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Use of in situ chemical oxidation with permanganate in PCE-contaminated clayey till with sand lenses

Hønning, Jirij; Bjerg, Poul Løgstrup; Broholm, Mette Martina

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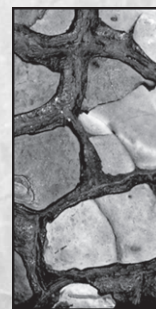
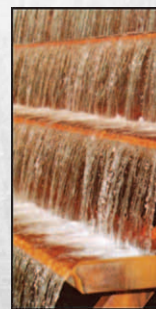
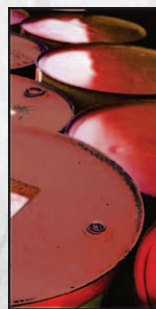
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Use of *in situ* chemical oxidation with permanganate in PCE-contaminated clayey till with sand lenses

Jirij Hønning

INSTITUTE OF ENVIRONMENT & RESOURCES



**Use of *in situ* chemical oxidation with
permanganate in PCE-contaminated
clayey till with sand lenses**

Jirij Hønning

Ph.D. Thesis
May 2007

Institute of Environment & Resources
Technical University of Denmark

***Use of in situ chemical oxidation with permanganate in
PCE-contaminated clayey till with sand lenses***

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TABLE OF CONTENTS

Preface	iii
Acknowledgements	v
Abstract	vii
Dansk sammenfatning	x
1. Introduction	1
2. Characteristics of subsurface materials	3
2.1. Classification of subsurface materials	3
2.2. Sedimentary organic matter	4
2.3. Inorganic components	6
3. Distribution and fate of PCE	9
3.1. Use of PCE in dry-cleaning industry	9
3.2. Physical-chemical properties of PCE	9
3.3. Subsurface migration of PCE	10
3.4. Fate of PCE in the subsurface	11
4. <i>In situ</i> remediation technologies for chlorinated solvents	15
4.1. Overview of remediation technologies	15
4.2. Physical remediation technologies	15
4.3. Chemical remediation technologies	17
4.4. Biological remediation technologies	18
5. <i>In situ</i> chemical oxidation for site remediation	19
5.1. Overview of oxidants	19
5.2. Ozone	19
5.3. Hydrogen peroxide/Fenton's reagent	20
5.4. Persulfate	22
5.5. Permanganate	23
5.6. Choosing an oxidant	24

6. Reaction between MnO_4^- and the sediment	25
6.1 Natural oxidant demand	25
6.2 Reaction kinetics	27
6.3 Effect of sedimentary organic matter on NOD	28
6.4 Effect of inorganic components on NOD	30
6.5 Diffusion of MnO_4^- in low permeable sediments	31
6.6 Geochemical conditions after chemical oxidation	33
7. Oxidation of chlorinated solvents using MnO_4^-	35
7.1 Reaction mechanisms	35
7.2 Oxidation of chlorinated solvents present as DNAPL	35
7.3 Oxidation of dissolved chlorinated solvents	38
7.4 Oxidation of chlorinated solvents in low permeable media	41
8. Conclusions and perspectives	43
9. References	47
10. Appendices	61

Preface

This thesis is based on research done for a PhD project undertaken from 2003 to 2007 at the Institute of Environment & Resources, Technical University of Denmark. The primary supervisor was Professor Poul L. Bjerg and co-supervisor was Associate Research Professor Mette M. Broholm, Institute of Environment & Resources, Technical University of Denmark. The project was funded by the Technical University of Denmark, the Danish Environmental Protection Agency and RECETO (Research School of Environmental Chemistry and Ecotoxicology).

As part of my PhD project I have conducted field and laboratory experiments, participated in three international conferences, visited four universities in North-America, been a member of a project group on one project for the Danish EPA, participated in several Danish meetings and contributed to Danish popular journals.

The thesis is composed of a summary of the subject “Use of *in situ* chemical oxidation with permanganate in PCE-contaminated clayey till with sand lenses” as well as 3 journal papers (1 accepted for publication, 1 submitted and one manuscript). The in-text references and the titles of the papers are:

(**I**, Hønning et al., 2007a; **II**, Hønning et al., 2007b; **III**, Hønning et al., 2007c)

I Hønning, J., Broholm, M.M., Bjerg, P.L. Quantification of potassium permanganate consumption and PCE oxidation in subsurface materials. *Journal of Contaminant Hydrology*, Vol. 90, pp. 221-239.

II Hønning, J., Broholm, M.M., Bjerg, P.L. The role of diffusion in chemical oxidation of PCE-contaminated clayey till with interbedded sand lenses. *Submitted manuscript*.

III Hønning, J., Koch, C.B., Bjerg, P.L. The role of Fe(II) in layer silicates on the consumption of MnO_4^- by subsurface materials during chemical oxidation. *Manuscript*.

The papers are not included in this www-version but can be obtained from the Library at the Institute of Environment & Resources, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Kgs. Lyngby (library@er.dtu.dk).

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Jirij Hønning
April 2007

Abstract

This thesis is composed of a summary of the subject “Use of *in situ* chemical oxidation with permanganate in PCE-contaminated clayey till with sand lenses” and three journal papers describing the work undertaken for this Ph.D. project.

Chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE) have been widely used in the industry because of their low flammability and reactivity, and their ability to quickly and efficiently dissolve a wide range of organic substances. PCE is most commonly known for its use in the dry-cleaning industry, whereas TCE primarily has been used as a degreasing solvent. Due to their widespread use, they are commonly detected groundwater contaminants. The two contaminants have been detected in groundwater in more than 50% of Superfund sites in USA and found in more than 20% of all sites with groundwater pollution in Denmark, with many of these sites being dry cleaning facilities. As contamination from dry cleaning facilities is a focus area in Denmark, PCE has been the contaminant of interest in this thesis.

The large extent of groundwater contamination with these compounds has led to use of various innovative remediation technologies. *In situ* chemical oxidation (ISCO) with MnO_4^- has been suggested as an innovative technology for remediation of sites contaminated with chlorinated solvents, especially at sites with sandy aquifer sediments. The experience with applications of ISCO in low permeable media is limited as is the knowledge of the governing processes. This makes it difficult to predict how effective ISCO with MnO_4^- will be. Therefore, field investigations and experimental work are essential to understand the relative importance of the transport and oxidation processes.

ISCO performance may be impaired by consumption of MnO_4^- from reaction with a variety of non-target sedimentary reductants such as organic matter and/or inorganic species. The consumption of MnO_4^- by the sedimentary reductants is referred to as the natural oxidant demand (NOD) and is expressed as the mass of oxidant consumed per mass of dry solid. Both organic and inorganic species in the subsurface sediment contribute to the NOD, where organic carbon is found to be the primary reactive species with regards to the total MnO_4^- consumption in the reaction with the sediment.

The experimental work in this thesis demonstrated that the sediment does not act as an instantaneous sink for MnO_4^- . The consumption of MnO_4^- by reaction with the sedimentary reductants is the result of several parallel reactions, during which the reaction between PCE and MnO_4^- also takes place. The long term consumption of MnO_4^- and oxidation of PCE can not be described by a single rate constant. However, a first order reaction is observed in the first hours of contact. Short term first order rate constants for consumption of MnO_4^- and oxidation of PCE are $0.05\text{-}0.5\text{ hours}^{-1}$ and 0.5-

4.5 hours⁻¹, respectively. Application of low MnO₄⁻ concentrations was found to oxidize PCE even though MnO₄⁻ was consumed quickly by reaction with the sediment. This was due to faster reaction rates for the oxidation of PCE and because the NOD does not need to be met fully before PCE is oxidized. The high oxidant demand exerted by the sediment compared to the oxidant demand exerted by dissolved PCE showed that dissolved PCE in concentrations up to 100 mg/l in the investigated sediments is not a significant factor in the consumption of MnO₄⁻.

The total MnO₄⁻ consumption increases with a higher initial MnO₄⁻ concentration for all sediment types, implying that a fixed NOD value can not be assigned to any sediment. In quantifying the NOD, laboratory scale batch and column experiments should always be conducted with relevant MnO₄⁻ concentrations in order to quantify the MnO₄⁻ consumption in soil/water systems, especially in silty and clayey sediments which exert a high oxidant demand.

The experimental work in this thesis has underlined the necessity of shifting the focus from the contaminant oxidant demand to the contribution of the sedimentary reductants, when designing field scale remediation of sediments contaminated with chlorinated solvents. Typical levels for the NOD in Danish subsurface materials have been established as part of this thesis. The NOD for sandy aquifer sediments are 0.5-2 g MnO₄⁻/kg dw, 1-8 g MnO₄⁻/kg dw for sandy till and 5-20 g MnO₄⁻/kg dw for clayey till. One of the challenges for application in low permeable media in this aspect is the diffusion process. Even though diffusion of MnO₄⁻ into low permeable media has been shown to take place, the rate of oxidant loss to NOD is large compared to the rate of diffusion of MnO₄⁻ into the clay, which retards the extent of oxidant penetration. This decreases the amount of oxidant available to react with the contaminants impairing the ISCO performance as NOD competes with the target contaminants for MnO₄⁻.

In general, the literature reviewed and the experiments conducted suggest that ISCO using MnO₄⁻ is a feasible remediation technology in low permeable media, such as clayey till. Successful application of ISCO requires good contact between contaminant and oxidant, which can be a challenge in low permeable media. To make ISCO more effective the focus should be on optimizing the contact between MnO₄⁻ and PCE. This could be done by using an iterative oxidant loading approach with a low oxidant dose MnO₄⁻, giving PCE time to diffuse out from the low permeable media before being treated. Fracturing could also be used as a tool for shortening the distance between sand lenses and fractures, thereby minimizing the diffusion distance required. However, successful remediation can be difficult to achieve with a single remediation technology. Hence the advantages and prospects of using chemical oxidation as the first step in a treatment train should be investigated by further research.

Dansk sammenfatning

Denne afhandling består af en sammenfatning af emnet “Anvendelsen af *in situ* kemisk oxidation med permanganat i PCE-forurenede moræner med sandlinser” samt tre artikler der beskriver det udførte arbejde i dette ph.d.-projekt.

Klorerede stoffer som perklorethen (PCE) og triklorethen (TCE) har været benyttet i større omfang i industrien grundet deres lave antændelighed og reaktivitet samt deres evne til hurtigt og effektivt at opløse en bred vifte af organiske stoffer. PCE er primært kendt for sit omfattende brug ved rensning af tøj, hvorimod TCE primært er benyttet som affedningsmiddel. På grund af den omfattende brug er klorerede stoffer ofte fundet i forurenede grundvand. De to stoffer er fundet i mere end 50% af 'Superfund sites' i USA samt observeret i over 20% af alle danske lokaliteter med grundvandsforurening, hvor en stor del af de danske lokaliteter er renserigrunde. PCE har været undersøgt nærmere i dette projekt, grundet den store fokus på forurening fra renserier i Danmark.

Den omfattende forurening med disse stoffer har ledt til forsøg med forskellige nye oprensningsteknologier. *In situ* kemisk oxidation (ISCO) med MnO_4^- er blevet foreslået som en ny oprensningsteknologi til oprensning af lokaliteter forurenede med klorerede stoffer, især på lokaliteter med sandede akvifer sediment. Erfaringen med anvendelsen af ISCO i lavpermeable aflejringer ligesom kendskabet til de fremherskende processer er begrænset. Dette gør det vanskeligt at beregne effektiviteten af oxidation med MnO_4^- . Derfor er det vigtigt at foretage både feltundersøgelser og laboratorieeksperimenter for at forstå den relative betydning af transport og oxidationsprocesserne.

Udbyttet af ISCO kan blive hæmmet af, at stoffer, der er naturligt forekommende i sedimentet såsom organisk stof og/eller uorganiske stoffer reagerer med og forbruger MnO_4^- . Stoffernes forbrug af MnO_4^- betegnes som det naturlige oxidant forbrug (NOD) og udtrykkes som massen af forbrugt oxidationsmiddel per masse tørstof. Både organiske og uorganiske stoffer i sedimentet bidrager til NOD, hvor organisk kulstof kan betragtes som værende den primære reaktive komponent med hensyn til forbruget af MnO_4^- i reaktionen med sedimentet.

Forsøgsarbejdet i denne afhandling demonstrerede at sedimentet ikke forbruger MnO_4^- øjeblikkeligt. Forbruget af MnO_4^- i reaktionen med de reducerede stoffer i sedimentet er resultatet af flere parallelle reaktioner. Forbruget af MnO_4^- og oxidationen af PCE kan på lang sigt ikke beskrives med en enkel rate konstant. Imidlertid er der observeret en første ordens reaktion for de første timer, hvor første ordens reaktions raterne for forbruget af MnO_4^- og for oxidationen af PCE er henholdsvis $0,05 - 0,5 \text{ timer}^{-1}$ og $0,5 - 4,5 \text{ timer}^{-1}$. MnO_4^- i lavere koncentrationer har vist sig at kunne oxidere PCE selv om MnO_4^- er blevet hurtigt forbrugt i reaktionen med sedimentet. Dette skyldes de hurtigere

reaktionsrater for oxidationen af PCE samt at NOD ikke skal opfyldes før PCE oxideres. Det høje NOD i sedimentet sammenlignet med forbruget af oxidationsmiddel fra den opløste PCE viste, at opløst PCE i koncentrationer på op til 100 mg/l i de undersøgte sedimentter ikke er en signifikant faktor i forbruget af MnO_4^- .

Det totale forbrug af MnO_4^- stiger for samtlige typer sedimentter ved højere startkoncentrationer af MnO_4^- . Dette indikerer at der ikke kan fastslås en fast NOD værdi for noget sediment. Laboratorieskala batch- og kolonneforsøg bør altid udføres med relevante MnO_4^- koncentrationer med henblik på at beregne NOD og på at kvantificere forbruget i jord/vand systemer. Dette er især relevant i silt- og lerholdige sedimentter med et højt oxidantforbrug.

Forsøgsarbejdet i denne afhandling har understreget behovet for at skifte fokus fra forureningsstoffet til de reducerede stoffer i sedimentet idet der skal tages højde for NOD i designet af oprensningen i sedimentter forurenede med klorerede stoffer. I denne afhandling er det typiske niveau for NOD i danske sedimentter blevet fastslået. NOD i sandede akvifer sedimentter er 1,5–2 g MnO_4^- /kg tørstof (ts), 1–8 g MnO_4^- /kg ts i sandet moræneler og 5–20 g MnO_4^- /kg ts i moræneler. En af udfordringerne for anvendelsen i lavpermeable aflejringer, er problematikken omkring diffusionsprocessen. Selv om diffusion af MnO_4^- ind i lavpermeable aflejringer har vist sig at finde sted, er tabet af MnO_4^- til NOD høj sammenlignet med raten af diffusion af MnO_4^- ind i ler, hvilket sinker omfanget af oxidationsmiddel der trænger ind i leret. Dette nedbringer omfanget af oxidationsmiddel til rådighed for reaktionen med forureningen og hæmmer udbyttet af ISCO idet NOD konkurrerer med forureningsstoffet om MnO_4^- .

