IRON MATERIALS FOR THE REMEDIATION OF DNAPL-POLLUTED GROUNDWATER

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Abstract

Tetrachloroethylene and its daughter-products represent a group of contaminations which are frequently found at sites with industrial activities, such as metal processing, electrotechnical and pharmaceutical industries as well as dry cleaning of clothing and the production of colours, paints and laquers. Due to their toxicity and persistence under natural conditions “denser-than-water” non aqueous phase liquids are substantial threats to the subsurface environment as well as the surface ecosystems including human beings. During the last two decades a number of technical solutions has been presented to enhance the situation of contaminated areas. One of the more recently established concepts are permeable reactive barriers. Permeable reactive barriers are passive in situ treatment zones containing a reactive material suitable to remove the contamination from the groundwater. They are installed downgradient from the pollution source perpendicular to the groundwater flow direction to immobilise or degrade the dissolved pollutants in the groundwater as it flows through.

This project was organised in two main parts. The first part assessed seven different iron powders in batch experiments to determine the most efficient powder in terms of degradation velocity. The second part of the study employed this powder in a column experiment using different mixing ratios with sand to evaluate its performance under simulated subsurface conditions in a permeable reactive barrier. The aim of this experiment was to obtain a more detailed description of the behaviour and performance of the selected material. In the batch experiment the most promising iron powder produced a half-life of tetrachloroethylene of 2.36 h. The column study demonstrated that cis-dichloroethylene has the longest half-life compared to tetrachloroethylene and trichloroethylene with 1.65 h. Having the longest half-life of all chloroethylenes included in this investigation the cis-dichloroethylene concentration will determine the dimensioning of a permeable barrier for remediation purposes.

keywords:
chlorinated ethylene; iron; reductive dechlorination; groundwater; batch experiments; column experiment;
### List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>1,1-DCE</td>
<td>1,1-dichloroethylene</td>
</tr>
<tr>
<td>cDCE</td>
<td>cis-dichloroethylene</td>
</tr>
<tr>
<td>DNAPL</td>
<td>“denser-than-water” non-aqueous phase liquid</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>LNAPL</td>
<td>“lighter-than-water” non-aqueous phase liquid</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometer</td>
</tr>
<tr>
<td>NAPL</td>
<td>non-aqueous phase liquids</td>
</tr>
<tr>
<td>PCE</td>
<td>tetrachloroethylene</td>
</tr>
<tr>
<td>PRB</td>
<td>permeable reactive barrier</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVC</td>
<td>polyvinyl chloride</td>
</tr>
<tr>
<td>TCE</td>
<td>trichloroethylene</td>
</tr>
<tr>
<td>tDCE</td>
<td>trans-dichloroethylene</td>
</tr>
<tr>
<td>VC</td>
<td>vinyl chloride</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compound</td>
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1 INTRODUCTION

The awareness of damages and threats to nature caused by human activities has grown constantly during the last decades. The avoidance and reduction of impacts on the environment are nowadays important aspects in modern planning and development strategies. Beside this minimisation approach the cleaning-up of polluted sites gained attention and importance in the same way the general awareness of the environment increased. A large number of technical solutions have been presented to enhance the situation of contaminated areas. But the task to find appropriate measures for remediation schemes is aggravated by the enormous number of different contaminants found and varying conditions from site to site. The “one-for-all-circumstances” solution has not been found and, most likely, will never be found.

Tetrachloroethylene and its daughter-products represent a group of contamination which is frequently found at sites with industrial activities, such as metal processing, electrotechnical and pharmaceutical industries as well as dry cleaning of clothing and the production of colours, paints and laquers. Due to their toxicity and persistence under natural conditions chlorinated ethylenes are substantial threats to the subsurface environment as well as the surface ecosystems including human beings. Different methods have been proposed and developed during the last two decades to clean-up contaminated sites, in particular polluted groundwater resources. One of the more recently established concepts are permeable reactive barriers. Permeable reactive barriers are passive in situ treatment zones containing a reactive material suitable to remove contaminations from the groundwater. They are installed downgradient from the pollution source perpendicular to the groundwater flow direction to immobilise or degrade the dissolved pollutants in the groundwater as it flows through. These barriers seem to be a promising approach to degrade pollutants in situ using zero-valent metals to transform the highly toxic dissolved chlorinated ethylenes to environmental harmless ethene. Although the degradation mechanism is still under research pilot installations showed impressive results in treating plumes of dissolved pollutants. Furthermore, permeable reactive barriers are not limited to chlorinated hydrocarbons, also trace metals and anion contaminations can be removed from the groundwater.

This thesis project was a co-operation between Höganäs AB, Sweden, VBB Viak, Linköping, and the Royal Institute of Technology, Stockholm, to assess the suitability of seven different iron powders produced by Höganäs AB as reagents in permeable barriers. The study is the follow-up of a similar investigation carried out at Stockholm University in 1999 (Nordqvist, 1999 and Wiklander, 1999). Parallel to the ongoing research efforts Sweden’s first permeable barrier was installed in Linköping in May 2000.

1.1 Objectives

The main objective of the study is to assess the suitability and effectiveness of seven iron powders as reducing agent for dissolved chlorinated ethylenes in groundwater. The project was organised in two main parts. The first part assessed the iron products in batch experiments to determine the most efficient powder. The second part of the study employed this powder in a column experiment to evaluate its performance under simulated subsurface conditions in a permeable reactive barrier. This column experiment aimed at a more detailed description of the behaviour and performance of the selected material under more realistic conditions.

2 THEORETICAL BACKGROUND

2.1 PCE and its degradation products in soil and groundwater

The groundwater pollutants Tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cDCE), trans-1,2-dichloroethene (tDCE), 1,1-dichloroethene (1,1-DCE) and vinyl chloride (VC) are in the main focus of this work. All substances consist of two double-bound carbon atoms and a varying number of chloride and hydrogen atoms. Chlorinated ethylenes belong to the group of halogenated unsaturated aliphatic hydrocarbons; they have relative low boiling points and densities above one (except VC). All compounds are highly resistant to biotic and abiotic degradation under natural subsurface conditions. But due to the oxidised state of the carbon is it more likely to degrade the substances, biologically or abiotically, under reducing conditions (Orth et al., 1996).

In industrialised countries pollution caused by leaks, spills and historical disposal practices of chloroethylenes is a frequently occurring problem, which reflects their wide spread use. PCE and its degradation products, TCE, cDCE, tDCE, 1,1-DCE and VC, are/were employed in different areas, such as the degreasing, cleaning and induration of metals, as solvents for glues, paints and laquers, as agent in dry-cleaning of clothing and in the pharmaceutical and electrotechnical industries.

2.1.1 “Non-aqueous phase liquids” in soil and groundwater

Non-aqueous phase liquids (NAPLs), like PCE and the related less chlorinated ethylenes, belong to a group of organic substances, which are immiscible with water. A further distinction of this class corresponding to their density would be “denser-than-water” non-aqueous phase liquids (DNAPLs - such as TCE, PCE, heavy oils) and “lighter-than-water” non-
aqueous phase liquids (LNAPLs - such as diesel, aviation fuel, gasoline).

Once spilled into the ground a multiphase system of interrelated contamination in soil and groundwater develops. The four occurring phases are (Schnoor, 1996):
- the NAPL phase
- dissolved contaminant (in pore water and groundwater)
- sorbed contaminant – residual product (attached to the soil matrix in saturated and unsaturated zone)
- gas phase (soil air)

TCE and its daughter-products are DNAPLs, because of their high density. In case of a release to the ground, DNAPLs are transported by gravity through the unsaturated and the saturated zone into lower soil layers until they encounter a low-permeability zone of an aquitard. In the following, the pollutant descents to the lowest unit and forms a pool of organic liquids. The direction of movement in the saturated zone, in particular if the movement takes place on top of an aquitard, is not necessarily the direction of the groundwater flow (see Figure 1) (Schnoor, 1996).

**Figure 1: DNAPL spill in saturated and unsaturated zone (Domenico et al., 1997)**

Once arrived at the bedrock or an aquitard the DNAPLs may become entrapped in fractures or pores. As the dissolution rate is mainly determined by the surface area of the contaminant blobs the NAPLs dissolve very slowly. Subsequently, the organic liquids entrapped need more time to dissolve due to the decreased interface area between water and contaminant resulting in a long-term source of groundwater pollution (Schnoor, 1996).

Depending on the sorption capacity of the unsaturated zone not all spilled NAPLs reach the aquifer. The soil retention capacity for NAPLs is about 3 to 5 l/m³ in case of high permeability and about ten times higher (30 to 50 l/m³) for low permeability soils (Schnoor, 1996).

### 2.1.2 Physical properties

The chlorinated hydrocarbons, subject to this study, belong to the group of volatile organic compounds (VOC). This group is characterised by low boiling points, normally below 150°C (Hölting, 1996). The investigated substances are denser than water (see section 2.1) and their solubility is low, but still toxic for organisms (see section 2.2).

VOCs volatilise at relative low surrounding temperatures. The rate of volatilisation is mainly determined by the size of the molecule measured in terms of molecular weight and its solubility in water (Schnoor, 1996).

Models for this process are often based on Lewis and Whitman’s two-film-theory describing that volatilisation is a function of the Henry’s constant (Schnoor, 1996). According to Henry’s law formulating that the solubility of a gas at a given temperature is proportional to the partial pressure above the solution, the distribution of a volatile substance between the solvent and the gas phase can be described by the following equilibrium (Mortimer, 1996):

\[
[c_{\text{aq}}] \Phi \rightarrow [c_{\text{g}}]
\]

Stating this relation the Henry's constant can be defined as follows:

\[
K_H = \frac{c_d}{P_g}
\]

where \(c_d\) is the solubility of the substance in the solvent and \(P_g\) the partial pressure above the solution. A second possibility to define the constant is the ratio between the aqueous-phase concentration \(c_d\) and the gas-phase \(c_g\) concentration of the substance under consideration by

\[
K_H^w = \frac{c_d}{c_g} = K_H \times RT
\]

where \(R\) is the gas constant and \(T\) the temperature in Kelvin (Sander, ~1999).

