inhaled vapor must be calculated via a “shower model”, and the model of Foster and Chrostowski (ABB ES, 1992a) is used for this purpose. For a more detailed study see Picazo (1996).

2.6.2 Results

In the bioremediation scheme two cases are presented because the amount of TeCA that is degraded cannot be estimated due to lack of data. Two cases are then applicable: one wherein all TeCA is degraded, and one where all the TeCA remains in the groundwater. TeCA is more likely to be degraded, and a pilot study will be useful to determine the level of TeCA degradation. Table F-11 shows the resulting concentrations.

Table F-11: Contaminant levels after cleanup through bioremediation.

<table>
<thead>
<tr>
<th></th>
<th>µg/L</th>
<th>PCE</th>
<th>TCE</th>
<th>DCE</th>
<th>TeCA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>0.6</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Average</td>
<td>0.2</td>
<td>0.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Case 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>0.6</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>Average</td>
<td>0.2</td>
<td>0.3</td>
<td>0</td>
<td>0</td>
<td>6.8</td>
</tr>
</tbody>
</table>
In the case where TeCA may not be subject to bioremediation, as mentioned above, a pump and treat system is necessary to remove the TeCA. In this case the resulting contaminant concentrations are tabulated below (Table F-12).

<table>
<thead>
<tr>
<th>µg/L</th>
<th>PCE</th>
<th>TCE</th>
<th>DCE</th>
<th>TeCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>5</td>
<td>5</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Average</td>
<td>5</td>
<td>5</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

The risks associated with the various schemes can be viewed graphically in Figures F-12 and F-13. The graphs show that, following EPA guidelines, the plume must be remediated. Since it is possible to almost completely remove all contaminants from the groundwater, the best case for all remediation strategies involves no risk.

**Figure F-12: Carcinogenic risk.**
2.6.3 Discussion

The process of calculating risk involves the use of approximations and conservative assumptions. Thus the risks calculated are generally estimates. Keeping in mind that the primary purpose of risk assessment in this project is the comparison of alternative remediation strategies, these values then become meaningful. All the uncertainties inherent in the calculations apply to each remediation scenario, and therefore the risks can be compared across remediation strategies. The assessment can also show which of the contaminants poses the greatest risk.

It is apparent that simply allowing the plume to proceed unabated can result in unacceptable risk, at least from a regulatory standpoint. In addition, the calculated risks do not take into account any potential ecological risk if groundwater contaminants are discharged into surface waters such as Coonamessett Pond.

From Figure F-12 it can be seen that all calculated non-carcinogenic risks are well below the Hazard Index limit of 1.0, and do not seem to pose a threat to human health. Carcinogenic risks, however, vary up to two orders of magnitude from case to case. Figure F-13 shows that in contrast to non-carcinogenic risks, carcinogenic risks for the no
action alternative are above the limit. The various treatment schemes yield risks within acceptable range, except for the bioremediation case where TeCA is assumed to resist degradation. In this case a pump and treat system is necessary to remove TeCA.

From a risk point of view, any of the alternatives which reduce the risk to permissible levels is acceptable. Therefore the pump and treat system, and the bioremediation scheme (assuming satisfactory TeCA degradation). A pilot test will be useful in determining the actual TeCA degradation, as well as the actual degradation of the other contaminants. The bioremediation scheme which assumed complete TeCA removal results in the lowest calculated risk, but if this is true then use of pump and treat system to polish the cleanup will lower the risk even more. Aside from the lowered risk, the pump and treat system serves as a back-up to the bioremediation, especially during the start-up period. This combination assures the satisfactory removal of the groundwater contaminants.

It should be noted that the incremental risk of developing cancer is minute compared to the background cancer risk of 0.25. Aside from this, the likelihood that a well will be installed in the vicinity of the plume is small. Despite this, the public perception is that this level of increased threat of cancer is unacceptable, and therefore the water must be cleaned up and the threat removed.