Generelt antyder både den anvendte litteratur og de udførte eksperimenter, at ISCO med MnO_4^- er en brugbar afværgeteknologi i lavpermeable aflejringer såsom moræneler. Fuldt udbytte af ISCO kræver imidlertid god kontakt mellem forureningsstoffet og oxidationsmidlet. En god kontakt mellem oxidationsmiddel og forureningsstof er nødvendig for en succesrig anvendelse af ISCO, hvilket kan være en udfordring i lavpermeable aflejringer. For at effektivisere ISCO mere effektiv bør der fokuseres mere på at optimere kontakten mellem MnO_4^- og PCE. Dette kan for eksempel gøres ved at anvende en lave koncentrationer af MnO_4^- i gentagne doseringer, hvorved PCE får tid til at diffundere ud fra det lavpermeable sediment inden det behandles igen. Man kan også benytte sig af frakturering for at afkorte distancen mellem sandlinserne og sprækkerne og derved minimere diffusionsafstanden. Imidlertid kan en succesrig oprensning være svær at opnå ved kun at anvende en enkel oprensningsteknologi. I den forbindelse bør fordele og muligheder ved at anvende kemisk oxidation som første trin i en sekventiel oprensning undersøges videre.

1. Introduction

Groundwater contamination by chlorinated solvents, particularly tetrachloroethene (PCE) and trichloroethene (TCE) is widespread in the United States (USEPA, 2004a; Moran et al., 2007) as well as in Denmark (Miljøstyrelsen, 1996; Københavns Amt, 2006). TCE is a widely used degreasing solvent, whereas PCE is most commonly known for its use in the dry-cleaning industry (Doherty, 2000a and 2000b). The two contaminants have been detected in groundwater in more than 50% of Superfund sites in USA (USEPA, 2004a) and observed in more than 20% of all registered sites with groundwater pollution in Denmark, with many of them being dry cleaning facilities (Miljøstyrelsen, 2006). As contamination from dry cleaning facilities is a focus area in Denmark (Miljøstyrelsen, 2006), PCE will be the contaminant of interest in this thesis.

PCE is characterized as a dense non-aqueous phase liquid (DNAPL), which will migrate into the subsurface in an unpredictable pattern (Pankow and Cherry, 1996). The migration and depth of penetration are mainly governed by the size of the spill and the geological settings. The downwards migration of PCE will often leave behind zones of residual PCE (Illangasekare et al., 1995; Bedient et al., 1999) where long term diffusion of DNAPL compounds into low permeable media can generate a zone of contaminant concentrations that may act as a long term source of groundwater contamination following the removal or disappearance of the original DNAPL mass (Hood et al. 2002; Chapman and Parker, 2005; McGuire et al., 2006).

Earlier remediation approaches for groundwater contaminated with chlorinated solvents have included pump-and-treat applications (USEPA, 1997). However this is more a containment method as little or no subsequent reduction of the contamination takes place (Pankow and Cherry, 1996). The need for alternative ways of remediating the source zone have led to an increase in the use of *in situ* technologies in both soil and groundwater over the last 25 years (USEPA, 1997; USEPA, 2004a) with *in situ* chemical oxidation (ISCO) emerging as a useful remediation technology (SCRD, 2004).

ISCO is potentially applicable on a wide range of contaminant concentrations from source area mass reduction to intercepting of plumes to removing mobile contaminants (Siegrist et al., 2001) and can be applied with different oxidants (ozone, hydrogen peroxide, persulfate and permanganate) depending on the type of pollution and the type of sediment treated. The oxidants working through indirect oxidation (ozone, Fenton's reagent, activated persulfate) have a high reaction rate and are primarily distributed through advection. Permanganate (MnO_4^-) on the other hand is more stable, easy to handle and applicable over a wide pH range. A large part of the Danish subsurface consists of carbonated clayey till where MnO_4^- is assessed to be the most applicable oxidant for ISCO and therefore used as the oxidant of interest in this thesis.

ISCO with MnO_4^- has been proven effective for the oxidation of chlorinated solvents as demonstrated for sandy sediments in laboratory column studies (Schroth et al., 2001; Huang et al., 2002), in laboratory 2D box studies (Conrad et al., 2002; MacKinnon and Thomson, 2002) as well as in the field (Nelson et al., 2001; McGuire et al., 2006). However, the knowledge with applications in low permeable media such as clayey till where diffusion is an important transport mechanism is limited.

Due to its stability in the subsurface MnO_4^- is able to diffuse into low permeable media and react with the target contaminant (SCRD, 2004; USEPA, 2006). However, the matrix diffusion of MnO_4^- may be limited the consumption of MnO_4^- from reaction with a variety of non-target sedimentary reductants such as reduced species associated with subsurface material (e.g., ferrous, manganous, sulfidic species) and/or organic matter. The consumption of MnO_4^- by reaction with the sedimentary reductants is referred to as the natural oxidant demand (NOD) and is expressed as the mass of oxidant consumed per mass of dry solid (Mumford et al., 2005).

As successful application of ISCO requires good contact between contaminant and oxidant, the ISCO performance may be impaired by the NOD as it competes with the target contaminants for MnO_4^- (Hood et al., 2002; MacKinnon and Thomson, 2002), thereby decreasing the amount of oxidant available to react with the contaminants. NOD should therefore be taken into consideration as a design criterion when evaluating ISCO at potential remediation sites.

The aim of this thesis was to understand the transport and oxidation processes during chemical oxidation and to evaluate the applicability of ISCO with MnO_4^- for the removal of PCE in clayey till with sand lenses by: (1) Determining the rates of PCE oxidation and MnO_4^- consumption in a soil/water system, (2) Evaluating the competition between the oxidation of PCE and the sedimentary reductants for the consumption of MnO_4^- , (3) Quantifying the consumption of MnO_4^- by reaction with the sedimentary reductants, (4) Determining and quantifying the relative importance of organic and inorganic sediment constituents on the consumption of MnO_4^- and (5) Evaluating the role of diffusion of PCE and MnO_4^- in low permeable media from laboratory experiments and field observations.

The experimental work in this thesis included field observations after a full scale ISCO at a dry cleaner site contaminated with PCE where core samples were obtained and experimental work in the laboratory, including (A) Batch experiments with sandy and clayey subsurface sediments exposed to various concentrations of PCE and MnO_4^- and (B) Two-dimensional (2D) box experiments with MnO_4^- simulating the flow in a sand lens and the diffusion into a clay matrix.

2. Characteristics of subsurface materials

To understand the reduction capacity of the sediment, knowledge of the amount, type and reactivity of sedimentary reductants in the subsurface is crucial. This chapter will give the necessary background for understanding the chemical reactivity of sediments and thereby the exerted impact on the fate and behavior of substances in the subsurface.

2.1. Classification of subsurface materials

Subsurface materials can generally be classified in three broad types of geologic media: (1) porous media or granular media, which mainly consists of sand and gravel; (2) fractured porous media, where fractured silty and clayey deposits as well as fractured sedimentary rocks are common examples, and (3) fractured non-porous media, which mainly is found in fractured crystalline rocks (Pankow and Cherry, 1996). Throughout Denmark, the unconsolidated surface is composed almost entirely of glacial sediments (Ernstsen, 1998). The Danish subsurface mainly consists of the first two types of geologic media, where the porous media is commonly found in the unconsolidated surface in the western part of Denmark as well as in sand and gravel aquifers. The fractured porous media consists mainly of clayey till found in the eastern part of Denmark (**Figure 1**).

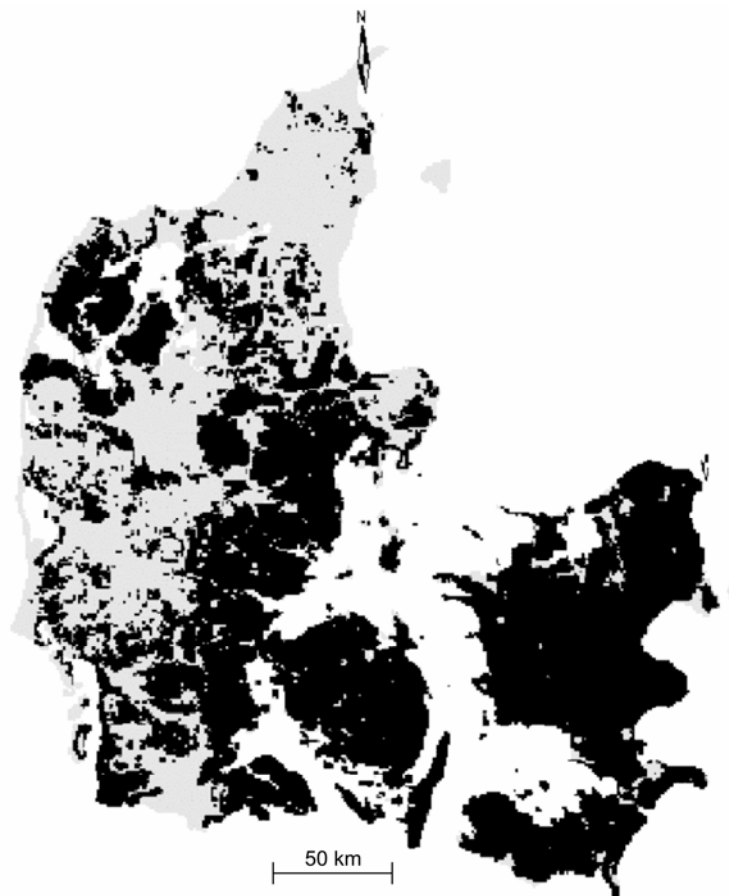


Figure 1. Regional extent of deposits with > 15 w% clay. From Nilsson et al. (2000)

The solid matter making up the porous media and fractured porous media can be identified in two major components, that is the sedimentary organic matter (SOM) and the inorganic or mineral components, which typically represent more than 90% of the solid matter (Sposito, 1989; Brady and Weil, 1996). Mineral products of weathering, collectively referred to as secondary minerals, are typically clay sized and contribute substantially, along with decomposed SOM (humus), to the chemical reactivity of the sediment (McBride, 1994; Brady and Weil, 1996; Essington, 2004). Consequently, the focus will be on the structure and reactivity of clay minerals and humus.

2.2. Sedimentary organic matter

Sedimentary organic matter consists generally of two groups: (a) original plant tissue and its partially decomposed equivalents and (b) the humus, which is the more reactive part of SOM. The bulk of SOM consists of humus (Pignatello, 1998; Weber et al., 2001; Cuypers et al., 2002). Humus is not a specific compound nor does it have a single structural markup. It is comprised of biomolecules, including carbohydrates which may account for up to one-half of the organic carbon in soils and organic acids containing the reactive carboxylic group $-\text{COOH}$ (Sposito, 1989; Dixon and Weed, 1989), as well as the humic substances, which can be separated into three classes; fulvic acid, humic acid and humin (Sposito, 1989; McBride, 1994; Brady and Weil, 1996).

A conceptual model has been proposed in which SOM is described as being comprised by highly amorphous (soft, rubbery) and relatively condensed (hard, glossy) domains (Weber et al., 1999; LeBoeuf and Weber., 2000; Young and LeBoeuf, 2000; Cuypers et al., 2002). Cuypers et al. (2000) showed that amorphous SOM was oxidized by reaction with persulfate, whereas the condensed SOM remained unchanged. This demonstrated that some part of the SOM may be chemically refractory towards oxidation. The availability of SOM may also be decreased by the sorption to mineral surfaces (Mayer, 1994; Salmon et al., 2000). Sorption of SOM can take place on the reactive surface of the clay minerals or oxide particles, with a positive correlation between resistant SOM and amount of total iron oxides and clay content (Eusterheus et al., 2005; Kahle et al., 2004; Tombácz et al., 2004; Mikutta et al., 2005). A study by Eusterheus et al. (2005) indicated that only a small part of the SOM was protected by sorption to clay minerals, where the sorption to iron oxides was more important. The content of SOM is up to 5% by weight in a topsoil, less in the clayey subsurface and typically very low in aquifer sediments (Pedersen, 1992; Brady and Weil, 1996, Hartog et al., 2004).

A general model compound representing SOM is proposed with the structural formula, $\text{C}_7\text{H}_8\text{O}_4$, where organic carbon is considered a principal reactant in SOM with the oxidation state of C^0 (Pedersen, 1992). The OC content in the model compound is 54% by weight, which is similar to values from Brady and Weil (1996) where the OC content

in SOM is reported to be between 45% and 58%. Other studies have suggested a simple carbohydrate, CH₂O as an expression for SOM, where the average oxidation state of carbon is C⁰ (Essington, 2004, Mumford et al., 2005). Using the model compound, C₇H₈O₄, the contribution of SOM to oxidant demand can be quantified leading to the assumption that sediments with a higher content of SOM and thereby higher OC content can exert a higher oxidant demand.

Quantifying the SOM content of sandy and clayey subsurface sediments has also formed a part of this thesis (I, Hønning et al., 2007a). The sandy aquifer sediments used in this thesis were samples from (Christensen et al., 1996) where the OC content in Danish sandy aquifer sediments was determined in the interval 0.01%-0.5%. These values were similar to OC values for sandy aquifer sediments from both Danish studies (Pedersen, 1992; Heron et al., 1997; Clausen et al., 2002) and international studies (Barcelona and Holm, 1991; Hartog et al., 2004; Hrapovic et al., 2005).

A positive relationship is found between the specific surface area and the OC content in aquifer sediments (Hartog, 2003). The general trend found in Hartog (2003) compares favorably with data for clayey sediments (Allen-King, 1996; Kennedy et al., 2000), indicating that clayey sediments will have higher OC content. This was shown in Clausen et al. (2002) and Hønning et al. (I, 2007a) for Danish aquifer sediments and clayey till, where the OC content was higher in the clayey sediments with a range of 0.2%-0.4% OC on oxidized clayey till and a range of 0.4%-1.7% OC in reduced clayey till. However, the results also revealed a large variation in the OC content.

Even though SOM is considered the principal sedimentary reductant, the relative contribution of SOM to oxidant consumption during sediment oxidation depends on the reactivity of other reductants present (Hartog, 2003). This is illustrated by the oxidized and reduced clayey till from two sites shown in Table 1, which formed part of this thesis (I, Hønning et al., 2007a). Measurements of chemical oxidant demand (COD) of the four sediments suggested that even though the OC content in both the oxidized and reduced clayey till is similar, there is still a distinct higher reactivity in the Hvidovre sediment. This could be due to higher availability of SOM but more probably due to higher reactivity from the inorganic species, which the Fe_{total} content could indicate.

Table 1. Sediment characteristics and geological description for oxidized and reduced clayey till from 2 sites. Modified from Hønning et al. (I, 2007a).

	Unit	Dalumvej		Hvidovre	
		Oxidized	Reduced	Oxidized	Reduced
Redox state		Oxidized	Reduced	Oxidized	Reduced
Lithology		Clayey till	Clayey till	Clayey till	Clayey till
OC content	%	0.21	0.41	0.21	0.41
COD	g O ₂ /kg	3.9	6.0	5.5	13.7
Fe _{total} content	%	0.19	0.18	1.03	1.26

2.3. Inorganic components

The inorganic components or minerals are defined as naturally occurring homogeneous solids with a definite chemical composition and crystalline structure (Dixon and Weed, 1989). However, only some of them are important with regards to the reactivity of the minerals and their interaction with the sediment. The major minerals can be divided into 4 groups: (a) Carbonates, (b) Sulfides, (c) Oxides and Hydroxides, and (d) Silicates (Dixon and Weed, 1989). A majority of the discussion of minerals is devoted to the silicates, the most common and abundant class of minerals, and especially the clay minerals, which are an important reactive group within the phyllosilicates.