The values for the Henry's constant as well as for the solubility available in the literature can vary considerably. Due to that it is difficult to find one “ideal” choice for the constants.

The most important physical properties for the chlorinated hydrocarbons tetrachloroethene, trichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,1-dichlorethen and vinyl chloride are presented in the following table (Table 1). To account for the mentioned problems related to the Henry’s constant the corresponding columns list two different values. The first of the three columns contains the smallest, the second one the largest value cited in the literature (see also section 3.4)

### 2.2 Harm potential of chlorinated hydrocarbons

The substances PCE, TCE, CDCE, tDCE, 1,1-DCE and VC can be considered as dangerous and toxic to both humans and ecosystems. PCE, TCE and VC are especially toxic for humans due to their long-term effects on eyes, liver, kidney and the central nervous system. Furthermore, all three compounds are
Iron Materials for the remediation of DNAPL-polluted groundwater

genetically toxic and carcinogenic. The intake into the organism occurs by inhalation, absorption through the skin and the respiratory tract.

The three isomers of dichloroethene are also highly toxic but not as dangerous as the compounds mentioned above.

The isomers can also cause damage to the central nervous system, the respiratory tract and inner organs.

All substances are toxic to aquatic life forms and therefore should not enter natural waters, such as surface or subsurface waters. Additionally, PCE, TCE and 1,1-DCE are also toxic in seawater (University of Vermont Safety Information Resources, Inc., ~1993).

There are of course limits for the maximum contaminant level (MCL) set by the U.S. Environmental Protection Agency will be listed additionally (see Table 2).

Table 2: Limits for the concentration of chlorinated hydrocarbons in groundwater and drinking water (sources: a Lide, 1998; b Schnoor, 1996; c Gavaskar et al., 1998; d Naturvårdsverket, 1999; e U.S. Environmental Protection Agency, ~1998)

<table>
<thead>
<tr>
<th>substance (abbreviation)</th>
<th>molecular weight a [g/mol]</th>
<th>density a [kg/l]</th>
<th>boiling point a [°C]</th>
<th>solubility b (in water) [mg/l]</th>
<th>vapour pressure b [M/atm]</th>
<th>Henry's constant c [dimensionless]</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrachloroethene (PCE)</td>
<td>165.83</td>
<td>1.62</td>
<td>121.0</td>
<td>150.4 – 400</td>
<td>2×10²</td>
<td>3.4×10⁻²</td>
</tr>
<tr>
<td>trichloroethene (TCE)</td>
<td>131.39</td>
<td>1.46</td>
<td>87.0</td>
<td>110.4</td>
<td>8×10⁻²</td>
<td>7.5×10⁻²</td>
</tr>
<tr>
<td>cis-1,2-dichloroethene (cDCE)</td>
<td>96.94</td>
<td>1.28</td>
<td>49.0</td>
<td>3500</td>
<td>0.26</td>
<td>1.3×10⁻¹</td>
</tr>
<tr>
<td>trans-1,2-dichloroethene (tDCE)</td>
<td>96.94</td>
<td>1.26</td>
<td>60.0</td>
<td>6300</td>
<td>0.45</td>
<td>7.1×10⁻²</td>
</tr>
<tr>
<td>1,1-dichloroethene (1,1-DCE)</td>
<td>96.94</td>
<td>1.22</td>
<td>31.7</td>
<td>2500</td>
<td>0.66</td>
<td>6.5×10⁻²</td>
</tr>
<tr>
<td>vinyl chloride (VC)</td>
<td>62.5</td>
<td>0.91</td>
<td>-14.0</td>
<td>90.0 – 2800</td>
<td>3.4</td>
<td>8.2×10⁻⁴</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>substance</th>
<th>molecular weight a [g/mol]</th>
<th>density a [kg/l]</th>
<th>boiling point a [°C]</th>
<th>solubility b (in water) [mg/l]</th>
<th>vapour pressure b [M/atm]</th>
<th>Henry's constant c [dimensionless]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>150.4 – 400</td>
<td>0.110</td>
<td>0.005</td>
<td>1.10</td>
<td>0.20</td>
<td>0.005</td>
</tr>
<tr>
<td>TCE</td>
<td>110.4</td>
<td>0.20</td>
<td>0.005</td>
<td>0.20</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>cDCE</td>
<td>3500</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>1.0</td>
<td>0.01</td>
</tr>
<tr>
<td>tDCE</td>
<td>6300</td>
<td>-</td>
<td>0.007</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,1-DCE</td>
<td>2500</td>
<td>-</td>
<td>0.007</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.3 Degradation of perchloroethylene in presence of zero-valent iron

The chemical principles and reactions that build the basis for the remediation of chlorinated solvents in groundwater, have been known and used in organic synthesis for the last 150 years (Matheson et al., 1994). Generally, the occurring mechanism is a reductive dehalogenation where the zero-valent iron is oxidised and the halogenated hydrocarbons are reduced. Reductive dehalogenation reactions can be distinguished in two different processes: the hydrogenolysis and the reductive elimination. Both reactions occur competitively during the degradation and each of them is accompanied by a net-transfer of two electrons. In case of the reductive elimination two chloride ions are released from one molecule, that is reduced, where the hydrogenolysis accounts for the replacement of one chloride by one hydrogen atom (Roberts et al, 1996). To reduce PCE completely to ethene a transfer of eight electrons is needed. Very generally depicted the reduction can be written as follows (Matheson et al., 1994):

$$ Fe^0 + e^- + H^+ \rightarrow Fe^{2+} + H_2 $$

where R symbolises the hydrocarbon molecule under consideration. Investigating these three equations more closely three major actors responsible for the occurring reaction can be identified:
1. the iron dissolving in water and as place of the reaction
2. the chlorinated hydrocarbons being reduced
3. a proton donator, in the system under consideration - water

The detailed mechanism of the reduction is still under research, but the hypothesised reaction sequence is shown in Figure 2.

**Figure 2: Hypothesised reaction sequence from PCE to ethene (Arnold et al., 1998)**

Starting with PCE the degradation ends with ethene as final product, a non-toxic and easily biodegradable compound. A further reduction of ethene to ethane is possible but is not necessarily occurring (Orth et al., 1996). The intermediate steps of the dehalogenation are characterised by different reaction mechanisms and velocities (see section 2.3.2).

Beside ethene and ethane as the dominating products other products such as methane, propene, propane, 1-butene and butane have been reported. It is not always obvious where those substances origin, additional processes (e.g. the reduction of dissolved carbon dioxide) have to be considered responsible for their occurrence (Orth et al., 1996). In total, the chlorinated degradation products, TCE, isomers of DCE and VC account for less than 5% of the converted PCE (Farrell et al., 2000). As the chlorinated degradation products are also toxic and environmental dangerous a complete characterisation of all daughter- and intermediate products is necessary to assess the inherent risks and essential to optimal barrier design. In particular cDCE and VC are fairly persistent and of environmental concern (Roberts et al., 1996).

Beside the halogenated ethylenes chlorinated acetylenes are listed as reaction products. Those arising acetylenes are highly poisonous (Lide, 1998), but fortunately they are not formed in significant amounts compared to the mass of PCE or TCE.

During the reaction sequence they show an accumulation and decay behaviour typical of a reaction intermediate. (Roberts et al., 1996; Arnold et al., 1998).

Describing the reaction mechanism in a more general way it can be stated that:

- the reductive dehalogenation is an abiotic reaction taking place at the surface of the involved iron particles (Orth et al., 1996).
- the velocity of the reduction decreases with a decreasing number of chloride atoms (Arnold et al., 1998).
- the reduction capacity is related to the specific iron surface (Matheson et al., 1994; Orth et al., 1996; Arnold et al., 1998).

### 2.3.1 Factors influencing the degradation process

Examining the process of reductive dehalogenation of chlorinated ethylenes it can be observed that the values for reaction rate constants are highly variable and very sensitive to operation conditions (Johnson et al., 1996). There are various factors affecting the development of the iron-water-contaminant system; furthermore, those factors are interacting and influencing each other. The most important determinants, which will be discussed below, are iron corrosion, temperature, pH and redox potential, the iron material and the groundwater chemistry.

#### Iron corrosion

The zero-valent iron is exposed to different processes in water. Beside its oxidation both aerobic and anaerobic corrosion occur in the iron-water-system according to the following equations (Matheson et al., 1994):

**aerobic:** \[ \text{Fe}^0 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{Fe}^{2+} + 2\text{OH}^- \]

**anaerobic:** \[ \text{Fe}^0 + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}^{3+} + \text{H}_2 + 2\text{OH}^- \]

Both redox reactions cause an increase of the pH in weakly buffered systems due to the release of two moles of hydroxyl ions per mole iron. This effect is more pronounced for aerobic condition because the aerobic corrosion is undoubtedly faster than the anaerobic. Oxygen is the preferred oxidant for zero-valent iron with regard to the reaction with chlorinated hydrocarbons. This leads to a reaction between iron and oxygen until all dissolved oxygen is consumed and the reduction of PCE and its degradation products can take place (Matheson et al., 1994). This preference is the reason that the dissolved oxygen concentration and the redox potential drop very quickly over a few centimetres as the water enters the iron cell in the permeable reactive barrier.

The increased pH caused by iron corrosion favours the formation of iron hydroxide and other metal precipitates depending upon the natural aquatic chemistry of the groundwater. These precipitates may inhibit further reactions by forming a surface layer on
the reactive sites of the iron particles or decreasing the permeability of the iron barrier (Orth et al., 1996). Additionally, the groundwater chemistry and constitution plays an important role for the corrosion process and the formation of precipitates. Gu et al. (1999) report that for example the presence of HCO$_3^-$ enhances the iron corrosion.

**Temperature**

The temperature dependence of the dehalogenation process varies for the different compounds. cDCE and VC show no or only little sensitivity to surrounding temperatures. The degradation of PCE, TCE and tDCE is more likely to be affected by temperature. For example, the degradation rate for TCE declines by factor 1.4 for a change in temperature from 23°C to 15°C (U.S. Environmental protection agency, 1998). Furthermore, temperature is an important parameter regarding solubility and distribution of the pollutants in water and gas phase (see section 2.1.2).

**pH and redox potential**

pH and redox potential are important parameters for the occurrence and the availability of the zero-valent iron. As already stated the reductive dehalogenation causes an increasing pH (Matheson et al., 1994) and a lowered redox potential (Orth et al., 1996). There are four different reactions responsible for any change in pH (Mufikan et al., 1995; Orth et al., 1996); but until now no direct link has been found between the bulk solution pH and the reaction rate constants for the dehalogenation (Farrell et al., 2000):

- **dissolving of iron:** $Fe^3+ + 2e^- \rightleftharpoons Fe^{2+}$
- **dissociation of water:** $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$
- **anaer. corrosion:** $Fe^0 + 2H_2O \rightleftharpoons Fe^{2+} + H_2 + 2OH^-$
- **oxidation of iron:** $Fe^0 + 2H^+ \rightleftharpoons Fe^{2+} + H_2$

The second important parameter is the redox potential. The redox couple of Fe$^{0}$/Fe$^{2+}$ has a standard potential of -0.440 V. This negative potential enables Fe$^0$ to act as a reducing agent relative to redox-labile compounds such as PCE or TCE with an estimated standard reduction potential between +0.5 and +1.5 V at pH 7. Furthermore, the solubility of Fe$^{2+}$ in water depends on both, pH and redox potential, with decreasing Eh and pH increases the solubility of Fe$^{2+}$ (Scheffer et al., 1998). The behaviour of iron in water for varying pH and redox potential is displayed in Figure 3.

**Iron material**

As mentioned earlier, the metallic iron surface plays an important role for the initialisation, mediation and course of the reaction. Under most environmental conditions the iron surface will be covered by various kinds of oxides, sulfides and/or carbonates (Oregon Graduate Institute of Science and Technology, ~1999). Despite this surface layer the dehalogenation has to take place while the chloroethylenes are attached to the iron surface. The probability for an instantaneous transfer of eight electrons seems to be exceedingly low. But the low concentrations of intermediate products found give rise to the hypothesis that the organic molecules must remain attached to the iron surface for a sufficient period of time for eight electrons to be transferred (Orth et al., 1996).

![Figure 3: Pourbaix diagram for the Fe$^0$ - $H_2O$ system at 25°C (Puigdomenc, ~1999)](image)

Taking this into account Scherer et al. (1998) postulated three mechanisms how the electron transfer to the organic compound could proceed (see Figure 4).

![Figure 4: Mechanisms at the iron surface (Oregon Graduate Institute of Science and Technology, ~1999)](image)

The first pathway “physical barrier” shows the direct electron transfer from the zero-valent iron to the hydrocarbon in a corrosion pit or similar gap in the
covering layer of oxides, sulfides and/or carbonates. The second model shows the oxide layer working as a semiconductor transporting electrons to the organic substrates. The last proposed pathway displays the oxide layer working as a co-ordinating surface containing Fe$^{2+}$ to reduce the chlorinated substances (Oregon Graduate Institute of Science and Technology, ~1999).

But not only the passivation layer has effects on the development of the reaction. The iron composition strongly influences the formation of the surface layer of iron oxides, sulfides and carbonates (Farrell et al., 2000) as well as it has impacts on the degradation characteristics. Su et al. (1999) concluded that variations of specific reaction rate constants for different iron materials but identical experimental designs and conditions imply that material characteristics such as iron impurity, crystallinity and morphology may be important factors influencing the degradation behaviour.

**Groundwater chemistry**

Aside the discussed factors, the composition of the groundwater, where the permeable barrier will be situated, plays an important role regarding reaction rate constants and the development of the iron surface passivation (Farrell et al., 2000). Today, the importance and effects of different groundwater constituents such as sulphate and hydrocarbonate ions are fairly unknown. In particular sulphate and hydrocarbonate are corrosive to zero-valent iron resulting in a disruption of the surface passivation and additional “consumption” of zero-valent metal (Gu et al., 1999). The increased corrosion of iron leads to a higher amount of iron precipitates and subsequently to mineral precipitation, both of them causing cementation and decreased permeability of the iron barrier. Finally, this deterioration of the iron material ends in slower degradation of the contaminant. The conclusion, which has to be drawn from this, is that the compatibility between the iron material and the subsurface on has to be checked very carefully for every project.

### 2.3.2 Kinetics of the degradation mechanism

The detailed kinetics taking place during the reduction of PCE are still subject to a number of different studies. The occurring reactions are pseudo-first-order with respect to the substrate (Matheson et al., 1994; Orth et al., 1996; Roberts et al., 1996). Transferred into mathematical terms the reaction can be written as:

$$\frac{C}{C_0} = e^{-k_{obs} t} = \ln \left( \frac{C}{C_0} \right) = -k_{obs} t$$

where C stands for the substance concentration, $C_0$ is the initial concentration of pollutant, $k_{obs}$ is the observed reaction rate constant and t is time. Investigating this equation more closely a further relation for $k_{obs}$ can be postulated. As the process is mainly determined by the specific surface area of the iron product $k_{obs}$ can be expressed by

$$k_{obs} = k_{str} \rho \rho_{m}$$

Here $k_{str}$ stands for the specific reaction rate constant [Lm$^{-2}$h$^{-1}$], $\rho_{str}$ is the specific surface area of the zero-valent iron [m$^2$g$^{-1}$], $\rho_m$ is the mass concentration of Fe$^0$ in the solution [gL$^{-1}$] and $\rho_s$ is the surface area concentration of iron [m$^2$L$^{-1}$] (Johnson et al., 1996).

The introduced value $k_{obs}$ can also be used to determine the half-life, $t_{1/2}$, for different species according to the equations below.

$$t_{1/2} = \frac{\ln 2}{-k_{obs}}$$

The process of dechlorination is generally faster at saturated carbon centers (e.g. tetrachloromethane) than unsaturated carbon centres (e.g. PCE, TCE) and high degrees of halogenation favour rapid reduction (Johnson et al., 1996). Typical half-life values for PCE and its degradation products for commercially available iron products are listed in Table 3. These values present a summary of published values found by Gillham (1996) during a literature review. The values are normalised to 1 m$^3$ per ml of solution.

<table>
<thead>
<tr>
<th>substance</th>
<th>half-live [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>2.1 – 10.8</td>
</tr>
<tr>
<td>TCE</td>
<td>1.1 – 4.6, 2.4, 2.8</td>
</tr>
<tr>
<td>cDCE</td>
<td>10.8 – 33.9, 47.6</td>
</tr>
<tr>
<td>tDCE</td>
<td>4.9, 6.9, 7.6</td>
</tr>
<tr>
<td>1,1-DCE</td>
<td>37.4, 15.2</td>
</tr>
<tr>
<td>VC</td>
<td>10.8 – 12.3, 4.7</td>
</tr>
</tbody>
</table>

It is noticeable that the reduction of PCE, TCE and tDCE are much faster than the degradation of cDCE, 1,1-DCE and VC. The removal of PCE, TCE and tDCE by zero-valent iron takes only minutes to some hours, but the dechlorination of the intermediate products needs much more time. Arnold et al. (1998) present a quite reasonable explanation for this. As mentioned before different mechanisms proceed in a competitive way. It seems that chlorinated ethylenes with at least two chlorine atoms in a trans-$\alpha$-$\beta$-position show a preference for the pathway of two-electron $\beta$-elimination resulting in the formation of acetylene or chlorinated acetylenes (see Figure 5, pathway B). Subsequently, the chloroacetylene undergoes hydrogenolysis to form acetylene, which may be further reduced to ethene or ethane. Compounds not bearing chlorine atoms in a trans-$\alpha$-$\beta$-position, such as cDCE, 1,1-DCE and VC, need more time to be degraded via hydrogenolysis (Figure
5, pathway A), which explains the smaller reaction rate constants. One implication of this behaviour is that the dimensioning of permeable reactive barriers has to be adjusted to the concentrations of cDCE, 1,1-DCE and VC to guarantee sufficient time for those substances to be dechlorinated.

Furthermore, independent of the initial concentration of chlorinated ethylenes the reaction rate constant has a linear relation to the metal loading of the solution. The metal loading describes the size of specific iron surface per litre solution. So, with an increasing iron surface, the dechlorination process will speed up (Arnold et al., 1998).

As the whole process is considered to be a surface process it must be assumed that there is an upper limit for the concentration of organohalides where the reactive sites are saturated. Orth et al. (1996) showed that up to concentrations of 61 mg TCE/l the process is still of pseudo-first reaction order. The usually found concentrations are far below this value and it seems reasonable to treat the reaction as a pseudo-first-order process.

![Figure 5: Degradation of TCE via reductive-β-elimination and hydrogenolysis (U.S. Environmental protection agency, 1998)](image)

**2.4 Remediation of polluted sites**

**2.4.1 Permeable reactive barrier**

The “Permeable reactive barrier” (PRB) is one method of in-situ remediation of groundwater developed during the 1980s. It is an alternative solution to expensive conventional pump-and-treat remediation techniques, which are only limited applicable for large amounts of polluted subsurface waters and not greatly effective.

The PRB is a passive in situ treatment zone containing reactive material suitable for the contaminants that should be removed. Possible reactive media, which can be used in PRBs, are zero-valent metals, sorbants and ion, exchangers, bacteria and oxygen-releasing compounds (Oregon Graduate Institute of Science and Technology, ~1999).