Carbonate minerals are usually stable and their presence is extensive in the Danish fractured porous media, such as clayey till (Ernstsen, 1998), where they act as a strong buffer. This has an impact on the choice of oxidant for application of chemical oxidation, which will be discussed in chapter 4. The most common mineral of the sulfide group, pyrite can be formed under strongly reducing conditions. It is unstable in an oxidizing environment and can exert a high oxidant demand when present. Pyrite also produces high amounts of acid when it weathers (Dixon and Weed, 1989). Oxides and hydroxides are generally associated with the latter stages of silicate weathering. They are primarily present as colloid precipitants between or on the soil particles (Brady and Weil, 1996). Unlike layer silicate clays, the oxides have a very low cation exchange capacity even with large surface areas. However, the surfaces have considerable capacity to adsorb metal ions as well as inorganic and organic anions (McBride, 1994).

Silicate minerals dominate the soil mineral phase; with the primary minerals, such as quartz and feldspars dominant in the coarse size fraction or the sand ($>50 \mu\text{m}$) and in the silt fraction (between $2 \mu\text{m}$ - $50 \mu\text{m}$). Quartz is the most common silica with no weak structural points. Consequently, quartz is persistent in sediments and not amenable to react (McBride, 1994). Thus, indicating that sandy aquifer sediments, which is primarily made up of quartz and feldspars will have a low reactivity and a low oxidant demand.

The secondary minerals formed by the weathering of less resistant minerals are also present in the silt fraction, but they are dominant in the very fine clay fraction ($< 2 \mu\text{m}$) where they are responsible for the reactivity of soils (McBride, 1994; Brady and Weil, 1996; Essington, 2004). The original structure and chemical composition of the secondary minerals have changed through weathering and consists mainly of layered silicates (phyllosilicates), with the clay minerals being an important group (Pedersen, 1992). The clay minerals are chemically and structurally analogous to other phyllosilicates but contain varying amounts of water and allow more substitution of their cations. They are often the last to chemically breakdown in weathering processes and thus constitute a significant amount of soils and fine grained sedimentary rocks.

A positive correlation between the reductive capacity of clay minerals and the Fe(II) content could indicate the importance of Fe(II) as a reactive compound (Nzengungu et al., 2001; Lee and Batchelor, 2003). However, not all Fe(II) present is available for reaction, which is mainly based on the type of Fe(II) species. Three types of Fe(II) species in fundamentally different chemical environments may be present simultaneously, i.e. structural Fe(II), Fe(II) complexed by surface hydroxyl groups at edge surfaces, and Fe(II) bound by ion exchange at basal siloxane surfaces (Murayed et al., 2000; Hofstetter et al., 2003). Structural bound and complexed Fe(II) have been found to be very reactive and relevant as sedimentary reductants (Ernstsen et al., 1998; Hofstetter et al., 2003), thereby making it interesting to examine the structural and mineralogical composition of the clay minerals.

Clay minerals are usually classified into three layer types (1:1 layer, 2:1 layer and 2:1 layer with hydroxide inter layer), distinguished by the number of tetrahedral and octahedral sheets combined, and further into five groups (kaolinite, smectite, vermiculite, illite and chlorite), differentiated by the cation substitutions that occur (Sposito, 1989; McBride, 1994; Brady and Weil, 1996).

The 1:1 layer type with one tetrahedral and octahedral sheet is represented by the kaolinite group. Kaolinite has no significant cation substitution taking place (McBride, 1994) and does not contain structural bound Fe(II). The 2:1 layer type has two tetrahedral sheets that sandwich an octahedral sheet and are represented by three groups (smectite, vermiculite and illite). Smectites can be rich in Fe(II) and have a relatively low layer charge, which allows it to separate to large dimensions in water, conferring unique and dramatic swelling properties to this mineral group. Vermiculites are common in the clay fraction of soils and can be Fe(II) rich. However, the structural Fe(II) is bound between the two tetrahedral sheets where it is relatively protected from reaction, which is also the case with Fe(II) in Illite. The last group is the 2:1 group with a hydroxide inter layer, represented by the chlorite group (Sposito, 1989). Fe(II) can be very rich in Fe(II) where it is more readily active compared to the other clay minerals.

The different crystalline structures make it possible to identify the clay minerals by X-ray diffraction (XRD). Hønning et al. (III, 2007c) determined the composition of the clayey tills in Table 1 by comparing the d-spacing of the common layer silicates from four diffractograms (**Figure 2**). The four diffractograms were, air-dried (RT), ethylene glycol-solvated at 60°C/2 days (EG), subsequently heated to 350°C/2 h (350) and to 550°C/2 h (550). The investigations show that the reduced parts of the two clayey till both contain illite (1.0 nm basal spacing), kaolinite (0.7 nm basal spacing), vermiculite (1.4 nm basal spacing collapsing to 1.0 nm on heating), chlorite (1.4 nm heat resistant basal spacing) and to a minor degree some smectite (1.8 nm after glycolation).

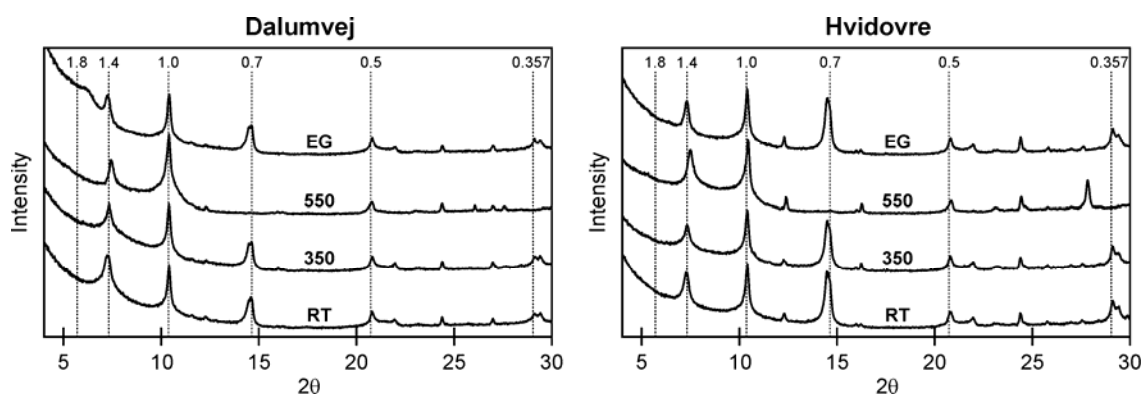


Figure 2. X-ray diffractograms for the clay fraction from the reduced clayey till from Dalumvej and Hvidovre. From Hønning et al. (III, 2007c).

The clayey tills from both sites showed none very low content of smectite with the main difference between the two sites being the higher content of chlorite in the clayey till from Hvidovre, which could explain the higher Fe content (Table 1). Because of the higher Fe content of the clay fractions in general, the speciation of Fe was investigated in these fractions using Mössbauer spectroscopy (III, Hønning et al., 2007c), which is shown in **Figure 3**. The Mössbauer spectra show a distinct higher content of Fe(II) in the clayey till from Hvidovre reflecting the higher Fe content and higher COD value (Table 1).

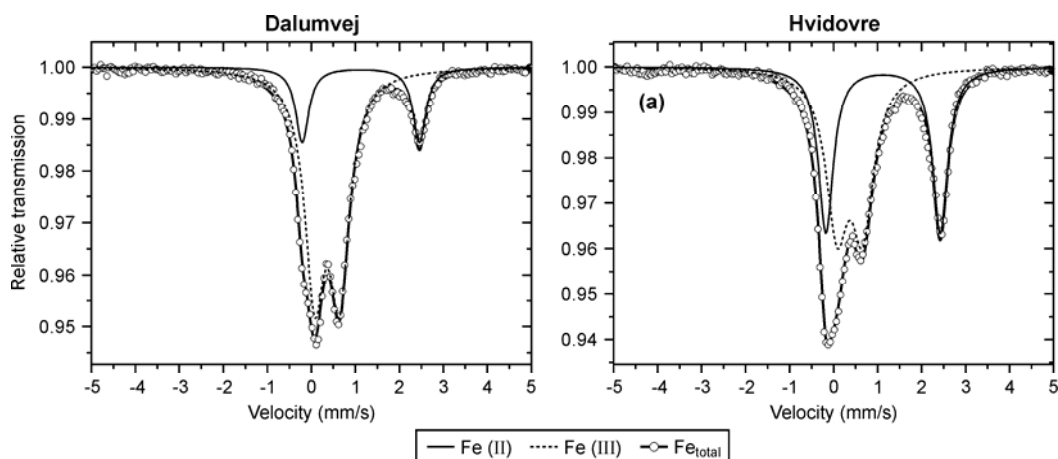


Figure 3. Mössbauer spectra measured at room temperature of the untreated clay fraction from Dalumvej and Hvidovre. Modified from Hønning et al. (III, 2007c).

Ernstsen (1998) conducted a comprehensive study of mineralogical composition of clayey tills in the eastern part of Denmark and the investigations in Hønning et al. (III, 2007c) showed that the clayey tills presented in Table 1 are representative for the clayey tills in this region, except for the low content of smectite.

3. Distribution and fate of chlorinated solvents

The distribution and fate of chlorinated solvents in fractures porous media in the subsurface will be described in this chapter. The distribution is focused on the migration processes, where the fate of the chlorinated solvents is described by the partitioning processes after cessation of flow.

3.1. Use of PCE in the dry-cleaning industry

PCE is most commonly known for its wide use in the dry-cleaning industry, where it was introduced in the late 1930s, it has been used in other industries such as metal cleaning, paint removal and the printing industry (Doherty, 2000a). The use of PCE in the United States increased heavily in the 1950s and by 1960 PCE was the dry-cleaning solvent of choice in the United States, with the dry-cleaning industry responsible for 90% of the PCE consumption (Doherty, 2000a) and around the same time the import of PCE to Denmark started (Figure 4). The use of PCE peaked in Denmark around 1970 and steadily decreased after that, primarily due to improvements in the efficiency of dry-cleaning equipment (AVJ, 2001). The use of PCE has steadily declined after 1970 due to both economic and regulatory factors and fell to 10% of the use during the peak period by the year 2000. Despite the increased regulation and huge decline, PCE remains the solvent of choice for most dry-cleaners and launderers (Moran et al., 2007).

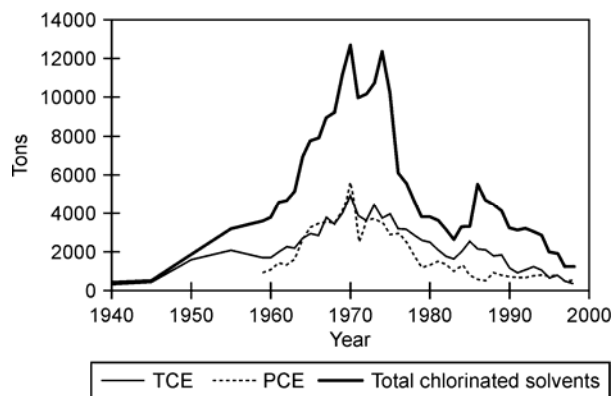


Figure 4. Import of chlorinated solvents to Denmark. Adapted from AVJ (2001).

3.2. Physical-chemical properties of PCE

The distribution and fate is governed by their physical and chemical properties as well as the geological conditions in the subsurface. PCE is a volatile compound, with a lower viscosity and a higher density than water as well as a relatively high solubility in water (Table 2). The low K_{ow} value indicates that the sorption of PCE will be limited. Thus, PCE can be characterized as a dense non-aqueous phase liquid (DNAPL) with different behavior and properties from those of dissolved contaminants.

Table 2. Physical-chemical properties of PCE at standard temperature and pressure (25°C and 101.325 kPa) unless otherwise mentioned according to MacKay et al. (1993).

Property	Unit	Value
Molar weight	g/mol	165.8
Density (20°C)	g/cm ³	1.63
Viscosity	cP	0.84 ^a
Solubility in water	mg/L	150-240
		200-240 ^b
Henry's constant, K_H^*	--	0.72 ^b
Log K_{OW}	--	2.88

^a Lide, D.R. (2002) ^b Pankow and Cherry (1996)

3.3. Subsurface migration of PCE

The migration takes place through two different processes in the fractured porous media: (1) Advective transport through either vertical and horizontal fractures or high permeable layers, driven by pressure gradients and (2) a slower diffusive transport in the soil matrix driven by concentration gradients as illustrated in **Figure 5**.

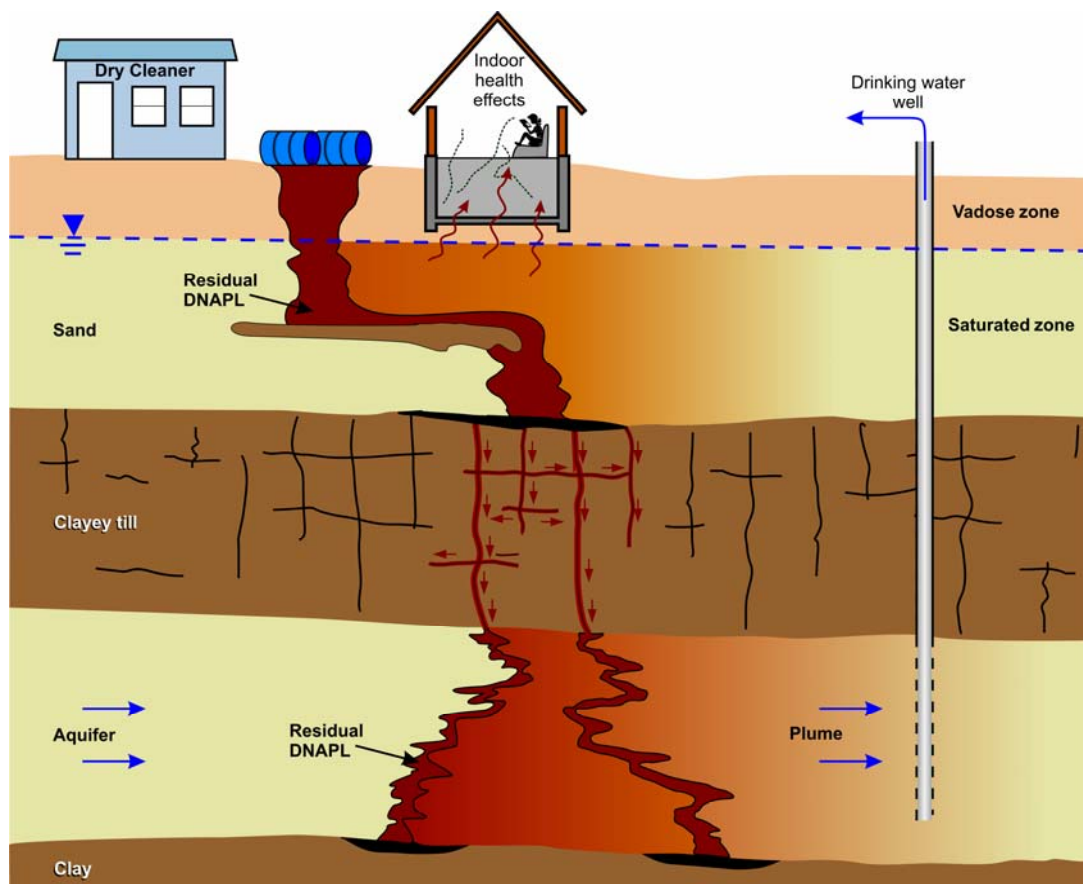


Figure 5. Routes of DNAPL migration and potential problems from contamination with chlorinated solvents.