The barrier is installed in a zone downgradient from the contamination source perpendicular to the groundwater flow direction. It immobilises or degrades the dissolved pollutant as the groundwater flows through it (see Figure 6). The barrier is installed by replacing a part of the aquifer material with the chosen reactive medium. The transport of the groundwater through the barrier occurs without any input of energy by additional pumping only due to the natural gradient of the groundwater table (U.S. environmental protection agency, ~2000). The reactive medium intercepts the plume and transforms the contaminants to a non-toxic species via degradation, sorption, precipitation or removal of the pollutant. This technique can be employed for various substances such as chlorinated hydrocarbons, trace metals (e.g. chromium, nickel, lead, uranium, cadmium) and anion contaminants (e.g. sulphate, nitrate, phosphate, arsenic) (U.S. Environmental protection agency, 1998).

![Figure 6: Scheme of a permeable reactive barrier (Powell & Associates, ~2000a)](image)

Reactive barriers can be designed in different ways. The two most common designs are the funnel-and-gate design and the continuous trench (see Figure 7). In the funnel-and-gate design only the gate area is filled with reactive material and sheet pilings are used to direct the plume towards the gate. Using the continuous trench the whole barrier is filled with reactive media and the plume passes the barrier on its entire length.

![Figure 7: Basic installation designs for permeable reactive barriers (Powell & Associates, ~2000b)](image)

During the design of a PRB four important issues have to be addressed. First, the reactive medium employed should be compatible with the subsurface environment to minimise undesired changes of the chemical conditions. Second, the material should persist over a long time to keep the costs low. The third important aspect is that the permeability of the barrier has to be higher or equal to the permeability of the aquifer to avoid dispersion of the flowing waters around the reactive zone (U.S. Environmental protection agency, 1998). The probably most essential point to consider are the physical properties of the site.
on hand and the degree of contamination and the
distribution of the pollutant in the subsurface. It is
necessary to describe the physical characteristics, such
as hydraulic conductivity, bulk densities, geological
structure, groundwater flow conditions and chemistry
as well as the contamination, its composition and
concentration very carefully. A detailed description
of these parameters facilitates the decision if a permeable
reactive barrier might be a promising measure and
enables a proper design of the barrier to meet the
actual site conditions in an optimal way. The
characterisation of the remediation site should also
include groundwater flow modelling to locate the
most suitable position and design of the barrier

More general the advantages of permeable reactive
barrier can be summarised as follows:
- several forms of inexpensive materials are
  commercially available
- no above ground treatment facilities are needed
- space can be returned to its original use
- there are no or only little operation and
  maintenance costs
- no external energy is consumed – the system
  works passive
- no hazardous by-products need to be disposed
  or treated
- no effluent water needs to be treated
- potential for long-term operation with minimal
  efforts for supervising (Environmental security
technology certification program, 1999)

Comparing the conventional pump-and-treat
approaches with the PRB technology it can be stated
that the initial capital investment for the PRB is higher
due to the increased construction activities. In the
middle and long-term the higher investments efforts
can be refinanced by the crucial lower maintenance
and operational costs. For a 20 to 30 year remediation
period between 29 and 64% cost savings can be
achieved compared to a pump-and-treat remediation
of the same site over a period of 6 to 8 years
(Environmental security technology certification program, ~2000).

2.4.2 Alternative and conventional remediation
methods

There are different technologies available for in situ
remediation schemes of DNAPLs. Not all techniques
are already commercially available, some are still in a
pilot phase to prove their effectiveness. In the
following the most important approaches will be
named and shortly explained.

Biological processes / biodegradation – pollutants are used as
substrate or co-substrate by bacteria, fungi and other
microorganisms and completely or partially
metabolised. Introduction of additional oxygen,
substrates and co-substrates or improvement of the
soil structure by using materials such as straw or cork
enhance the biodegradation. Relatively new is the
approach to stimulate the anaerobic biological
degradation by adding of Hydrogen Releasing
Compounds (HRC®) distributed by Regenesis, USA
(California).

Containment – the source of pollution is contained by
slurry walls or sheet pile walls to prevent the plume
from moving. Additionally measures of ground
modification including stabilisation and solidification
can be employed. Containment does not aim at the
removal of the contamination but at its isolation to
limit its spreading.

Soil washing – the contaminated area is cleaned by
flushing or flooding of the effected area with
surfactants or co-solvents to dissolve the DNAPLs in
the ground. The dissolved DNAPLs, together with
the solvent, are pumped out of the soil and extracted from
the solvent. More recently the remediation of DNAPL
contaminations by flushing the soil with alcohol was
developed.

Air stripping – by enhancing the airflow in the ground
due to extraction of soil air the volatile components of
DNAPLs can be removed. The flow paths are
strongly influenced by the heterogeneity of the
subsurface (Grupp et al., 1995).

Beside the mentioned methods for in-situ
remediations of DNAPL spills the conventional pump-
and-treat approach should be named, where the
contaminated ground water is pumped to the surface
and treated by various techniques including chemical,
physical and biological processes. With regard to PCE
two processes are applied in pump-and-treat systems.
The first possibility are systems stripping PCE and
transferring it to another medium. The contaminated
water is pump through a column with a counter
current stream of air. The ethylenes volatilise in the
gas bobbles and are adsorbed on activated carbon.
Another option is an advanced oxidation system
where hydrogen peroxide or ozone in conjunction
with irradiation by high intensity UV radiation is
added. Here, the ethylenes are first oxidised and
afterwards destroyed by the radiation (Muftikan, et al., 1995).

3 METHODS AND MATERIALS

3.1 Iron powders

All iron powders evaluated in this work are produced by
Höganäs AB, Sweden. The products differ
regarding their material characteristics such as specific
surface area, content of metallic iron, additives, grain
size and shape. Beside those differences all powders
are made of sponge iron or at least based on sponge
iron, which is produced from enriched iron ore of fine
grain sizes. Some of the powders are annealed some
are not. The process of annealing refers to a heat
treatment in a reducing atmosphere containing
hydrogen to decrease the contents of carbon and
oxygen. The main characteristics for each iron powder
are listed in Table 4 below. For reasons of simplicity
the three last powders will be renamed as listed in Table 4.

### 3.2 Specific surface measurement

To be able to evaluate and compare the different iron powders involved in this study (as well as those mentioned in the literature) it was necessary to determine the specific surface area of each product to establish a common point of reference. The specific surface area for the powders was ascertained using the single-point BET-method. The basic assumption for this technique is that a sample at the temperature of liquid nitrogen (boiling point –194.5°C) can adsorb gaseous nitrogen under formation of a monomolecular nitrogen layer (a nitrogen layer with a thickness of one nitrogen molecule) on its surface. Taking the amount of nitrogen gas adsorbed or desorbed and the surface area occupied by one nitrogen molecule the specific surface can be calculated. An accounting for the current climatic conditions, e.g. air pressure and temperature, is necessary (Micromeritics Instrument Corporation, 1996).

#### Table 4: Main characteristics of assessed iron powders (Höganäs product specifications)

<table>
<thead>
<tr>
<th>Iron product</th>
<th>Composition</th>
<th>Main grain diameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distaloy SA</td>
<td>Fe 96.6 %, C 0.01 %, Ni 1.93 %, Cu 1.65 %, Mo 0.55 %</td>
<td>150 – 106</td>
<td>annealed iron powder</td>
</tr>
<tr>
<td>SNC 100.24</td>
<td>Fe 98.8 %, C 0.01 %, S 1.15 %</td>
<td>150 – 106</td>
<td>annealed iron powder</td>
</tr>
<tr>
<td>CI 40</td>
<td>Fe 98.5 %, C 0.005 %, S 0.01 %</td>
<td>~ 40</td>
<td>Fe – metallic min 96.9 %; unannealed iron powder</td>
</tr>
<tr>
<td>CMS</td>
<td>Fe 93 %, C 0.35 %, S 0.02 %</td>
<td>&lt; 45</td>
<td>Fe – metallic 88 %; based on unannealed iron</td>
</tr>
<tr>
<td>02.20.214 renamed: E214</td>
<td>Fe 93 %, C 0.05 %</td>
<td>&lt; 45</td>
<td>Fe – metallic 88 %; based on unannealed iron</td>
</tr>
<tr>
<td>02.20.215 renamed: F215</td>
<td>Fe 93 %, C 0.5 %, S 0.02 %</td>
<td>&lt; 45</td>
<td>Fe – metallic 88 %; C fraction is activated carbon; based on unannealed iron</td>
</tr>
<tr>
<td>02.20.216 renamed: G216</td>
<td>Fe 93 %, C 0.5 %,</td>
<td>&lt; 45</td>
<td>Fe – metallic 88 %; C fraction is</td>
</tr>
</tbody>
</table>

All measurements were done with the Micromeritics FlowSorb II 2300; the gas used for the adsorption was a nitrogen-helium mixture (30% nitrogen, 70% helium). Before the measurements all samples were dried for 24 h at 105°C and additionally de-gased in the equipment for about 15 minutes at approximately 110°C.

First, a defined amount of sample was transferred into a glass tube and inserted into the equipment for degasing. A second sample, which was already degased during the preceding measurement, was moved to the measuring position and cooled with liquid nitrogen during the adsorption measurement. While the desorption rate was determined the glass tube containing the sample was submerged in water at room temperature. So, the specific surface area for each sample was measured two times, the first time during the adsorption process and the second time during the desorption process. Due to the higher accuracy of the desorption measurement this value is assumed to be the real specific surface area. To determine the accuracy of the measurement a Kaolinite sample (Micromeritics) with a given specific surface area of 15.9 ± 0.9 m²/g was used as a standard.

### 3.3 Chemical analyses

#### 3.3.1 Analysis of chlorinated hydrocarbons

The chemicals used as control standards during the analyses, for the preparation of the analytical method and the “synthetic-polluted” water for the batch experiment were tetrachloroethylene (Lancaster, 99 %), trichloroethylene (Lancaster 98+ %), cis,1,2-dichloroethylene (Tokyo Kasei, 99 %), trans,1,2-dichloroethylene (Aldrich, 98 %) and 1,1-dichloroethylene (Lancaster, 99%). Vinyl chloride was not included in the analytical parameters due to its fast volatilisation under the given experimental conditions and the relative uncertain analytical determination.

The content of chlorinated hydrocarbons was measured throughout the whole project using a Varian 3400 gas chromatograph linked to a Finnigan SSQ 7000 mass spectrometer (GC/MS). For the analysis 1 ml of the solution was transferred to 2 ml-vials with Teflon septa. Using a 100 µl gas-tight syringe 50 µl of the headspace were withdrawn from the 2 ml-vials and injected manually. The used GC-column was a DB5MS (ID: 0.25 mm, film-thickness: 0.25 μm, length: 30 m) with helium as carrier gas at a pressure of 10 psi (68.947 kPa). The temperature settings for the gas chromatograph were constant during the project and equal for all substances. The column temperature was 30°C and raised by 1°C per minute...
3.3 Batch experiment

To assess the effectiveness of the different iron powders several batch experiments were carried out. Each experiment was conducted in seven 25 ml-vials capped with Teflon/rubber septa. Each vial contained 1.0 g of iron powder and was filled without leaving headspace with “synthetic-polluted” water with a tetrachloroethylene concentration of 20 mg/l. The employed water was deionised water (average conductivity around 2.1 µS/cm). The vials where shaken on a vertical shaker (Heidolph Reax 2) at approximately 30 shakes per minute. Samples were taken after 0, 0.5, 1, 2, 4, 8 and 24 hours. For each time point one vial was used. This procedure is based on the assumption that the conditions in each vial with the same amount of iron powder and the same amount of pollutant will develop equally. The time points were kept with an accuracy of ± 2 min during the eight hours and about ± 15 min for the 24 hour sample.

Before taking the samples for the analysis the solution was filtrated using syringe filters (Cole Parmer, 0.45 µm PTFE syringe filters, 25 mm diameter) and 10 ml plastic syringes to remove the iron powder and intercept the degradation process. Double samples of 1 ml of the filtrated solution were transferred to 2 ml-vials. The first sample was analysed between 12 and 15 minutes after the sample taking, the second one after 24 to 27 minutes. Furthermore, a control sample from a vial without iron powder was analysed in the same way after 5 hours. Directly after the filtration the pH of the solution was measured using a Radiometer Copenhagen PHM 82 Standard pH Meter with a potassium chloride electrode for the pH. All experiments took place at 21.1 ± 0.7°C and artificial light.

As discussed earlier, chlorinated ethylenes volatilise fast (see section 2.1.2) and the partitioning of PCE between aquatic and gas phase is described by a dimensionless Henry’s law constant of 2.94. Assuming an initial amount of 1 µg PCE in the water phase when 1 ml of solution is transferred to a 2 ml-vial, after partitioning 0.746 µg PCE can be found in the water phase and 0.254 µg in the headspace. For the calibration of the analysis the concentration in the gas phase was set to be 1 µg even if in reality only 0.254 µg were present. Using this assumption the measurement taken from the gas-phase represented the whole system “2 ml-vial”. Despite the fact that the Henry’s law constant listed in Table 1 are valid at 25°C and the experiments took place at 21.1 ± 0.7°C no accounting for the temperature difference was considered. The PCE concentration in the headspace changes by two to three percent for a temperature change from 25 to 21.1 ± 0.7°C. Facing higher uncertainties, such as the tightness of the vials or the precision of the GS/MS, it was abstained from accounting for the shift in temperature.

3.5 Column experiment

3.5.1 Column design, set-up and sampling

The column experiment was carried out with four columns. The materials used to construct the columns were PVC tubes and caps. Each column was about 60 cm long and had an inner diameter of 10 cm. But only 50 cm of the length between inlet and outlet were later on filled with sand and iron material (see Figure 8). The column lid was made of a Plexiglas plate and tightened with silicone. Three sample ports were located along the length of the reactive part of the column at distances of 10, 20 and 40 cm from the inlet. Stainless steel needles were inserted through a small drill-hole as sample ports and glued to the column to enable sampling from the middle of the column. The bottom of the column was filled with a 2cm-layer of crushed glass and on top of the glass a polyethene filter was inserted to prevent the column filling from entering the glass layer and the inlet. The columns were run in reverse flow mode, they were percolated from bottom to top to drive out all air enclosed during the packing and maintain anaerobic conditions during the experiment.
Iron Materials for the remediation of DNAPL-polluted groundwater

To pump the water through the columns a peristaltic pump (Alitea UDx2l) with four channels was used; Viton tubing (Noax AB, 2.0 x 4.0 mm) passed through the pump roller assembly. All other tubing used in the set-up was PVC (see Figure 9).

The water percolated through the columns (see section 3.5.3) was stored in 20-l collapsible Teflon bags, which were covered with black plastic foil to protect them against sunlight and UV radiation. The Teflon bags were chosen to minimise the loss of contaminant due to volatilisation to a forming headspace as the source water is consumed. To stabilise the columns in the beginning about 10 pore volumes of deionised water were run through the columns. The columns were percolated with a velocity of about 0.75 m/day. At this speed about 1.5 pore volumes were pumped through the columns.

Additionally to the analysis on chloroethylenes the parameters pH, redox potential, dissolved oxygen and conductivity were analysed. The pH electrode was identical with the one used during the batch experiments. The redox potential was determined using a CDM 80 conductivity meter by Radiometer Copenhagen and the dissolved oxygen with a Russell RL425 oxygen meter.

Samples were taking from all sample ports approximately three times a week with a 10 ml plastic syringe. Prior to the sample collection 0.5 ml were withdrawn to remove stagnant water from the sample ports. For the analyses on chlorinated ethylenes 2.5 ml of water was withdrawn from the columns; double samples of 1 ml of the filtrated solution were transferred to 2 ml-vials. The syringe was rinsed several times with deionised water between the different samplings. For the determination of pH, dissolved oxygen, conductivity, redox potential and chloride concentration additional 10 ml of sample were extracted from each sample port. All samples were filtrated employing syringe filters (Cole Parmer, 0.45 µm PTFE syringe filters, 25 mm diameter). The column experiment took place at 21.2 ± 0.6°C.

The columns were operated for ten days with deionised water and for thirty days with a contaminated groundwater from the dry cleaning site in Liköping.

The columns were percolated between 83 and 92% of the total time. The pollutant concentrations were measured three times a week, parameters such as pH, dissolved oxygen, electric conductivity and chloride concentration only once a week due to the larger amount of sample that was needed for the measurement. Unfortunately, the mass spectrometer was not available for two weeks due to a defect turbo pump; the contaminant concentrations for this time are not available. During this period only the parameters pH, electric conductivity and chloride concentration were determined. The dissolved oxygen concentration in exchange for the redox potential was measured only during the last week of the experiment, because the earlier measurements of the redox potential resulted in relative imprecise and obviously uncertain values. In general the investigated substances were limited to PCE, TCE and cDCE because these compounds were the only pollutants found in significant amounts in the source water. In case of flow disturbances or interceptions prior to a scheduled sampling no samples were taken.

3.5.2 Column packing

Three of the four columns were filled with different mixtures of sand and iron powder. The fourth column was used as a control column and packed with pure sand. The sand/iron columns were set up with sand-iron ratios of 75/25%, 50/50% and 25/75% (percentages by weight). The sand used for the column packing was silver sand with an average grain size of 500 µm (see Figure 10).
3.5.3 Groundwater for column experiment

To ensure conditions relatively close to natural subsurface conditions a “real” groundwater was percolated through the column during the experiment. The water was taken from a site in Linköping/Sweden, where a dry cleaning company is operating since the 1950th. The plot has a size of about 50 m x 30 m and is situated in an industrial area close to the centre of Linköping.

The top layer of the soil is a layer of filling materials (sand and/or gravel) with a thickness between 0.2 and 0.5 m, at some places the thickness of this layer might increase up to 1.5 m. A sandy silt layer follows the sand/gravel layer, which is up to 5 m thick. A second sand layer of 0.5 to 4 m is situated under the silt layer. Finally, a moraine (between 0.5 and 6 m thick) forms the deepest layer. The groundwater table is about 3 m below the surface and the average hydraulic conductivity was determined to be between $10^{-5}$ and $5\times10^{-5}$ m/s.

The groundwater taken from this site is highly polluted with PCE and its degradation products. The maximal concentrations for chlorinated ethylenes found at this site are listed in Table 5.

### Table 5: Maximum concentration of chlorinated ethylenes (internal report of VBB Viak, 1999)

<table>
<thead>
<tr>
<th>substance</th>
<th>maximum concentrations found [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>6.6</td>
</tr>
<tr>
<td>TCE</td>
<td>22.0</td>
</tr>
</tbody>
</table>

In general, the groundwater shows a high alkalinity (around 400 mg HCO$_3^-$/l) and chloride concentration (around 50 mg/l). The pH of the water is around pH 7 (internal report of VBB Viak, 1999). The water was pumped directly from the sample tube into the collapsible Teflon bags. It was tried to minimise the aeration of the groundwater to avoid losses due to volatilisation.

Two times polluted groundwater was collected for the column experiment. The second time the water contained PCE as main contaminant and only traces of cDCE. To be able to determine the half-life of cDCE, it was added to the source water aiming at a concentration around 25 mg/l. So, the source water used during the last two weeks contained beside its “natural” pollution by PCE a significant amount of artificially added cDCE. Even if this contaminant was added it can be assumed that the water chemistry of the source water was not influenced significantly.