As water commonly occupies the smaller pores, the migration will primarily take place in larger pores and fractures in the soil matrix. Minor changes in the permeability can change the migration pattern and low permeable areas will often function as barriers for the distribution, where more permeable media will permit higher flow rates (Illangasekare et al., 1995). The physical–chemical properties (Table 2) show that PCE will migrate at rates comparable to, or faster than water in a given geologic media.

PCE will migrate into the subsurface in an unpredictable pattern and with a high mobility, due to its low viscosity. With the low interfacial tension it can enter small pores and fractures in the subsurface as long as the original entry point is active, facilitating deep entry into the subsurface (Pankow and Cherry, 1996). When the supply is exhausted a zone of residual PCE is formed. Residual PCE may act as continuing source of contamination to groundwater, as it is very difficult to remove once it is trapped in individual pores (Illangasekare et al., 1995; Bedient et al., 1999). A small mass of PCE in the vadose zone can produce a vapor plume migrating horizontally and vertically through molecular diffusion. The diffusion process is important in both the horizontal and vertical direction, as the diffusion coefficient is significantly higher than in water (AVJ, 2001). In low permeable media, such as clayey till, the migration in soil air primarily takes place through fractures or zones of higher permeability.

PCE will tend to penetrate through the vadose zone into the saturated zone. (Pankow and Cherry, 1996). The migration of the DNAPL in the saturated zone is governed by the soil layering, as the migration will continue downwards until a less permeable layer is reached. At this time a pressure will build up and a horizontal migration take place until the edge of the layer is reached or the entry pressure of the layer is reached (Illangasekare et al., 1995). In the latter case, the DNAPL will pass through the layer and continue its downward movement (Pankow and Cherry, 1996). Immobile residuals in the pore spaces will be left by the migration, as in the vadose zone. Migration of dissolved PCE in the saturated zone is dependent on the contaminant water solubility and groundwater flow and takes place through advective transport following the groundwater flow. The pollution plume will migrate both vertically and horizontally down gradient of the source, due to dispersion. The extent of the plume can be retarded from sorption processes or affected by degradation.

3.4. Fate of PCE in the subsurface

After the DNAPL flow has ceased, PCE will tend to partition among the phases in the subsurface, seeking equilibrium distribution conditions. In this context four partitioning processes are of particular interest: (1) vaporization of PCE as DNAPL into air; (2) dissolution of PCE as DNAPL into water; (3) sorption of dissolved PCE from water to

solid and (4) volatilization of dissolved PCE from water into air (Pankow and Cherry, 1996). Alongside the partitioning processes, microbial and chemical (abiotic) transformation processes will influence the ultimate fate of PCE.

Vaporization is the mass transfer of PCE as a DNAPL to the gas phase. Due to the high volatility of PCE, vaporization is considered to be the most significant phase transfer mechanism in the vadose zone (Pankow and Cherry, 1996). A conceptual model of the processes involved is shown in **Figure 6**.

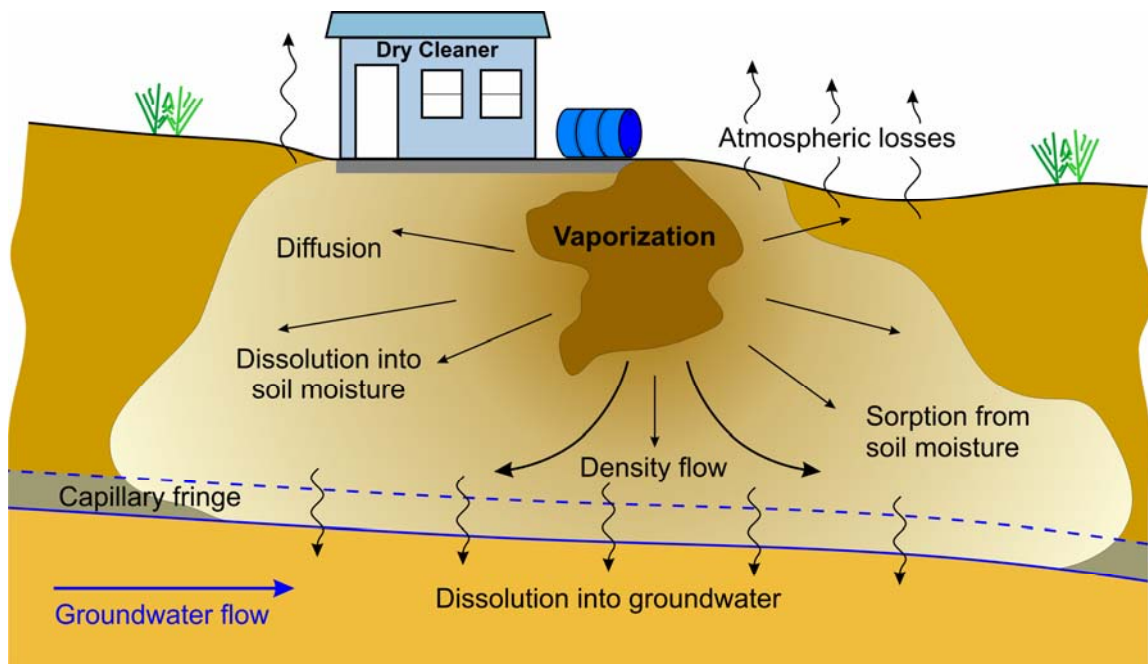


Figure 6: Conceptual model of vapor transport processes from a residual DNAPL source. Modified from Pankow and Cherry (1996).

Vaporization and vadose zone transport of PCE is facilitated by the high diffusion coefficients in the gas phase. In some cases this could cause a rapid depletion of the DNAPL phase and formation of significant vapor plumes. Partitioning into the gas phase is minimal to non-existent below the water table (Pankow and Cherry, 1996), where mass dissolution of the DNAPL is the most important phase transfer process.

The mass dissolution rate of PCE is a function of the solubility, the groundwater velocity, the mass and distribution of PCE, the pore distribution and the aqueous phase diffusion coefficient (Pankow and Cherry, 1996). With the relatively slow molecular diffusion in the aqueous phase and the advective transport it is expected that DNAPL pollution is able to contribute to a pollution plume for a great number of years.

Sorption is the uptake by soil of dissolved PCE from the aqueous phase. The movement of dissolved PCE is retarded by sorption from water to solids, thus reducing the rate of contaminant transport. However sorption can also increase the pumping required to flush the compound out of an aquifer thus affecting transformation rates (Pankow and Cherry, 1996). Sorption of PCE will primarily be associated with the SOM fraction of the soil (Bedient et al. 1999). The degree of sorption in a given circumstance depends both on the chemical properties of PCE and the nature of the aquifer solids.

Volatilization is the mass transfer of dissolved chemical from the aqueous phase to the gas phase. The high volatility of PCE is utilized in several physical remediation technologies, which will be discussed in chapter 4. In the vadose zone, mass transfer to the soil air occurs directly from the dissolved phase as well as from the DNAPL phase, where vaporization is the mass transfer from the DNAPL phase.

Abiotic and microbial transformations have the ability to remove PCE from the contaminated system, either by degrading it to other organic compounds or by mineralization to carbon dioxide and water. The extent to which any transformation may influence the fate of PCE can be strongly influenced by the conditions of the local environment. The different transformation reactions will be discussed in the next chapter under chemical and biological *in situ* remediation technologies.

4. *In situ* remediation technologies used for chlorinated solvents

The fate of chlorinated solvents through microbial and chemical transformation processes will be described in this chapter alongside with the use of physical methods for removal of the contaminant mass.

4.1. Overview of remediation technologies

Early efforts to remediate contaminated soil and groundwater in DNAPL source zones has typically focused on excavation of the contaminated soil with subsequent treatment off-site, combined with plume or source zone containment by pumping and treating contaminated groundwater (USEPA, 1997; Siegrist et al., 2001). The problem with many of the pump and treat applications is that little or no subsequent reduction of the concentration has taken place except over very long time (Pankow and Cherry, 1996), consequently pump and treat applications are used more for source zone containment.

This has led to more innovative remediation technologies being pursued and subsequently the use of *in situ* technologies in both soil and groundwater has experienced a sharp increase over the last 25 years (USEPA, 1997; USEPA, 2004a). Remediation with *in situ* technologies can be grouped in two categories based on the way they treat the contamination: (a) mass transfer and recovery by use of physical methods or (b) in-place destruction methods by use of chemical and biological methods (Pankow and Cherry, 1996; Siegrist et al., 2001). However, some of the technologies may not fit into these categorizations, but instead have multiple modes of actions.

The application of *in situ* technologies for the remediation of PCE should be considered on the basis of the type of geologic media, the treatment goals and the applicability of the technology. The treatment technologies screening matrix proposed by USEPA (2007) could be used as a tool for this. Together with the list of applied remediation technologies used at dry cleaning facilities contaminated with chlorinated solvents from the State Coalition for Remediation of Drycleaners (SCRD, 2005), this gives an overview of possible *in situ* remediation technologies to be used against contamination with chlorinated solvents (Table 3).

4.2. Physical remediation technologies

There is no net loss of the contaminant mass when applying physical methods. Instead, the contaminant mass is transferred to the vapor or dissolved phase and subsequently pumped/extracted from the source for *ex situ* treatment and/or disposal off-site by using SVE, air sparging or MPE. The phase transfer can be stimulated by increasing the temperature using thermal treatment or by applying cosolvent/surfactant soil flushing.

Table 3. Overview of *in situ* remediation technologies for chlorinated solvents.

Remediation technology		Subsurface zone	Comments
Physical	Soil vapor extraction	Vadose	Removes contaminants by extracting soil vapor
	Air Sparging	Saturated	Strips contaminants from dissolved to vapor phase
	Multiphase extraction	Vadose/Saturated	Removes contaminants by simultaneously extracting soil vapor and groundwater
	Thermal treatment	Vadose/Saturated	Increases vapor pressure and contaminant mobility
	Soil flushing	Saturated	Enhances DNAPL solubility and mobility
Chemical	Chemical oxidation	Vadose/Saturated	Strong oxidants oxidize contaminants to mineralization
	Chemical reduction	Saturated	Reduction processes promote sequential dechlorination
Biological	Aerobic degradation	Vadose/Saturated	Only lower chlorinated species are susceptible to this process
	Anaerobic degradation	Saturated	Reductive dechlorination is the principle mechanism

SVE systems utilizes the contaminant's volatility by extracting the soil vapor under vacuum, where by a flow of air through the soil causes the chlorinated solvents to volatilize and partition into the vapor phase. SVE is one of the most widely used remedial methods for removal of contamination from the vadose zone when excavation is not feasible due to the presence of physical obstructions (SCRD, 2005). SVE is often used together with air sparging in conjunction with remediation in the saturated zone.

Air sparging involves injection of air into the saturated zone to strip the contaminants from the dissolved phase and transfer it to the vapor phase (Johnson, 1998). The vapor is then vented through the vadose zone to the atmosphere or more typically SVE systems is employed to more effectively control, treat and remove the vapor plume from the vadose zone (Waduge et al., 2004). The effectiveness of both air sparging and SVE is greatly affected by the soil permeability as they are best employed in porous media and greatly inhibited in low permeable zones.

Multi Phase Extraction (MPE) is a general term used for technologies that simultaneously extract soil vapor, groundwater and a separate phase liquid (USEPA, 1999). For this reason MPE is most effective at sites where the aquifer can be depressed. Sites with low to moderate permeable soils are ideal for using MPE. Low yield aquifers may allow the water table to be drawn many feet past the capillary fringe.

Cosolvent/surfactant soil flushing is a DNAPL removal technology, with the potential to remove large quantities of DNAPL in a short period of time (SCRD, 2005). The surfactant/cosolvent solutions lower the DNAPL/water interfacial tension and decrease the capillary forces in the aquifer, thus enhancing DNAPL solubility and mobility. However, mobilization of DNAPLs may lead to uncontrolled downward migration (Conrad et al., 2002). Favorable conditions for use of soil flushing include a relatively homogeneous aquifer or residual DNAPL in the more permeable zones (SCRD, 2005).

In situ thermal heating technologies are applied in order to enhance contaminant transport in order to volatilize, mobilize, or degrade contaminants (Heron et al., 2005). Currently, three thermal treatments are applied, e.g. steam enhanced extraction (SEE), electrical resistive heating (ERH) and thermal conductive heating (TCH). SEE is best suited for moderate to high permeability zones, in which steam is injected into the source zone (Heron et al., 2005). ERH in which electrical current is passed through the contaminated zone, increasing the subsurface temperature is particularly suited to the treatment of low permeable media (Friis et al., 2006). TCH in which surface or subsurface conductive heating elements are used to create a high-temperature zone differs from the other heating methods (SEE and ERH) in that it does not rely solely on steam as a heat source or water as a conductive path (USEPA, 2004b).

4.3. Chemical remediation technologies

The two applicable chemical transformations for chlorinated solvents are oxidation and reduction (Vogel et al., 1987). The abiotic transformation is very slow under natural conditions, but it can be increased considerably by injecting or emplacing strong oxidants (Siegrist et al., 2001) or by metal-enhanced dechlorination (Zhang, 2003).

In situ Chemical Oxidation (ISCO) is a remedial process where strong oxidants are introduced into the subsurface to react with the contaminants of concern (Siegrist et al., 2001). Oxidants used to date include ozone, sodium and/or potassium permanganate, persulfate, hydroxide peroxide, and Fenton's Reagent (ITRC, 2005; USEPA, 2006). During ISCO contaminants are mineralized without producing toxic daughter products, with the destruction taking place when the oxidant is brought into contact with the contaminant. However, the principal limitation of any ISCO method comes in delivering the oxidant into physical contact with the contaminant. Another limitation is the sedimentary reductants as they will compete for the injected oxidants and thereby negatively affect the efficiency of the oxidation (Mumford et al., 2005; I, Hønning et al., 2007a). Chemical oxidation will be discussed further in chapter 5.

Remediation by chemical reduction is currently being achieved by using zero-valence iron (Fe^0) in nanoscale or granular form (Gillham and O'Hannesin, 1994; Orth and

Gillham, 1996; Lien and Zhang, 2001; Zhang, 2003). A common method used to employ Fe^0 is by use of permeable reactive barriers (O'Hannesin and Gillham, 1998; Wilkin, 2003; Jeen et al., 2006). The barriers may consist of a funnel-and-gate system designed to direct water through a treatment zone, continuous treatment walls, or wells spaced to maximize contact with the barrier material. The effective use of Fe^0 in permeable barriers can be decreased by carbonate precipitates (Jeen et al., 2006) or by the composition of the groundwater (D'Andrea et al., 2005).

4.4. Biological remediation technologies

Biological treatment of chlorinated solvents involves both aerobic and anaerobic degradation and involves the engineering of the subsurface environment to facilitate biological degradation to non-toxic end products (e.g. ethene) using native or engineered organisms (ITRC, 2002; Field and Sierra-Alvarez, 2004).

Aerobic degradation can occur by direct oxidation or cometabolically, which rarely occurs in contaminated groundwater systems, except on the edge of the contaminant plume where dissolved oxygen has not been depleted (Bradley, 2000). However only lower chlorinated compounds are susceptible to this process and PCE will therefore not be subject to aerobic degradation (Field and Sierra-Alvarez, 2004).