# Results

## 4.1 Specific surface measurements

As already stated, the value of the desorption measurement was used as the specific surface area of the samples due to its higher accuracy compared to the result of the adsorption (see section 3.2). The compiled data of the surface measurements for the different iron powders is listed below (see Table 6). CI 40 and CMS show the largest specific surface area with 0.541 and 0.230 m²/g, respectively.

The standard sample, Kaolinite, has a specific surface of $15.9 \pm 0.9$ m²/g. The surface measured for this sample was 15.842 m²/g, this supports the assumption that the accuracy of the determined values is very high. Furthermore, the results reflect the size of the surfaces as Höganäs AB specified them. Only the last two samples, F215 and G216, have clearly higher specific surfaces compared to the rest of the samples showing specific surfaces of the same magnitude (except CI 40). Both powders are based on CMS but include 0.5 % of activated carbon. It seems very reasonable that the relatively high specific surface of the activated carbon adds to the measured value. Taking into account the uncertainty of those two surface values the surface areas determined for CMS and E214 are employed for further calculations on G216 and F215. Another conclusion that can be drawn from the results is that sulphur in the sample seems to reduce the surface area. E214 and F215 contain 0.5 % of sulphur. The surfaces of the corresponding samples without sulphur, CMS for E214 and G216 for F215, are about 20 to 30 % larger compared to those with sulphur.
Iron Materials for the remediation of DNAPL-polluted groundwater

Table 6: Results of specific surface measurements

<table>
<thead>
<tr>
<th>iron powder</th>
<th>specific surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distaloy SA</td>
<td>0.089 m²/g</td>
</tr>
<tr>
<td>SNC 100.24</td>
<td>0.115 m²/g</td>
</tr>
<tr>
<td>CI 40</td>
<td>0.541 m²/g</td>
</tr>
<tr>
<td>CMS</td>
<td>0.230 m²/g</td>
</tr>
<tr>
<td>E214</td>
<td>0.172 m²/g</td>
</tr>
<tr>
<td>F215</td>
<td>1.801 m²/g (0.172 m²/g)</td>
</tr>
<tr>
<td>G216</td>
<td>2.173 m²/g (0.230 m²/g)</td>
</tr>
<tr>
<td>Kaolinite (standard)</td>
<td>15.842 m²/g</td>
</tr>
</tbody>
</table>

4.2 Batch experiments

The results for the degradation of PCE as well as the development of the chloride concentration and the pH for the seven tested iron powders are displayed in Figure A 1 to Figure A 7 in APPENDIX A – RESULTS OF BATCH EXPERIMENTS.

The different concentrations were calculated using the average of the two analyses for each time point and batch. Table 7 summarises the most important analytical results gained during the batch experiments.

The last four products, CMS, E214, F215 and G216, show clearly the fastest degradation of PCE during the batch experiments with \( k_{\text{obs}} \) values approximately > 0.3. CI 40 has also a very high degradation potential, but due to its high price CI 40 is not of economical interest and not included in further evaluations.

The kobs - values are based on the analytical results only of the first 8 hours of the experiments (for definition of \( k_{\text{obs}} \) and \( k_{\text{SA}} \) see section 2.3.2). The concentrations measured after 24 hours seem to incorporate some uncertainties. In two cases the pollutant concentrations in the 24h-vial differed significantly from the concentration that were predicted by the reaction rate constants derived from the degradation results collected during the first eight hours (SNC 100.24 and F215). Furthermore, one 24h-vial was not tight and no reliable measurement was possible due to volatilisation losses (Distaloy). The considerations regarding the degradation kinetics were limited to PCE, because daughter products of the reduction process could not be traced in all batch experiments due to a declining detection quality of the mass spectrometer with an increasing number of batches.

Table 7: Observed reaction rate constants for the different iron powders

<table>
<thead>
<tr>
<th>powder</th>
<th>specific surface area</th>
<th>surface area conc.</th>
<th>( k_{\text{obs}} )</th>
<th>( R^2 ) ((k_{\text{obs}}))</th>
<th>( k_{\text{SA}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI 40</td>
<td>0.541</td>
<td>21.64</td>
<td>0.3857</td>
<td>0.99982</td>
<td>0.0178</td>
</tr>
<tr>
<td>Distaloy</td>
<td>0.089</td>
<td>3.56</td>
<td>0.1355</td>
<td>0.8569</td>
<td>0.0381</td>
</tr>
<tr>
<td>SNC</td>
<td>0.115</td>
<td>4.60</td>
<td>0.1190</td>
<td>0.9511</td>
<td>0.0259</td>
</tr>
</tbody>
</table>

The control samples for all batch experiments contained with one exception (CI40, 73 %) between 95 and 104 % of the initial concentration of PCE. The pH rose for all systems over the time. The highest increase was observed for F215 with pH 11.4, on the other hand the increase in pH was minimal for CI40 to pH 8.6.

4.2.1 Conclusions from surface measurements and batch experiments

Combining the results of the surface area measurement with the product specification from Höganäs four hypotheses can be derived, which should be possible to prove with the data from the batch experiments. Those hypotheses are:

- The degradation of PCE is fastest using CI40, because CI40 has the largest surface area of the compared powders.
- SNC 100.24 and Distaloy show similar performance based on their comparable surface area.
- CMS and E214 should perform relatively similar regarding their specific surface.
- F215 and G216 produce the highest declining of substance due to the included activated carbon (adsorption of contaminant by activated carbon).

All four assumptions can be validated with the data found in the batch experiments (see Table 7). The outline of this project was to examine the most promising iron powder in column experiments. Using the observed reaction rate constants the last four powders based on CMS seem to be the best choice. But including the control experiments, the chloride analysis, into this consideration the situation changes. The chloride concentration after 24 hours for F215 and G216 is only about 50 % of the chloride concentration for CMS and E214 after the same time (see Figure 11 to Figure 14). This fact supports the assumption that parts of the PCE were adsorbed by the activated carbon and not available for the degradation mechanism. Based on this observation and the faster degradation of PCE using CMS in comparison to E214 and the lower costs of CMS it seems reasonable to employ CMS in the column experiments.
4.3 Column experiment

4.3.1 Physical column characteristics

It was put much effort on ensuring equal conditions regarding bulk density and porosity for all four columns during the packing and operation to facilitate comparisons between the columns. The porosity and subsequently the pore volume of each column is of special interest because the reaction rate constants are referenced to the available specific iron surface per unit solution or pore volume respectively. Having equal or comparable conditions regarding porosity and bulk density it is easier to compare the results of each column and to ensure equal flow conditions in the different columns.

The columns were supposed to be packed with a bulk density of 1.6 to 1.8 g/cm³ and a porosity of 30 to 35 %. It turned out to be difficult to pack all columns aiming at equal conditions due to the relative big difference in particle size between the iron powder and the sand. The physical data for all four columns is given in Table 8.

<table>
<thead>
<tr>
<th>Column</th>
<th>sand (%)</th>
<th>iron powder (%)</th>
<th>bulk density [g/cm³]</th>
<th>porosity [%]</th>
<th>pore volume [l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>1.655</td>
<td>35.35</td>
<td>1.39</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>25</td>
<td>1.655</td>
<td>54.97</td>
<td>2.16</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
<td>1.808</td>
<td>62.25</td>
<td>2.44</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>75</td>
<td>1.986</td>
<td>66.37</td>
<td>2.61</td>
</tr>
</tbody>
</table>

The porosity was calculated using the given formula:

\[
\text{% porosity} = 100 - \left(\frac{\text{bulk density}}{\text{particle density}}\right) \times 100
\]

For the mixed columns a weighted particle density was used to calculate the porosity reflecting the iron-sand ratio in the column. The particle density for the sand was 2.56 g/cm³ and 7.02 g/cm³ for CMS (personal communication Fredrik Eklund). Corresponding to the differences in porosity between the four columns the size of one pore volume varied and subsequently
the residence time for one pore volume. Another effect of the grain size differences was settlements in column 3 and 4 due to a lacking integrity/stability of the grain matrix. Over the duration of the experiment a settlement of approximately 12% by volume was encountered for both columns. The bulk density was estimated to be about 2.054 for column 3 and 2.257 for column 4 decreasing the porosity to 57.12% and 61.78%, respectively.

4.3.2 Degradation results

In the following the degradation results will be presented for the different columns. The detailed analytical data such as contaminant concentration and pH of the source water, which was used as a point of reference to evaluate the results of the column experiment, is shown in Appendix B – Analytical data of source water.

100% sand column

The control column was set up to determine the influence of the silver sand, the PVC columns and the tubing material (flexible PVC) on the measurements and the results. Under optimal experimental conditions and an optimal selection of the materials no influence should be registered. In fact, the material showed no or only little effect on the pH and the dissolved oxygen concentration of the water as it was pumped through the column. Both parameters matched the value determined in the source water. Nevertheless, the pH of the effluent water increased slightly by approximately 0.15 units during the last week of the experiment. But the electric conductivity increased significantly while the water passed through the sand column. The rise in conductivity was between 150 and 400 µS/cm. A clear trend for this change regarding the residence time was not obvious.

Focusing on the contaminants very strong effects of the materials were observed. During the first week no PCE and/or TCE was detected in the water samples taken from the control column and only 70 to 75% of the initial cDCE concentration could be traced. A strong contaminant adsorption by the flexible PVC tubing seems to be the main reason for the substance loss. These adsorption losses over the time declined over the time. After three weeks about 50 to 60% of the initial PCE concentration was found in the samples, this percentage increased up to 80% after four weeks. The cDCE concentration even exceeded the initial contaminant concentration determined in the source water. The concentrations measured in the columns account for up to 120% of the cDCE concentration found in the source water. The origin of this “gain” of contaminant could not be identified. The detailed results of the control column are listed in Appendix C – Analytical data of column experiments. The chloride concentration, which was again used as control experiment for the degradation of the chlorinated compounds, matched the initial chloride concentrations of the source water. Based on this fact it can be concluded that no degradation took place and the loss of contaminant is only caused by adsorption and not by dechlorination, which would lead to increased chloride concentrations in the effluent water.

The flow rate varied during the study between 0.87 and 1.19 ml/min equalling a throughput of approximately 0.9 to 1.2 pore volumes per day. The settling of the column filling was < 3% and no major effects on porosity and hydraulic conductivity were encountered.

25% iron column

Looking at the column containing 25% CMS and 75% sand the pH, electric conductivity, dissolved oxygen concentration and chloride concentration are influenced significantly by the reduction of the chlorinated ethylenes in the column (see Appendix C – Analytical data of column experiments). The pH rose between the inlet and the first sample port (10 cm) from around 7 up to 10.5. Subsequently, the pH increased to a maximum of 11.2 in the effluent. Compared to the control column the electric conductivity did not increase in a similar style. The increase of electric conductivity as it was measured over the length of the column varied between 50 and 250 µS/cm. The dissolved oxygen concentration decreased from around 3.2 in the source water to values below 1 mg/l indicating a declining of the redox potential. The chloride concentration of the effluent water was clearly higher compared to in the source water due to the release of chloride ions during the dechlorination.

The PCE and the TCE concentrations measured during the first week were highly affected by the contaminant adsorption of the tubing. If PCE and TCE entered the column and if degradation took place it occurred in the first 10 cm of the column and was not accessible for the sampling and the analysis. The cDCE reached the column and was degraded with a normalized half-life (calculated for 1m² specific iron surface per 1 ml solution - see section 2.3.2) of 1.65 h and the observed reaction rate constant was 0.0727 h⁻¹ (R²=0.8175). Half-lives for PCE and TCE were not calculated, because of the little amount of available data to calculate the degradation kinetics. But even if those half-lives were not determined, it can be derived from the data that the half-lives of PCE and TCE are shorter compared to cDCE, which has the longest half-life of the chlorinated compounds on hand. A rough estimation for the reaction rate constant for PCE would be around 0.1 h⁻¹. To account for the adsorption effects and avoid impacts of this loss on the calculation of kobs, the concentration measured at the fist sample port in the column was not accessible for the sampling and the analysis. The PCE and TCE concentrations measured during the first week were highly affected by the contaminant adsorption of the tubing. If PCE and TCE entered the column and if degradation took place it occurred in the first 10 cm of the column and was not accessible for the sampling and the analysis. The cDCE reached the column and was degraded with a normalized half-life (calculated for 1m² specific iron surface per 1 ml solution - see section 2.3.2) of 1.65 h and the observed reaction rate constant was 0.0727 h⁻¹ (R²=0.8175). Half-lives for PCE and TCE were not calculated, because of the little amount of available data to calculate the degradation kinetics. But even if those half-lives were not determined, it can be derived from the data that the half-lives of PCE and TCE are shorter compared to cDCE, which has the longest half-life of the chlorinated compounds on hand. A rough estimation for the reaction rate constant for PCE would be around 0.1 h⁻¹. To account for the adsorption effects and avoid impacts of this loss on the calculation of kobs, the concentration measured at the fist sample port in the column was used as point of reference. The contaminant concentration in this point was used as C₀ and the concentrations in the following sample points related to this value using the equation below (see section 2.3.2):
At two time points no measurements were taken, because the column was not percolated, the first time due to a perforated pumping tube, the second time due to a power blackout. Sometimes, the sample taking was aggravated by fine iron particles and precipitates clogging the needles used as sample ports. The flow rate varied between 0.93 and 1.05 ml/min. This corresponds 0.62 to 0.7 pore volumes per day. No significant settling was registered for the 25% iron column.

**50% and 75% iron columns**

The operation of the columns containing 50 and 75% CMS was by far more difficult. The small average grain size of the iron particles in combination with the formation of iron precipitates led to frequent blockages of the sample ports making sampling impossible. With a relative large number of missing samplings it is very difficult to provide a coherent overview of the results of those two columns. In general it can be stated that the degradation reaction was faster compared to the column containing 25% iron particles. Due to the incomplete data sets it was abstained from including the detailed analytical results in this report and only some tendencies ill be presented in the following.

For the column with 50% iron the contaminant concentrations in samples withdrawn at the 40 cm sample port were already below the detection limit for PCE, TCE as well as cDCE. The dechlorination velocity seems to support the half-life of cDCE calculated for the 25% iron column. The pH increased up to 11.85 and the electric conductivity to 1015 µS/cm in the effluent water. The chloride concentration reached levels up to 34 mg/l indicating a high degree of purification. The average flow rate was between 0.94 and 1.04 ml/min corresponding to 0.59 to 0.64 pore volumes per day. The variation of pore volumes per day accounts also for the settling of the column filling (see section 4.3.1).

The column containing 75% CMS showed an even faster degradation of the pollutants. The cDCE concentration measured at the 20 cm sample port was already below the detection limit. But no complete column profile with samples from all sample ports taken during one day was obtained due to the formation of precipitates. The pH in the effluent reached the highest level in of all four columns with values up to 11.9. The electric conductivity was maximal, too, increasing up to 1681 µS/cm. The high electric conductivity was not only caused by the dechlorination and the release of iron and chloride ions to the solution but by fine iron particles in the effluent. The chloride concentration showed also maximal results with values up to 38 mg/l. The flow rate varied between 0.87 and 1.14 ml/min. This discharge is equivalent to a throughput of 0.52 to 0.63 pore volumes per day.

### 5 DISCUSSION AND CONCLUSIONS

#### 5.1 Degradation of chlorinated hydrocarbons

The conclusions that were drawn from the batch experiment were already presented in section 4.2.1 and the following discussion will focus on the results of the column experiment.

As outlined in section 2.3 the degradation is related to the available specific iron surface; with increasing specific surface of the iron particles decreases the time, which is needed for the dechlorination. The columns in this study showed the fastest degradation of chloroethylenes for the 75% iron column followed by the 50% column and the 25% iron column with the longest half-lives. The study on hand focused on the evaluation of the half-life of cDCE. Cis-dichloroethylene needs the longest time to be reduced compared to PCE and TCE. This leads to the conclusion that cDCE is the determining factor for the design of permeable reactive barriers. A PRB system containing zero-valent iron, which is designed to remove most of the cDCE from a contaminated groundwater, can easily remove all PCE and TCE from the same subsurface water.

The observed reaction rate constant for PCE (estimated to be around 0.1 h⁻¹) seems to be smaller compared to the batch experiment (0.2933 h⁻¹) resulting in a longer half-life. Gavaskar et al. (1998) report that half-lives for PCE and TCE exceed batch values by factor three and two. This would lead to the conclusion that the difference in reaction rate constants is not necessarily a mistake but a fact, which was observed in other studies too.

The flexible PVC tubing are the main reason for the faced problems in the determination of the reaction rate constants for PCE and TCE. With the choice of flexible PVC tubing for the experimental set-up a certain loss of contaminants to the tubing material was anticipated, but it seemed unlikely that two contaminants will be lost completely to the tubings during the first half of the experiment. Parker and co-workers (1996) investigated the effects of different flexible and rigid tubing materials on trace-level organics testing the adsorption effects of 20 different tubing materials on eight different organic substances including PCE, TCE and tDCE. They report adsorption of PCE, TCE and tDCE by flexible PVC tubing between 93 and 98% after one hour and initial contaminant concentrations between 10 and 16 ppm. Awareness of this fact in an earlier stage of the column set-up would have resulted in a different choice for the tubing material.

When the extent of the adsorption effects was discovered another problem was encountered. The polluted groundwater from the site in Linköping, contained PCE as main contaminant and only traces...
of cDCE. To be able to overcome the loss of contaminant due to adsorption and to determine the half-life of cDCE, cDCE was added to the source water. The high amounts of cDCE found in the control column accounting for up to 120% of the initial cDCE concentration are a kind of “miracle” in this study. It is not clear where those additional 20% of cDCE origin. The first idea might be that it is a degradation product of the PCE, but as the chloride concentration did not increase, the PCE concentration was stable over the length of the column and chlorinated daughter products account for less than five percent of the degradation products of PCE (Farrell et al, 2000) this possibility is very unlikely and can be excluded. The second hypothesis would be that the additional cDCE was adsorbed earlier by the tubing and “re-dissolves” in the source water while it was pumped through the tubing. The large amount of cDCE “occurring from nowhere” makes it relative unlikely that a dissolving process is the answer to the question of origin. Finally, a wrong analysis for the cDCE in the source water could account for the additional cDCE, but the source water was additionally analysed two times at different time points confirming the earlier results. So, it is not possible to assign a defined source to the occurring cDCE.

The dissolved oxygen concentration was measured instead of the scheduled redox potential. The measurements of the redox potential during the beginning of the column experiment resulted in relative imprecise and obviously uncertain values. In order to get at least an rough idea about the redox conditions in the column the dissolved oxygen concentration was recorded during the last week of the experiment, because.

The increase in pH is obviously related to the amount of iron in the columns. It seems that the higher the iron content in the column is the more pronounced will be the rise in pH. On the other hand the increase of the electric conductivity has two sources. The dechlorination releases iron and chloride ions to the solution. Most of the iron ions form precipitates and remain in the column material (Orth et al, 1996). The chloride ions behave like a conservative tracer. They are removed from the column by the water. But only the additional chloride ions cannot explain the sharp increase in conductivity. Furthermore, there is obviously a correlation between the sand content and the rise in electric conductivity in the effluent water. The sand used as column material had an additional impact on the conductivity as it can be seen from the results of the control column containing 100% sand. In a control experiment 40 g sand were stirred in 200 ml deionised water. The initial electric conductivity of pure deionised water of 1.2 µS/cm increased to 102.4 µS/cm after 15 min of stirring. So, the increase of the electric conductivity is a superposition of released ions from the dechlorination and the sand material adding to the conductivity.