Anaerobic degradation of PCE can occur by either reductive dechlorination or cometabolically, where reductive dechlorination is the principle biodegradation mechanism (Vogel et al., 1987; Bradley, 2000; Major et al., 2002). Reductive dechlorination involves the sequential replacement of chlorine atoms by hydrogen atoms. Dehalospiring microorganisms use PCE as their terminal electron acceptors in metabolism and gain energy from reductive dechlorination, where hydrogen produced by fermentation often is the electron donor. However, the subsurface conditions may not be anaerobic or there is a lack of donor. The addition of electron donor, such as lactate to aid the dechlorination process and stimulate the anaerobic conditions is termed biostimulation (Freeborn et al., 2005).

At some sites, dechlorination of PCE stalls at cis-1,2-dichloroethene resulting in an accumulation of partially dechlorinated products and these sites all have in common that the microorganism *Dehalococcoides ethogenes* is not present, as this is the only microorganism able to completely dechlorinate PCE to ethane (Major et al., 2002; Field and Sierra-Alvarez, 2004). Under these circumstances microbial amendments are applied to facilitate or enhance the microbial degradation, a process referred to as bioaugmentation (Major et al., 2002). Some of the challenges in this respect are the limited transport of electron donor and microorganisms in the subsurface as well as maintaining the microbial population (Bradley, 2000).

5. *In situ* chemical oxidation for site remediation

Four different oxidants are generally considered for *in situ* chemical oxidation (ISCO) applications, where the oxidants can react directly or indirectly through the formation of free radicals. The four oxidants which will be described in this chapter are ozone, hydrogen peroxide, activated persulfate and permanganate.

5.1. Overview of oxidants

ISCO is potentially applicable on a wide range of contaminant concentrations from source area mass reduction to intercepting of plumes to removing mobile contaminants (Siegrist et al., 2001). The use of ISCO for treatment of DNAPL poses a challenge, but is generally applicable. It is also viable against dissolved contaminants in the groundwater, but at low concentrations it may not be cost-effective (ITRC, 2005). ISCO can be applied with different oxidants, all depending on the type of pollution and the type of soil treated. The oxidants have different oxidative strengths as shown in Table 4.

Table 4. Oxidation potentials for oxidants used for *in situ* chemical oxidation. From Siegrist et al. (2001), ITRC (2005) and USEPA (2006).

Chemical species	Oxidation potential (V)	Comments
Hydroxyl radical (OH•)	2.8	Hydroxyl radical is formed as a result of Fenton's reagent or adding hydrogen peroxide to ozone
Sulfate radical (SO ₄ • ⁻)	2.6	Sulfate radical is formed when persulfate is activated
Ozone	2.1	Direct oxidation
Persulfate	2.0	Direct oxidation
Hydrogen peroxide	1.8	Direct oxidation
Permanganate	1.7	Direct oxidation

5.2. Ozone

Ozone (O₃) is used in many processes, such as aquaculture, bleaching, industrial effluent treatment and wastewater treatment (Marley et al., 2002) with ozonation being a very common municipal water treatment technology (ITRC, 2005). The concept of remediation by ozonation has evolved over the past 20 years (Nelson and Brown, 1994).

The use of ozone in remediation is unique as it involves the application of a gas. The use of ozone in remediation is done by either direct or indirect oxidation (Siegrist et al., 2001; Choi et al., 2002; ITRC, 2005). The direct oxidation (eq. 1) is typically used in water treatment under acidic pH and the indirect approach (eq. 2) in remediation with neutral to basic pH, with both methods yielding a strong oxidant (Table 4).



Equation 2 shows that the indirect approach works through the formation of hydroxyl radicals (OH[•]), which are highly reactive and possess a high oxidation potential. On the other hand hydroxyl radicals are very unstable and have a very short half life. Due to ozone's high reactivity and instability, ozone is produced onsite (Siegrist et al., 2001). To ensure radical formation, hydrogen peroxide is often added to the ozone/water system (eq. 3) resulting in enhanced OH[•] generation (ITRC, 2005).



Practically ozone is applied in two different ways, either as vadose zone injection of ozone gas or through ozone sparging below the water table (ITRC, 2005). Ozone is most utilized in the vadose zone due to the easy transportation of the ozone gas (Clayton, 1998; Choi et al., 2002), although the high reactivity and instability require relatively closely spaced delivery points. The presence of heterogeneous layers in the soil can limit the effectiveness of ozonation. They can lead to channeling of ozone thus limiting the transport into low permeable layers, due to high reactivity that limits the possibility of diffusion into the low permeable soil.

The rate of reaction of ozone with organics in a subsurface environment is dependent on the decomposition rate of ozone and the generation of free radicals (Siegrist et al., 2001). If the oxidation takes place through radical formation it is important to know the chemical composition of the water and the soil composition, as radical scavengers are common (Marley et al., 2002; ITRC, 2005). Key aquifer constituents that offer some level of concern with regard to radical scavengers are high levels of bacteria biomass, organic carbon, iron, manganese and carbonates. Even though these constituents react slowly they exist in the water and the soil in concentrations, that they may present a natural limit to the oxidation.

5.3. Hydrogen peroxide/Fenton's reagent

Hydrogen peroxide (H₂O₂) has many industrial applications (Marley et al., 2002). It has been used for *in situ* remediation for the last 30 years and is the most studied oxidizing compound, both in the laboratory (Watts et al., 1990; Tyre et al., 1991; Gates and Siegrist, 1995; Gates-Andersen et al., 2001) and in the field (Cline et al., 1997; Kauffman et al., 2002; Cho et al., 2002).

Hydrogen peroxide can be utilized in remediation through either direct or indirect oxidation, typically at low hydrogen peroxide concentrations (Siegrist et al., 2001; Chamarro et al., 2001; ITRC, 2005). Hydrogen peroxide can work on its own through direct oxidation (eq. 4), but at low concentrations (<0.1%) it is not kinetically fast enough to degrade the contaminants before it decomposes (ITRC, 2005). However, the

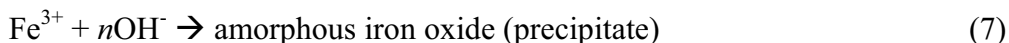
addition of a ferrous salt iron (Fe^{2+}) under acidic conditions (pH 2-4) dramatically increases the oxidative strength through the formation of hydroxyl radicals ($\text{OH}\cdot$), which are highly reactive and have a high oxidation potential (eq. 5). The reaction of iron catalyzed peroxide at pH 2-4 is called Fenton's reaction and is the most utilized application of hydrogen peroxide in connection with remediation processes.



The Fenton's reaction is not one isolated reaction; instead several competing reactions are involved in the free radical formation. Equation 5 shows the basic hydroxyl radical Fenton's reaction that initiates the chain-propagating sequence (Gates and Siegrist, 1995; Yin and Allen, 1999). Classical Fenton's system is not readily created *in situ* with low-peroxide concentration. In practice more concentrated solutions are injected (4-20%) with iron in acid solution. The deviation from traditional low-concentration peroxide/iron mixture is called "modified Fenton's system" (ITRC, 2005). Hydrogen peroxide can decompose in aqueous solutions (eq. 6) upon contact with mineral surfaces and carbonate/bicarbonate surfaces (Siegrist et al., 2001).



An important side reaction occurs and results in formation of precipitates (ITRC, 2005).



This reaction (eq. 7) is favored by a neutral pH, which makes it necessary to lower the pH or use chelating agents to maximize the available Fe^{2+} . The Fenton's reaction is most effective under very acidic conditions (pH 2-4) and becomes ineffective under moderate to strongly alkaline conditions (Chen et al., 2001; Siegrist et al., 2001). A high content of carbonate in the soil makes it difficult to acidify and control the soil matrix. The presence of free radical scavengers is also a limitation for the Fenton's reaction.

The oxidation process in Fenton's reaction is rapid and also strongly exothermic (ITRC, 2005). The exothermic reaction is more aggressive with a stronger peroxide solution (>10%). Due to the exothermic reaction and the lowering of the pH from the reaction, there can be ecological and environmental risks involved that need to be addressed. The Fenton's reaction is overall a very effective oxidant, which attacks the carbon-hydrogen bonds thus being effective against most organic compounds. Studies have shown effective oxidation of chlorinated solvents in the laboratory using hydrogen peroxide directly (Gates et al., 1995; Gates-Anderson et al., 2001), Fenton's reagent (Leung et al.,

1992; Gates and Siegrist, 1995; Weeks et al., 2000; Chen et al., 2001;) or modified Fenton's reagent (Kakarla et al., 2002). Several field studies have also reported effective oxidation of chlorinated solvents (Cho et al., 2002; DeHghi et al., 2002)

5.4. Persulfate

Persulfate ($S_2O_8^{2-}$) is widely applied in many industrial processes, e.g. polymerization, metal surface oxidation and organic chemical manufacturing (Huang et al., 2005). However the use of persulfate for *in situ* chemical oxidation has emerged within the last 5 years. Persulfate salts dissociate in water to persulfate anions ($S_2O_8^{2-}$) which are kinetically slow in destroying many organic contaminants. The most common salt is Sodium persulfate (ITRC, 2005).

Persulfate can be utilized in remediation through either direct or indirect oxidation. The direct oxidation (eq. 8) has a high oxidation potential (Table 4) but is generally slow at ambient temperatures (House, 1962; Huang et al., 2002a). However, the application of heat (eq. 9) or addition of Fe^{2+} (eq. 10) can activate the decomposition of persulfate and form sulfate radicals. The thermal activation (40-60°C) takes place at slightly acidic/neutral pH (Kolthoff and Miller, 1951; House, 1962; Cuypers et al., 2000). The metal activator in free radical formation can be naturally occurring or added during oxidant injection. The most common initiator in the field is Fe^{2+} (Kolthoff et al., 1951; Sperry et al., 2002).



As with the Fenton's reaction, the formation of sulfate radicals is not one isolated reaction. A chain-propagating sequence usually takes place with equation 9 being the chain-initiating reaction because the initial sulfate radical is formed. Fe^{2+} is involved in both chain-propagating (eq. 10) and chain-terminating reactions (eq. 11), making it important to know the Fe^{2+} concentration (Fordham and Williams, 1951; ITRC, 2005).

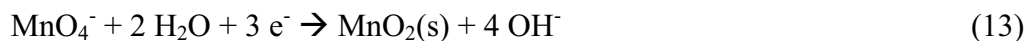
Fe^{2+} requires highly reducing conditions to remain in solution such as an acidic pH, so it may be necessary to lower the pH (as with peroxide systems). The effectiveness of iron activation degrades with time and distance, due to the iron precipitation in buffered soil. Chelating agents can be used to maintain the iron solubility. Another approach to activate the sulfate radical is the use of elevated pH (ITRC, 2005). Sulfate radicals have an unpaired electron which makes them highly reactive and short-lived, although they are more stable than the hydroxyl radical (Brown and Robinson, 2004). Chloride as well

as carbonate/bicarbonate can act as radical scavengers and reduce the effectiveness (Waldemer et al., 2007). Studies have shown effective oxidation of chlorinated solvents in the laboratory by thermally activated persulfate (Cho et al., 2002; Tsitonaki et al., 2006; Huang et al., 2005; Waldemer et al., 2007), iron activated persulfate (Sperry et al., 2002; Liang et al., 2004a) and activation by chelated iron (Liang et al., 2004b).

5.5. Permanganate

Permanganate (MnO_4^-) has been used in wastewater treatment for decades (Drescher et al., 1998; Marley et al., 2002) where the use of MnO_4^- for *in situ* remediation surfaced about 15 years ago (Gates et al., 1995; Hood et al., 2000). Potassium and sodium permanganate are the two common forms of permanganate (MnO_4^-) used for *in situ* treatment of chlorinated solvents (USEPA, 2006). KMnO_4 is a crystalline solid from which aqueous MnO_4^- solutions up to 4% (40 g/l) can be prepared on site, where NaMnO_4 is supplied as a concentrated liquid (40%) that is diluted on site and applied at lower concentrations (Siegrist et al., 2001; USEPA, 2006).

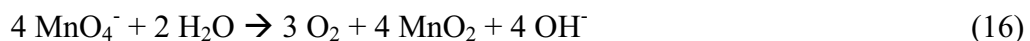
The oxidation process strictly involves direct electron transfer, rather than free radical processes that characterize the other oxidants (Siegrist et al., 2001). Permanganate is applicable over a wide pH range with the process following three primary redox reactions according to the pH. The reaction follows equation 12 under acidic conditions ($\text{pH} < 3.5$) and in the typical environmental range ($3.5 < \text{pH} < 12$) the primary reaction follows equation 13, with MnO_2 as a reaction byproduct and finally at high pH ($\text{pH} > 12$) the reaction follows equation 14 (Lide, 1992; Siegrist et al., 2001; USEPA, 2006).



In acidic solutions, the Mn^{4+} in MnO_2 can be reduced slowly to Mn^{2+} (eq. 15)



MnO_4^- can also react with water and auto decompose (Rees, 1987), but at very slow rates, resulting in non-productive depletion of permanganate and further generation of MnO_2 (equation 16).



Even though equation 16 shows that permanganate can auto decompose, it is still a very stable oxidant that can persist in the subsurface for months, thus making it possible for

MnO_4^- to diffuse into the soil matrix (ITRC, 2005). However, the presence of MnO_2 can catalyze the decomposition of MnO_4^- solutions (Rees, 1987, Siegrist et al., 2001), though the extent of the catalysis is not known. Thus, traces of MnO_2 initially present in the MnO_4^- , or formed by the reaction of MnO_4^- with reducing agents, such as organic matter or PCE may lead to a catalyzed decomposition of MnO_4^- . Even though MnO_4^- has the ability to diffuse into the soil matrix, there are still limitations on the use of MnO_4^- for ISCO. Equation 13 shows that $\text{MnO}_2(\text{s})$ is formed as a result of the oxidation (Crimi and Siegrist, 2004), which can lead to a reduction of the soil permeability due to precipitation. MnO_4^- is nonselective (as all oxidants) and will therefore react with the organic matter and the inorganic constituents in the soil. The reaction with the soil, termed the natural oxidant demand (NOD), may limit the effectiveness of ISCO (Haselow et al., 2003; Mumford et al., 2005; I, Hønning et al., 2007a)

5.6. Choosing an oxidant

Several parameters should be considered when identifying the most applicable oxidant for treatment with ISCO in heterogeneous aquifers. The key issues are: (a) Delivery and distribution of the oxidant, (b) Rate and extent of the natural oxidant demand, (c) Rate and extent of reaction with the contaminant and (d) Geochemical effects from the oxidation. With this in mind site specific information is a must before deciding the actual remediation strategy.

The Danish subsurface sediment consists largely of carbonated alkali clayey till making it difficult to apply both ozone and Fenton's reagent, except for the most western part of Denmark. The use of ozone also comes with higher capital costs as ozone must be generated on site as well as more restrictive safety procedures. The oxidants working through indirect oxidation (ozone, Fenton's reagent, activated persulfate) have a high reaction rate and are primarily distributed through advection. The high reaction rate makes it very important to deliver the oxidants very close to the pollution, as they will be limited by the non-target reactions.

MnO_4^- on the other hand has the ability to diffuse into low permeable media because it is more persistent. It is also applicable over a wide pH range which makes it useful in the Danish carbonated clayey till. There is no need to apply anything for MnO_4^- to react, unlike the oxidants that needs to be activated. On the downside there is formation of CO_2 and MnO_2 , which can affect the permeability. Taking the key issues into account and focusing on remediation in low permeable media, the overall assessment is that MnO_4^- seems to be the most applicable oxidant in the Danish clayey till.

6. Reaction between MnO_4^- and the sediment

Early studies by Barcelona and Holm (1991) investigated the reduction capacities of aquifer solids and found that the reduction capacities from aquifer solids may contribute significantly to the oxidant demand. This showed the importance of understanding the reaction between the oxidant and the sediment. The focus in this chapter will be on the parameters that can affect the oxidant demand in the reaction with the sediment.

6.1. Natural oxidant demand

The consumption of MnO_4^- from the reaction with the sedimentary reductants is referred to as the natural oxidant demand (NOD) and is expressed in g MnO_4^- /kg dry weight sediment (dw). In situations where contaminants are present the term TOD (total oxidant demand) is used with TOD equal to NOD + contaminant demand (Haselow et al., 2003). The NOD is the result of several reactions, taking place in parallel with the reaction between the contaminant and MnO_4^- (Mumford et al., 2005; I, Hønning et al., 2007a). While it has been known that sedimentary reductants can exert a demand for the oxidant and impact overall treatment efficiency, the focus has only recently shifted to quantifying and correlating their contribution to NOD. However, the contribution of the different sedimentary reductants on oxidant demand is still not well understood (Crimi and Siegrist, 2005; Mumford et al., 2005). Examples of laboratory studies focusing on NOD are listed in Table 5.

Table 5. Examples of laboratory studies investigating NOD.

Type of Study	Geology	MnO_4^- (g/l) ^a	NOD observations ^a	References
Batch	Sand	0.2 - 2	1.6 – 4.3 g/kg	Greenburg et al., 2004
Batch	Sand	3.7	0.2 g/kg	Mumford et al., 2004
Batch	Sand	0.2 - 37	0.06 – 9.8 g/kg	Crimi and Siegrist, 2005
Batch	Sand	3.7	1.2 g/k	Mumford et al., 2005
Batch	Sand	0.75 - 15	0.3 – 53 g/kg	Xu and Thomson, 2006
Batch	Sand	5 - 20	0.5 – 2 g/kg	I, Hønning et al., 2007a
Batch	Sandy till	0.05 - 20	1 – 8 g/kg	I, Hønning et al., 2007a
Batch	Clayey till	0.05 - 20	5 – 20 g/kg	I, Hønning et al., 2007a
Column	Silty clay	0.4 - 4	2.1 – 8.1 g/kg	Struse et al., 2002
Column	Sand	1.6 - 3.4	0.1-0.6 g/kg	Mumford et al., 2005
Column	Sand	0.75 - 15	0.2 – 27.5 g/kg	Xu and Thomson, 2006

^a The oxidant concentrations are reported as g KMnO_4 /l in most studies, but have been converted to g MnO_4^- /l for the purpose of comparison with the investigations in this thesis.

The overview of conducted laboratory studies shows that NOD investigations primarily have been performed on sandy aquifer sediments. The reported NOD values for sandy

aquifer sediments are generally low and NOD values from this thesis (I, Hønning et al., 2007a) are consistent with values reported from other investigations (Table 5). Reported NOD values for clayey soils are very scarce and the knowledge of MnO_4^- consumption in this type of media is limited. However NOD values reported by Struse et al. (2002) were similar to NOD values from this thesis (I, Hønning et al., 2007a).

The expected oxidant demand can be calculated or determined by laboratory experiments. However, a couple of studies have suggested the use of push-pull tests in the field as a useful and economical tool for evaluation of NOD (Mumford et al. 2004; Greenburg et al., 2004). The values obtained by push-pull testing in Mumford et al. (2004) were consistent with NOD values from laboratory scale batch experiments.

The reported NOD values in Table 5 have been shown to be dependent on the initial concentration of MnO_4^- used in the investigation. Under comparable conditions, the oxidant demand increases with an increase in the oxidant concentrations. This has clearly been demonstrated for the sandy aquifer sediments (Greenburg et al., 2004; Crimi and Siegrist, 2005; Xu and Thomson, 2006). However the knowledge in low permeable media is limited, as only a few investigations have focused on investigating this type of media. Investigating the effects of oxidant dose on the NOD value in low permeable media formed part of this thesis (I, Hønning et al., 2007a). A considerable increase in the MnO_4^- consumption is observed as the initial MnO_4^- concentration increases for all investigated sediment types and illustrated for clayey till in **Figure 7**.

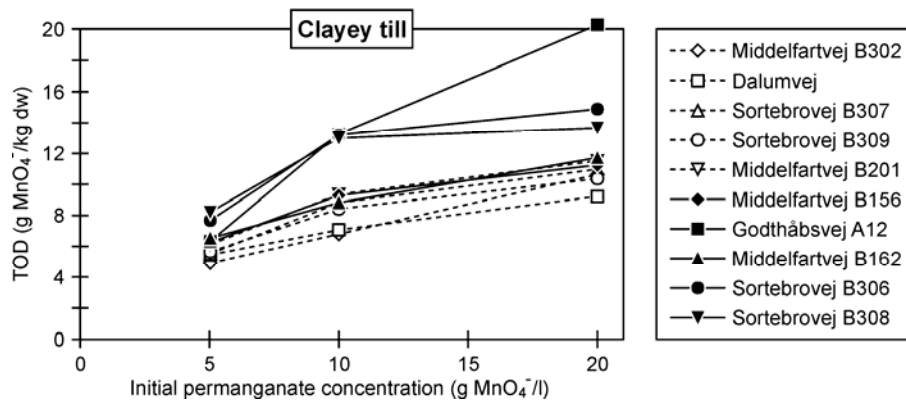


Figure 7. Oxidant demand as a function of the initial MnO_4^- concentration for ten clayey tills. Modified from Hønning et al. (I, 2007a).

The results point out that a fixed NOD value cannot be assigned to any type of sediment. The actual NOD value is dependent on the initial concentration of MnO_4^- and should therefore be reported together with the applied MnO_4^- concentration. To explain the difference in MnO_4^- consumption, knowledge of the amount, type and reactivity of sedimentary reductants present is crucial (Pedersen, 1992; Hartog et al., 2002). The

increased MnO_4^- consumption suggests that the sedimentary reductants react to a higher degree when the initial MnO_4^- concentration is increased, or that MnO_4^- decomposition by its reaction with water (equation 15, chapter 5) occurs to a greater extent.

6.2. Reaction kinetics

Recent studies by Mumford et al. (2005) and Xu and Thomson (2006) in aquifer sediments have shown that the NOD at a given MnO_4^- concentration is not an instantaneous reaction with a single valued quantity, but is kinetically controlled and dependent on the type of sedimentary reductants present. Jones et al. (2006) and Balu and Urynowicz (2006) reported an initial rapid depletion of MnO_4^- followed by a much slower depletion rate, with the fast reacting species following a first-order mass action law. The kinetically controlled consumption of MnO_4^- was also demonstrated in a column study with aquifer sediment (Jones et al., 2006), where incomplete breakthrough of MnO_4^- suggested the presence of a fast reaction responsible for the initial delay in MnO_4^- appearance and where a slow reaction between the sediment and MnO_4^- was still occurring at the end of the experiment. This general reaction pattern, where the rate of increase in NOD is declining with time was also demonstrated in low permeable media (I, Hønning et al., 2007a) as illustrated in **Figure 8**.

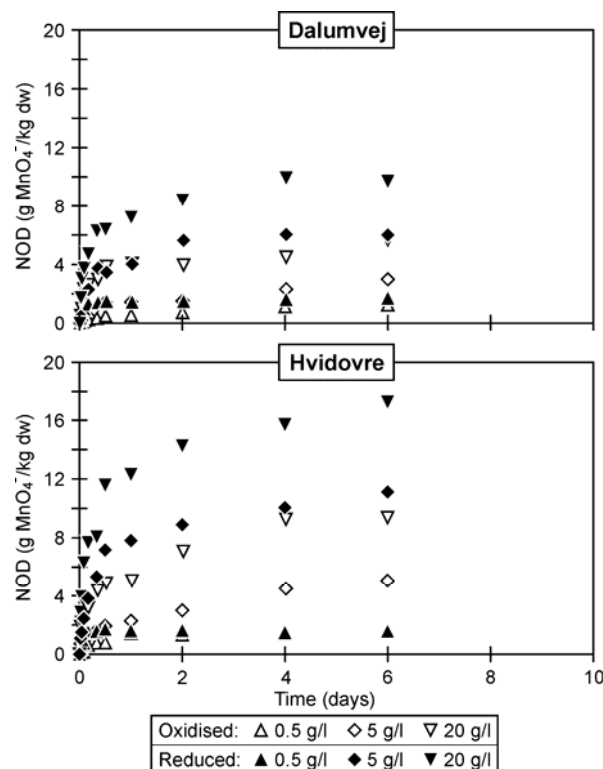


Figure 8. Consumption of MnO_4^- over time in oxidized and reduced clayey till from two different sites, Dalumvej and Hvidovre for three initial concentrations of MnO_4^- . From Hønning et al. (I, 2007a).

Hønning et al. (I, 2007a) showed that regardless of the sediment type and the initial MnO_4^- concentration the consumption of MnO_4^- followed the same reaction pattern (**Figure 8**). The consumption of MnO_4^- can not be described by a single rate expression for the entire duration of the experiment, which is in accordance with other studies where single rate expressions were found not to be applicable for long term consumption (Xu and Thomson, 2006; Jones et al., 2006). Hønning et al. (I, 2007a) found that the rapid increase in NOD, which occurs within the first 8-12 hours of reaction (**Figure 8**), accounted for 50-60% of the total NOD observed after three weeks in the sediments investigated. The kinetics for the shorter time frame shows that the MnO_4^- consumption follows a first order reaction in the first 8 hours in a laboratory slurry system with excess of MnO_4^- . The first order rate constants observed were in the order of 0.005-0.5 hours^{-1} , with higher rate constants in the reduced sediments (I, Hønning et al., 2007a). The first order rate constants can be used to predict the rapid initial consumption of MnO_4^- . However, using the short-term rate constants to predict the total consumption of MnO_4^- beyond the first 8 hours of reaction would overestimate the actual MnO_4^- demand and should therefore be used with caution.

6.3. Effect of sedimentary organic matter on NOD

In an early study Barcelona and Holm (1991) found that reduced organic matter in natural aquifer solids represented the bulk of both the measured and calculated reduction capacity in the total system. Organic carbon (OC) is the principal reactant in the sedimentary organic matter (SOM) with MnO_4^- in terms of NOD (Brown and Robinson, 2004; Mumford et al., 2005; I, Hønning et al., 2007a).

Several compounds have been suggested as a representative of SOM. Barcelona and Holm (1991) suggested phthalic acid ($\text{C}_8\text{H}_6\text{O}_4$) as a reasonable model compound for the reduction capacity in humic substances. More recently Brown and Robinson (2004) used fulvic acid ($\text{C}_{28}\text{H}_{30}\text{O}_{23}$) as a basis for the theoretical calculation giving a theoretical MnO_4^-/OC ratio of 7 (wt/wt), where Mumford et al. (2005) suggested using a simple carbohydrate (CH_2O , C in oxidation state C^0) where the complete oxidation yields a MnO_4^-/OC ratio of 13.2 (wt/wt). This corresponds well with the suggested reaction in Hønning et al. (I, 2007a) with $\text{C}_7\text{H}_8\text{O}_4$ (oxidation state C^0) as a model compound for SOM, giving a theoretical MnO_4^-/OC ratio of 13.2 (wt/wt). The theoretical reaction between OC and MnO_4^- can be described by:



The main constituents in sandy aquifer sediments are primary minerals, such as quartz. The primary minerals are characterized by their low reactivity, which can explain the low NOD values for any given MnO_4^- concentration in sandy aquifer sediments

compared to the MnO_4^- consumption in the more fine grained low permeable media, such as clayey till. The difference in measured MnO_4^- consumption for the different sediment types is likely a result of the difference in their soil composition and content of reactive species (organic carbon, inorganic species) in the sediment. The main contributor for NOD in sandy aquifers is organic carbon, while reduced iron, manganese and sulfides may also play a role in reduced aquifers (Barcelona and Holm, 1991, Heron et al., 1997, Siegrist et al., 1999, Brown and Robinson, 2004).

Struse et al. (2002) reported oxidation of 20-30% of OC during ISCO with MnO_4^- . Other studies have also investigated the oxidation of OC (Mumford et al., 2005; Balu and Urynowicz, 2006) with up to 60% of the OC being oxidized. The oxidation of up to 60% OC was also reported in Hønning et al. (I, 2007a) where the initial OC content in sandy aquifer sediments and clayey till was correlated to the measured NOD values.

Hønning et al. (I, 2007a) showed a good correlation between the initial OC content and the consumption of MnO_4^- in the sandy aquifer sediments, while there was no correlation in the clayey till, as illustrated in **Figure 9**.

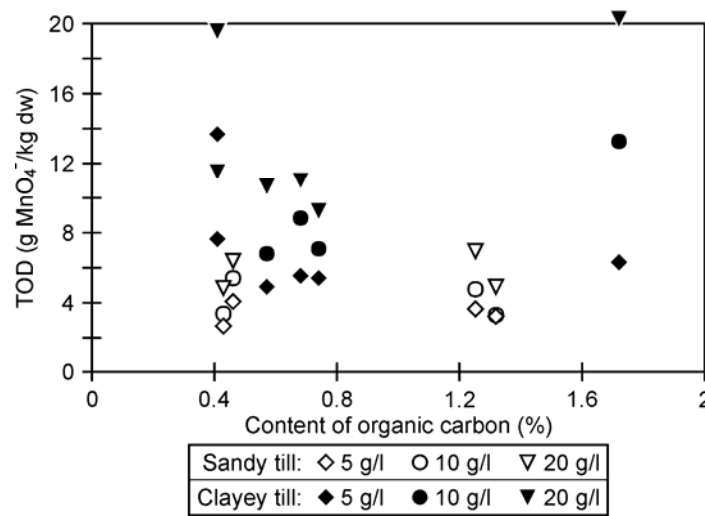


Figure 9. Consumption of MnO_4^- as a function of the initial OC content for sandy and clayey till. From Hønning et al. (I, 2007a).

The incomplete oxidation of OC which other studies also reported was in accordance with the description of SOM in chapter 2 stating that not all SOM was available for oxidation. However, even though the availability of SOM can differ in clayey tills, the large discrepancy in the MnO_4^- consumption in the clayey tills (**Figure 9**) indicate that OC is not the only constituent reacting with MnO_4^- .

6.4. Effect of inorganic components on NOD

Barcelona and Holm (1991) reported that inorganic components can contribute to the reductive capacity of the sediment. This was also suggested by Brown and Robinson (2004) where they reported the relative demands of the inorganic species with regards to MnO_4^- oxidation. However, the contribution of inorganic components has not been quantified and correlated to measured NOD values in other studies. Investigating the effects of inorganic components on the NOD value in low permeable media formed part of this thesis (III, Hønning et al., 2007c).