Summarising the results of this study, the iron product CMS seems to be a possible option for the design of a permeable barrier. Under the given conditions the half-life of cDCE was established to be 1.65 h. This value is the determining factor for the construction of a PRB. The residence time for the polluted groundwater must be high enough to degrade the dissolved cDCE. Residence time is long enough for the dechlorination of cDCE it will be sufficient for the degradation of PCE and TCE. But before CMS can be sold as a commercial product one important issue has to be addressed. The small grain size limits its usage. If a high permeability of the PRB is necessary it will be difficult to construct a barrier with CMS which is not sensitive to settlements and has a sufficient high structural stability to deal with possible forces and loads from the surface and the weight of the barrier itself. The columns containing 50 and 75% CMS demonstrated the limitation of CMS regarding settlements and structural integrity.

5.2 Errors and methodological uncertainties

There are some errors or methodological problems related to this study. The conclusions from the batch experiments are based only on one set of analyses for each iron product. After those runs were concluded the mass spectrometer was not operational due to technical/electronic problems. So, a second run for each powder was not conducted due to the defect of the mass spectrometer and a lack of time. This led to some data “gabs” and the lost opportunity to confirm the results of the first runs. But despite the occurring obstacles the collected data fits well with the theoretical background as it was developed in section 2 “Theoretical background”. Generally, the availability of the mass spectrometer and its performance influenced the outcome of this investigation. The spectrometer broke down three times during the work, each time for at least two weeks. Additionally, the response and sensitivity of the mass spectrometer changed sometimes randomly during the project duration. It was tried to compensate those effects by adjusting the calibration curves using control standards, which were analysed during the study.

Looking at the column experiment the employed flexible PVC tubings had the most significant impact on the results. The adsorption of PCE and TCE by the tubing aggravated the estimation of half-lives for these two compounds. But as the half-life of cDCE has the longest half-life of the substances under consideration it is no obstacle to the process that the degradation time for PCE and TCE could not be determined.

Furthermore, the Viton tubing passing through the roller assembly of the peristaltic pump was susceptible for aging. It was necessary to exchange the tubing in average once a week. This made it sometimes difficult to maintain a constant flow through the columns.
5.3 Prospects on future investigations

Concluding this project several points have to be considered before a future employment of CMS in remediation projects. The most important issue is the structural stability of a permeable barrier and its permeability, which have to be addressed. The columns with a CMS percentage of 50 and 75% showed settlements in a magnitude of 12% by volume. This led to a decreasing permeability and porosity of the columns. For field installations it will be relatively difficult to ensure the necessary bulk density of the permeable barrier. One requirement for the implementation of PRB was that the permeability of the barrier is equal or higher than the permeability of the surrounding subsurface environment to force the contaminated water through the barrier. It will be difficult to reach this goal for soils with low bulk densities if an iron content >25% for the barrier is planned. To improve the material with regard to permeability it might be necessary to evaluate carrier materials where the iron powder could be attached or glued to.

Beside the issue of permeability it might be interesting to assess possibilities to enhance the reactivity and performance of the iron material. Addition of vitamin B12 as second reducing agent (Burris et al., 1996), usage of hydroxypropyl-β-cyclodextrin or similar substances to enhance the solubility of chloroethylenes (Bizzigotti et al., 1997) or pyrite or aluminosilicate minerals minimise the shift in pH (Gavaskar et al., 1998) should be considered to strengthen a possible market position of CMS.

6 Acknowledgements

Several parties made it possible for me to complete this project successfully and in time. I am indebted to all of them for supporting and encouraging me. First of all I would like to thank my supervisor, Bengt Espeby, for his remarks, personal engagement, far-reaching support and freedom that he gave me during all phases of this work. Furthermore, I am very grateful to Fredrik Eklund from Höganäs AB for his confidence in me from the very beginning and providing me with the necessary knowledge about iron materials. In addition only the financial support of Höganäs AB made this project possible. The remarks of Johan Ericsson from VBB Viak in the beginning were a very useful orientation and provided guidance throughout my work.

It would have been impossible to conclude this investigation without the support and knowledge of Anna-Karin Borg-Karlsson and Johan Andersson (both from the Royal Institute of Technology, Department of Chemistry, Division of Inorganic Chemistry) in the analytical field. Despite all the problems occurring they did their best to help and support my efforts – they did a great job. Finally, I would like to thank Bertil Nielsson for his help and patience during the set-up and conductance of the column experiment.

Of course, I am also very greatful to Ann-Catrine Norrström for helping me during the final stage finalising this thesis and preparing my presentation.

7 List of Appendices

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix A</td>
<td>Results of batch experiments</td>
</tr>
<tr>
<td>Appendix B</td>
<td>Analytical data of source water</td>
</tr>
<tr>
<td>Appendix C</td>
<td>Analytical data of column experiments</td>
</tr>
</tbody>
</table>
8 Literature

8.1 Books and articles


Micromeritics Instrument corporation (1996): Instruction manual FlowSorb II 2300, Norcross (GA), USA


8.2 Internet sources


Oregon Graduate Institute of Science and Technology (~1999): Remediation with iron, http://cgr.ece.ogi.edu/iron/


University of Arkon, Department of Chemistry (~2000): Hazardous chemical database, http://ull.chemistry.uakron.edu/erd/


8.3 Other sources


Nordqvist, Anna (1999): Nedbrytning av klorerade kolväten met granulärt järn – en jämförelse av loka järnprodukter, Stockholm University, Department of Geology and Geochemistry, MSc-Thesis


Wiklander, Ann-Christine (1999): Nedbrytning av klorerade kolväten med granulärt järn – ett kolonnförsök, Stockholm University, Department of Geology and Geochemistry, MSc-Thesis
APPENDIX A – RESULTS OF BATCH EXPERIMENTS

Figure A 1: Development of PCE, chloride concentration and pH over time for CI 40
Figure A 2: Development of PCE, chloride concentration and pH over time for Distaloy

Figure A 3: Development of PCE, chloride concentration and pH over time for SNC 100.24
Iron Materials for the remediation of DNAPL-polluted groundwater

Figure A 4: Development of PCE, chloride concentration and pH over time for CMS

Figure A 5: Development of PCE, chloride concentration and pH over time for E214
Figure A 6: Development of PCE, chloride concentration and pH over time for F215

Figure A 7: Development of PCE, chloride concentration and pH over time for G216
**APPENDIX B – ANALYTICAL DATA OF SOURCE WATER**

<table>
<thead>
<tr>
<th>bag</th>
<th>PCE [mg/l]</th>
<th>TCE [mg/l]</th>
<th>cDCE [mg/l]</th>
<th>pH</th>
<th>electric conductivity [µS/cm]</th>
<th>chloride concentration [mg/l]</th>
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<tr>
<td>1</td>
<td>7.30</td>
<td>2.77</td>
<td>33.25</td>
<td>7.06</td>
<td>511</td>
<td>25</td>
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<tr>
<td>5</td>
<td>19.21</td>
<td>-</td>
<td>28.17</td>
<td>7.05</td>
<td>691</td>
<td>16</td>
</tr>
</tbody>
</table>

*cDCE added to source water, 00-08-14*

| 6   | 19.93      | -          | 27.70       | 7.03 | 674                          | 16                            |
| 7   | 18.94      | -          | 28.40       | 7.11 | 682                          | 15                            |
**APPENDIX C – ANALYTICAL DATA OF COLUMN EXPERIMENTS**

**column I – 100 % sand**

<table>
<thead>
<tr>
<th>position</th>
<th>PCE [mg/l]</th>
<th>TCE [mg/l]</th>
<th>cDCE [mg/l]</th>
<th>pH</th>
<th>dissolved oxygen [mg/l]</th>
<th>electric conductivity [μS/cm]</th>
<th>chloride conc. [mg/l]</th>
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<td>Start: 14.07.2000 – deionised water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.07.2000 – groundwater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>day 2, 26.07.2000, 42 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>2.77</td>
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<td>-</td>
<td>511</td>
<td>25</td>
</tr>
<tr>
<td>10 cm</td>
<td>&lt; 0,02 ?</td>
<td>&lt; 0,02 ?</td>
<td>24.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>20 cm</td>
<td>&lt; 0,02</td>
<td>&lt; 0,02</td>
<td>24.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>40 cm</td>
<td>&lt; 0,02 ?</td>
<td>&lt; 0,02</td>
<td>24.56</td>
<td>-</td>
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Contaminant concentrations marked with “?” were close to the detection limit, “-” marks measurements which were not taken.
column II – 25 % CMS and 75 % sand

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<td>Source Water</td>
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| Day 26, 19.08.2000, 622 h |          |              | 19.93 | < 0.02 | 27.70 | 7.03 | 3.07 | 674 | 16 |

*No samples taken due to disturbed flow (no flow)*

| Day 28, 21.08.2000, 666 h |          |              | 18.94 | < 0.02 | 28.40 | 7.11 | 3.26 | 682 | 15 |

*No samples taken due to disturbed flow (no flow)*

| Day 29, 22.08.2000, 691 h |          |              | 18.94 | < 0.02 | 28.40 | 7.11 | 3.26 | 682 | 15 |
| 10 cm       |          |              | 4.16  | < 0.02 | 24.00 | 10.50 | 0.37 | 691 | 19 |
| 20 cm       |          |              | < 0.02| < 0.02 | 18.26 | 11.09 | 0.82 | 753 | 23 |
| Outlet      |          |              | < 0.02| < 0.02 | < 0.02| 11.17 | -   | 824 | 26 |

*Sample port cloaked*

| Day 30, 23.08.2000, 715 h |          |              | 18.94 | < 0.02 | 28.40 | 7.11 | 3.26 | 682 | 15 |
| 10 cm       |          |              |       |        |       |      |    |    |
| 20 cm       |          |              |       |        |       |      |    |    |
| Outlet      |          |              |       |        |       |      |    |    |

*Analyses not reliable, results excluded*

Contaminant concentrations marked with “?” were close to the detection limit, “-” marks measurements which were not taken.