The possible contribution of inorganic components on the overall consumption of MnO_4^- can initially be evaluated by measuring the chemical oxidant demand (COD) and the total Fe content. The main part of the inorganic contribution can be evaluated by looking at ferrous iron, Fe^{2+} , before and after oxidation, as Fe^{2+} is considered an important reactive compound with regards to the reductive capacity (Nzengung et al., 2001; Lee and Batchelor, 2003). This was done in Hønning et al. (III, 2007c) for oxidized and reduced clayey till from two sites (Table 1, chapter 2). Even though the OC content of the clayey till is pair wise very similar the COD measurements and total Fe content are significantly different corresponding to the difference in NOD values, indicating the presence of inorganic species as shown in Table 5.

Table 5: Sediment characteristics and MnO_4^- consumption in oxidized and reduced clayey till from 2 sites. Modified from Hønning et al. (I, 2007a).

	Unit	Dalumvej		Hvidovre	
		Oxidized	Reduced	Oxidized	Reduced
Redox state					
NOD (5) ^a	g MnO_4^- /kg dw	3.3	7.7	6.2	13.7
NOD (20) ^a	g MnO_4^- /kg dw	7.3	11.5	11.4	19.6
OC content	%	0.21	0.41	0.21	0.41
COD	g O_2 /kg	3.9	6.0	5.5	13.7
Total Fe content	%	0.19	0.18	1.03	1.26

^a Initial MnO_4^- concentration (g MnO_4^- /l) given in brackets

The specific contribution of the inorganic species on MnO_4^- consumption can not be determined on the basis of the values in Table 5. However, the mineralogical analysis of the two sites reported in chapter 2, showed a distinct higher content of Fe^{2+} in the clayey till from Hvidovre reflecting the higher total Fe content and COD value (Table 5). Hønning et al. (III, 2007c) showed that Fe^{2+} in the clay minerals is oxidized by the reaction with MnO_4^- . The difference in Fe^{2+} content in the untreated oxidized and reduced bulk samples is used as a measurement of the maximum amount of Fe^{2+} that can react with MnO_4^- .

The difference between the Fe^{2+} content in the oxidized and reduced sediment from Dalumvej is $0.22 \text{ g Fe}^{2+}/\text{kg dw}$ (III; Hønning et al., 2007c) and with a relative demand for the Fe^{2+} species of $0.95 \text{ mg MnO}_4^-/\text{mg Fe}^{2+}$ (Brown and Robinson, 2004) this gives a maximum MnO_4^- demand of $0.2 \text{ g MnO}_4^-/\text{kg dw}$ for Dalumvej. The same calculation for Hvidovre gives an maximum MnO_4^- demand of $3.9 \text{ g MnO}_4^-/\text{kg dw}$, which reveals that Fe^{2+} in the Hvidovre sediment can be a significant factor in the total MnO_4^- consumption. The calculations show that Fe^{2+} from the clay minerals in some cases can be a substantial parameter in reduced clayey till with regards to the consumption of MnO_4^- . Whether or not the sedimentary reduction capacities are important in specific situations may depend on the strength and specificity of the oxidant and the reactivity of components of the reduction capacity (Barcelona and Holm, 1991).

6.5. Diffusion of MnO_4^- in low permeable sediment

Diffusion of MnO_4^- is an important transport mechanism at the field scale (LaChance et al., 1998; Hood et al., 2002), where MnO_4^- can diffuse into low permeable media and react with the target contaminant. While the reaction with the contaminant may enhance the rate of diffusion by increasing the MnO_4^- concentration gradient, MnO_4^- will continue to react with the sedimentary reductants. In many cases it is expected that the loss of MnO_4^- to NOD will be larger than the oxidant demand exerted by the reactions with the target contaminants (Hood et al., 2002; II, Hønning et al., 2007b).

Diffusion concentration profiles for MnO_4^- were modelled by Hood et al., (2002) and demonstrated that the distance of MnO_4^- penetration into the clay decreases as the NOD increases. The rate of oxidant loss to NOD is large relative to the rate of diffusion of MnO_4^- into the clay, and hence retards the extent of oxidant penetration in the clay until NOD is depleted. It is likely that even a slow rate of catalytic MnO_4^- decomposition will significantly limit the extent of oxidant penetration (Hood et al., 2002). Hønning et al. (II, 2007b) showed that the diffusion into the clay matrix is rapid at first with the progress slowing down over time, which is in accordance with observations in a field study by Siegrist et al. (1999). The diffusion of MnO_4^- into a clay matrix was visually observed in 2D laboratory box experiments (II, Hønning et al., 2007b) through the development of a dark brown colored oxidation front in the clay (**Figure 10**).

The dark brown colored oxidation front in **Figure 10** showed a visual observation of the ongoing MnO_4^- diffusion into a clay matrix. According to equation 17 OC and MnO_2 can be used as monitoring parameters for the diffusion and subsequent reaction between MnO_4^- and the sedimentary reductants, which is in accordance with observations in Struse et al. (2002) on the diffusion process. Hønning et al. (II, 2007b) showed that visual observations of MnO_4^- diffusion into a clay matrix correlated well with the monitoring parameters, as illustrated in **Figure 11**.

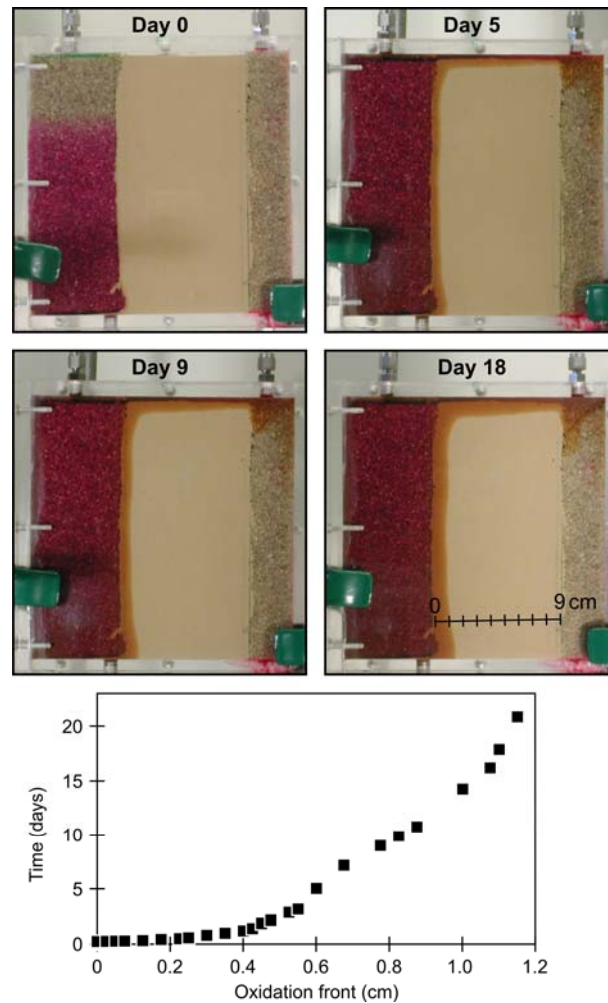


Figure 10. Observed diffusion of MnO_4^- into a clay matrix by development of a dark brown colored oxidation front. From Hønning et al. (II, 2007b).

Hønning et al. (II, 2007b) calculated diffusion rates for the diffusion of MnO_4^- into a clay matrix in a laboratory scale 2D box experiment. The diffusion rates were found to be between 0.04-0.06 cm/day, which corresponds well to observations in the field in the same study, where a diffusive reactive zone was reported to extend 15 cm into oxidized clayey till and 3 cm into reduced clayey till 12 months after initial MnO_4^- treatment. These rates are lower than those reported by Struse et al. (2002) of 0.1 cm/day for MnO_4^- in silty clay in a laboratory scale 1D experiment. The diffusion rates in Struse et al. (2002) correspond well with field observations in silty clay by Siegrist et al. (1999). The lower diffusion rates in the silty clay from Struse et al. (2002) and Siegrist et al. (1999) corresponded well with the simulation by Hood et al. (2002) as the NOD for the clayey till (12 g/kg) in Hønning et al. (II, 2007b) is higher than the NOD for the silty clay.

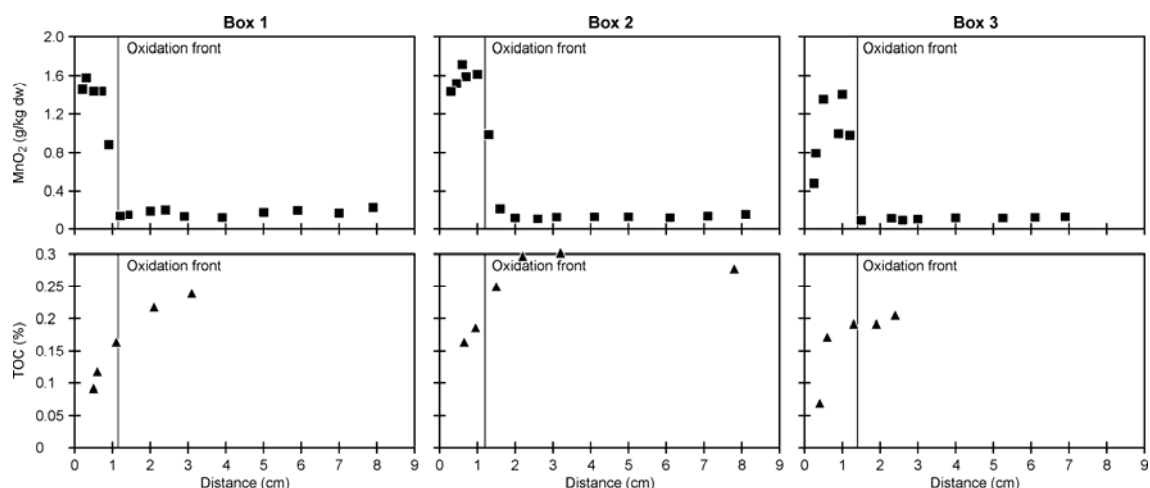


Figure 11. Concentrations of MnO₂ and TOC in the clay matrix, at the termination of the box experiments. Modified from Hønning et al. (II, 2007b).

6.6. Geochemical conditions after chemical oxidation

ISCO with MnO₄⁻ can be applied over a wide pH range between 3.5 and 12, which is common in carbonate buffered sediments, such as clayey till. The reaction involves the formation of CO₂ and solid MnO₂. MnO₄⁻ can also react with water itself and decompose (equation 15) resulting in further formation of MnO₂, although this reaction is very slow (Siegrist et al., 2001). The reaction can be catalyzed by the presence of solid MnO₂ in the system (Rees, 1987). Genesis of MnO₂ particles is faster and more extensive with greater concentrations of MnO₄⁻ and the contaminant (Crimi and Siegrist, 2004). If pH drops below 3.5 which can happen in systems with negligible buffering capacity as the oxidation reaction also forms H⁺, manganese will be reduced to Mn²⁺ with no precipitation of the MnO₂ solid. The effect on the permeability due to particle genesis and CO₂ is not clear, as some studies have observed decreased permeability (Schroth et al., 2001; Reitsma and Randhawa, 2002) whereas the permeability change was negligible in other cases (Nelson et al., 2001; II, Hønning et al., 2007b). Part of the explanation could be that the MnO₂ precipitants can be present as colloids or as coating on mineral surfaces in the sediment.

Elevated levels of metals in the subsurface from the application of ISCO with KMnO₄ can be due to mobilization of the metals from the oxidation reaction or addition of metal through impurities in the applied KMnO₄ (Siegrist et al., 2001; Crimi and Siegrist, 2003; Bjerg et al., 2005). Metals sorbed to the sediment under ambient conditions could be mobilized during ISCO due to decrease in pH or the amount of SOM. KMnO₄ solids are derived from mined potassium ores and contain impurities, including salts and metals (Siegrist et al., 2001; Crimi and Siegrist, 2003). The KMnO₄ solids used for MnO₄⁻ solutions applied during the experimental work in this study have been analyzed for content of trace metals and compared to a persulfate (S₂O₈²⁻) solution in typically

applied concentration levels (Table 6). Several sediment samples treated with MnO_4^- were also analyzed to investigate the metal content in the sediment after ISCO.

Table 6. Metal content ($\mu\text{g/l}$) in a MnO_4^- solution (10 g/l), a $\text{S}_2\text{O}_8^{2-}$ solution (25 g/l), and in two clayey tills before and after addition of MnO_4^- . Modified from Bjerg et al. (2005).

Sample	Al	Cd	Cr	Cu	Hg	Ni	Pb
MnO_4^- (aq.)	3500	150	330	1500	6	680	620
$\text{S}_2\text{O}_8^{2-}$ (aq.)	<1	<0.05	2	2	0.1	1	<0.2
B162 (before) ^a	<1	0.2	<0.5	3	3	4	1
B162 (after) ^a	<100	26	338	351	8	258	116
B201 (before) ^a	<3	0.1	<0.5	1	3	3	0.3
B201 (after) ^a	2100	15	345	142	12	108	44

^a Clayey till from two wells (B156, B201) at Middelfartvej (**Figure 7**)

The comparison between the aqueous MnO_4^- and $\text{S}_2\text{O}_8^{2-}$ solution demonstrates the level of impurities in MnO_4^- , which raises concern for the water quality standards after ISCO with MnO_4^- . The levels in the two clayey tills before and after MnO_4^- application clearly show that the metal concentrations are significantly increased from the addition of MnO_4^- , as other studies also have demonstrated (Moes et al., 2000; Crother et al., 2002). However, the metal concentrations are in most cases significantly lower in the sediment sample treated with MnO_4^- compared to the applied MnO_4^- solution, which most likely is due to sorption of the metals to the sediment. The sorption of metals to the sediment is most likely facilitated by the genesis of MnO_2 particles, as they act as a strong sorbent towards the metals (Siegrist et al., 2001; Nelson et al., 2001; Crimi and Siegrist, 2003). It has also been demonstrated that the mobilization effects may be attenuated by natural processes after completion of ISCO and a return to the natural conditions (Siegrist et al., 2001; Crother et al., 2002).

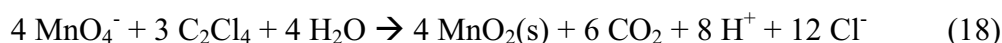
7. Oxidation of chlorinated solvents using MnO_4^-

The use of MnO_4^- for oxidation of chlorinated solvents in granular media has been demonstrated in many studies. However the challenges arising for applications in low permeable media using MnO_4^- are not well documented. The oxidation of chlorinated solvents in low permeable media has formed an integral part of this thesis and will be discussed in this chapter.

7.1. Reaction mechanisms

The generally accepted mechanism of oxidation of chlorinated solvents by MnO_4^- is that MnO_4^- initially reacts with the carbon-carbon double bond to form an unstable cyclic hypomanganate ester (Yan and Schwartz, 1999). Kinetic modelling for TCE by Yan and Schwartz (2000) showed that this initial reaction is independent of pH and can be considered as the rate-determining step. This has been suggested to be true for all chlorinated solvents (Waldemer and Tratnyek, 2006). From the unstable cyclic ester several transient intermediates can be formed (including formic, glyoxylic and oxalic acids) through several oxidative or hydrolysis pathways depending on the pH, until carbon dioxide (CO_2) are formed as the final product. (Yan and Schwartz, 1999; Yan and Schwartz, 2000; Siegrist et al. 2001; Waldemer and Tratnyek., 2006).

The reaction mechanism for the oxidation of PCE was investigated in Huang et al. (2002c) with the reaction pathway similar to the oxidation of TCE. However, under acidic conditions (e.g. around pH 3), PCE tends to be directly mineralized into CO_2 and chloride through the intermediate phosgene instead of oxalic acid that appears to be the major intermediate prior to complete mineralization of PCE in neutral and alkaline conditions (Huang et al., 2002c). The overall reaction stoichiometry was described by:



Equation 18 shows a significant amount of chloride being formed during the reaction and with a rate of chloride production nearly equal to the rate of PCE degradation it makes chloride a good constituent for the quantification of PCE destruction (Huang et al., 2002c). A $\text{MnO}_4^-/\text{PCE}$ ratio (wt/wt) of 0.97 is found, which is significantly lower than the MnO_4^-/OC ratio (wt/wt) of 13.2 presented in chapter 6.

7.2. Oxidation of chlorinated solvents present as DNAPL

The overview of conducted laboratory and field studies (Table 7) shows that DNAPL investigations in the field have been conducted with very high MnO_4^- concentrations compared to the laboratory studies. It is also evident that the majority of the studies have been performed in sandy aquifer sediments with TCE as the contaminant of concern.

Table 7. Examples of laboratory and field studies with DNAPL's using MnO_4^- .

Type of study	Geology	MnO_4^- ^a (g/l)	Focus	References
Batch ^b	Aqueous	22.5	Investigating MnO_2	Li and Schwartz, 2004a
Batch ^b	Aqueous	0.25 - 2.5	MnO_2 film around DNAPL	Urynowicz and Siegrist, 2005
Column ^b	Sand	0.75	Effective TCE treatment Precipitation of MnO_2	Drescher et al., 1998
Column ^c	Sand	5.5 - 7.5	Effective PCE treatment	Schnarr et al., 1998
Column ^b	Sand	0.6	Investigating CO_2 and MnO_2 around DNAPL	Schroth et al., 2001
Column ^b	Sand	3	Effective TCE treatment Precipitation of MnO_2	Huang et al., 2002b
Column ^c	Sand	9	Effective PCE treatment Precipitation of MnO_2	Hønning and Skou., 2003
Column ^b	Sand	1.9	Effective PCE treatment Rebound of PCE	Hrapovic et al., 2005
Column ^b	Silt/clay	0.4 - 3.7	Effective TCE treatment in area with diffusion	Struse et al., 2002
Box ^c	Sand	0.75	Investigating CO_2 and MnO_2 around DNAPL pool	Dan and Reitsma, 2002a
Box ^b	Sand	0.75	Investigating MnO_2 around DNAPL pool	Conrad et al., 2002
Box ^c	Sand	7.5	Investigating MnO_2 around DNAPL pool	MacKinnon and Thomson, 2002
Box ^b	Sand	0.15	Investigating MnO_2 around DNAPL pool	Li and Schwartz, 2004b
Field studies				
Pilot ^b	Sand	11-22.5	Effective TCE treatment No formation plugging	Mott-Smith et al., 2000
Pilot ^c	Sand	7.5-22.5	Effective PCE treatment	Nelson et al., 2001
Pilot ^b	Sand/silt	not given	Local efficient treatment but not overall	McKay and Berini, 2002
Pilot ^b	Silt/clay	37.5	Local efficient treatment but not overall	Moes et al., 2000
Full ^b	Sand	19	Local efficient treatment but not overall	West et al., 1998
Full ^b	Sand	30	Effective TCE treatment No rebound of TCE	Parker et al., 2002

^a The oxidant concentrations are reported as g KMnO_4/l in most studies, but have been converted to g MnO_4^-/l for the purpose of comparison with the investigations in this thesis.

^b TCE was investigated in this study

^c PCE was investigated in this study

Several laboratory and field investigations have focused on the use of ISCO for remediation of DNAPLs and have showed a good efficiency in the DNAPL treatment when MnO_4^- was applied in sandy sediments (Drescher et al., 1998; Huang et al., 2002; Hønning and Skou, 2003; Hrapovic et al., 2005). However the overall efficiency was limited when MnO_4^- was applied in low permeable media, as the distribution of MnO_4^- within the low permeable media was discontinuous (Moes et al., 2000; McKay and Berini, 2002; Struse et al., 2002). Schnarr et al. (1998) concluded that the effectiveness of ISCO would depend on the DNAPL distribution and dissolution, as oxidation of chlorinated solvents occurs in the dissolved phase after dissolution from DNAPL.

The rate of dissolution from the DNAPL is generally considered to be the limiting factor when using ISCO (Pankow and Cherry, 1996; LaChance et al., 1998), due to the fast reaction kinetics for the reaction between the dissolved contaminant and MnO_4^- , compared to the rate of dissolution. A conceptual model, referred to as the stagnant film model, for the dissolution of DNAPL has been suggested by Pankow and Cherry (1996) in which the dissolution is governed by a mass flux between the DNAPL and the aqueous phase in a stagnant border layer, as shown in **Figure 12**. The dissolved concentration will diminish as a result of the oxidation process, thereby increasing the concentration gradient across the stagnant film. This will result in an increased rate of DNAPL dissolution (LaChance et al., 1998; Schnarr et al., 1998; Hood et al., 2002).

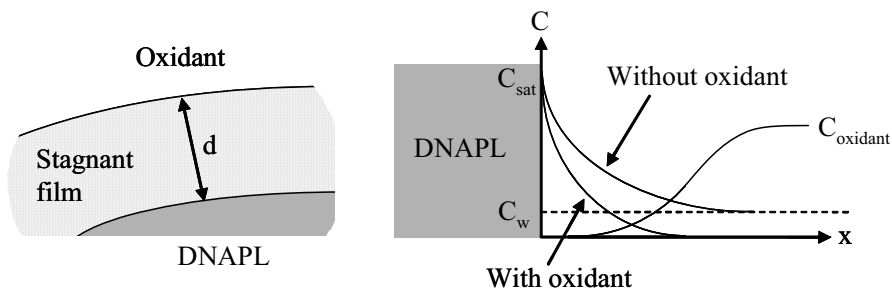


Figure 12: Conceptual model for the dissolution of DNAPL with the dissolved concentration (C_w) and the boundary layer concentration (C_{sat}). Modified from Pankow and Cherry (1996).

MnO_2 formation and CO_2 evolution can also limit the effectiveness of the oxidation process (Schroth et al., 2001). The accumulation and precipitation of MnO_2 is not taken into account in the stagnant film model. However, the accumulation of MnO_2 can interfere with the mass transfer by forming a rind around the DNAPL saturation zones (Conrad et al., 2002; Dai and Reitsma, 2002a; Li and Schwartz, 2004b) or by decreasing the flow locally around the DNAPL (MacKinnon and Thomson, 2002) as a result of bulk aqueous phase deposition of MnO_2 , thereby limiting the contact between MnO_4^- and the DNAPL. MnO_2 can also form a thin film at the DNAPL interface, which also limits the contact (Uryniewicz and Siegrist, 2005).

Laboratory studies have shown that extensive permeability reduction and even complete plugging due to MnO₂ precipitation and CO₂ production can occur during application of MnO₄⁻ flushing (Schroth et al., 2001; Huang et al., 2002b; Siegrist et al., 2002; Reitsma and Randhawa, 2002). However in field applications the same degree of permeability plugging does not seem to occur (Schnarr et al., 1998; Chambers et al., 2000; Mott-Smith et al., 2000; Nelson et al., 2001). However it is possible that local permeability reductions during field application do occur but only in the vicinity of DNAPL zones.

7.3. Oxidation of dissolved chlorinated solvents

Table 8. Examples of laboratory and field studies with dissolved chlorinated solvents using MnO₄⁻.

Type of study	Geology	MnO ₄ ⁻ ^a (g/l)	Focus	References
Batch ^{bc}	Aqueous	0.1	Investigating reaction kinetics	Yan and Schwartz, 1999
Batch ^c	Aqueous	3.7 - 22.4	Investigating reaction kinetics	Hood et al., 2000
Batch ^c	Aqueous	0.1 - 3.7	Investigating reaction kinetics	Dai and Reitsma, 2002b
Batch ^c	Aqueous	7.5 - 30	Investigating reaction kinetics and reaction mechanisms	Huang et al., 2002c
Batch ^c	Sand/silt	0.7 - 18.7	Investigating oxidation efficiency	Gates-Anderson et al., 2001
Batch ^c	Sand/clay	0.05 - 20	Investigating reaction kinetics and oxidation efficiency	I, Hønning et al., 2007a
Column ^b	sand	3	Investigating MnO ₂ formation and permeability reduction	Siegrist et al., 2002
Column ^c	sand	1.5	Investigating MnO ₂ formation and permeability reduction	Reitsma and Randhawa, 2002
Box ^c	Sand/clay	1	Investigating diffusion process	II, Hønning et al., 2007b
Field studies				
Pilot ^b	Sand	not given	Effective TCE treatment	Allen et al., 2002
Pilot ^b	Sand	7.5-22.5	Effective TCE treatment	Balba et al., 2002
Pilot ^b	Sand/silt	30-37.5	Effective TCE treatment Little or no rebound of TCE	Chambers et al., 2000
Pilot ^b	Silt/clay	Solids	Effective TCE treatment close to fractures	Siegrist et al., 1999
Full ^b	Sand	15-22.5	Effective TCE treatment Slight rebound of TCE	Smith et al., 2006
Full ^c	Clay till	Solids	Treatment close to sand lenses Rebound of PCE	Westergaard et al., 2004

^a The oxidant concentrations are reported as g KMnO₄/l in most studies, but have been converted to g MnO₄⁻/l for the purpose of comparison with the investigations in this thesis.

^b TCE was investigated in this study

^c PCE was investigated in this study

The overview of conducted laboratory and field studies (Table 8) shows that laboratory scale batch studies with PCE as the contaminant of concern primarily have focused on the oxidation efficiency and on investigating the reaction kinetics, where column and box studies have focused on MnO₂ formation and permeability reduction as a function of the oxidation process and on the diffusion processes in low permeable media. Field studies have focused on treatment efficiency with TCE as the contaminant of concern.

Early studies by Yan and Schwartz (1999) showed that chlorinated solvents can be rapidly degraded by MnO₄⁻ in aqueous solutions with half lives of TCE and DCE ranging from 0.4 to 18 min, with a MnO₄⁻ concentration of 1 mM (0.1 g/l). PCE however has a slow degradation rate with a half life around 4 h, due to an electron deficiency with the four chlorines in the carbon-carbon double bond equivalent to a first order rate constant of 0.16 h⁻¹ (Yan and Schwartz, 1999). Other studies for PCE in aqueous solution have shown that the rate constants increase with increasing temperature (Dai and Reitsma, 2002b; Huang et al., 2002c), with the rate constant twice as high when the temperature increases from 10°C to 20°C. The rate constants also increase with an increase in MnO₄⁻ concentration (Hood et al., 2000; Huang et al., 2002c). However, the first order rate constants in aqueous solution are overall similar with values around 0.5-0.6 h⁻¹ for an initial MnO₄⁻ concentration of 0.5 g/l and around 3-4 h⁻¹ at a MnO₄⁻ concentration of 5 g/l at 20°C. Hønning et al. (I, 2007a) reported similar rate constants for the short term kinetics in soil/water systems (Table 9).

Table 9. First order rate constants for the short term kinetics in a soil/water system for the oxidation of PCE in oxidized and reduced clayey till. From Hønning et al. (I, 2007a).

Parameter	MnO ₄ ⁻ ^a	Dalumvej			
		Oxidized		Reduced	
		10 mg/l ^b	100 mg/l ^b	10 mg/l ^b	100 mg/l ^b
k ₁ (hours ⁻¹)	0.5	0.71	0.47	0.60	0.39
	5	4.36	4.24	4.43	3.48

^a Initial MnO₄⁻ concentration given as g MnO₄⁻/l, ^b Initial PCE concentration given as mg PCE/l

The rate constants in Table 9 appear to be independent of the redox state of the clayey till. Together with the similarity to the aqueous rate constants this suggests that the rate of oxidation of dissolved PCE is independent of the presence of sediment in the system. The first order rate constants for PCE in Table 9 are considerable higher than the rate constants for consumption of MnO₄⁻ (0.005-0.5 h⁻¹, chapter 6) suggesting that the oxidation of dissolved PCE will be quick and effective when MnO₄⁻ is present. The effective oxidation of dissolved chlorinated solvents in soil/water systems has been demonstrated with MnO₄⁻, primarily for sandy sediments, both in the laboratory (Gates-Anderson et al., 2001, I, Hønning et al., 2007a) and in the field (Allen et al., 2002; Balba et al., 2002; Chambers et al., 2000; Smith et al., 2006).

The oxidation of PCE in a soil/water system is illustrated in **Figure 13**. The oxidation of PCE is rapid at first, with the main part of the oxidation occurring within the first 3 hours. The short term (3 h) rate constants are given in Table 9. The results also point out that a low concentration of MnO_4^- (0.05 g/l) can oxidize up to 50% of the PCE, even though MnO_4^- is consumed within the first couple of hours (I, Hønning et al., 2007a). This suggests that the sediment does not act as an instantaneous sink for MnO_4^- and that MnO_4^- reacts simultaneously with both PCE and the sediment, which is in accordance with findings by Mumford et al. (2005).

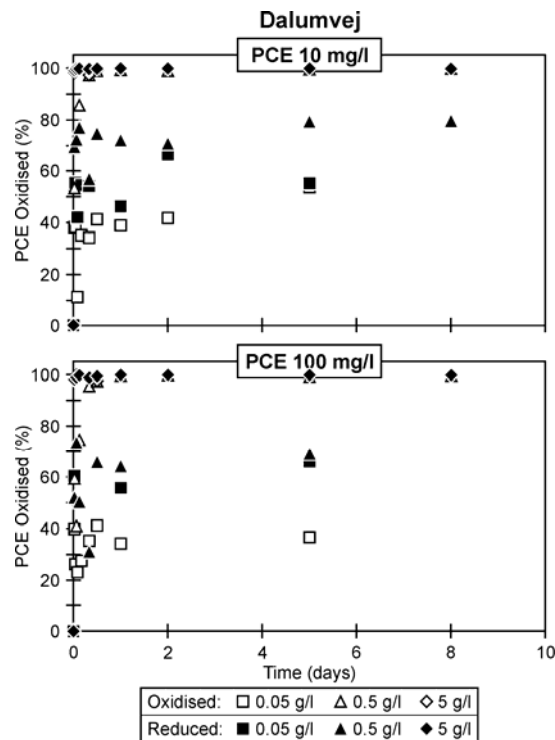


Figure 13. Oxidation of PCE over time for oxidized and reduced clayey till. The results are shown for two initial PCE concentrations. From Hønning et al. (I, 2007a).

The relative influence of dissolved PCE and the sedimentary reductants to the total consumption of MnO_4^- can be estimated, based on the theoretical reaction equations for the oxidation of PCE (equation 18) and the reaction between MnO_4^- and the sediment (equation 17, chapter 6). This was done in Hønning et al. (I, 2007a) for a 1 m^3 aquifer contaminated with PCE (Table 10).

Table 10. Theoretical consumption of MnO_4^- in a PCE polluted aquifer (1 m^3). From Hønning et al. (I, 2007a).

Parameters	OC		Parameters	PCE	
	Low	High		Dissolved	Sorbed
OC content (%)	0.02	0.2	PCE concentration	100 mg/l	29 mg/kg
MnO_4^- demand (kg)	2.8	28.1	MnO_4^- demand (kg)	0.06	0.05

Table 10 shows that the MnO_4^- consumption from sediment with a low OC content still is 25 times higher than from reaction with the total dissolved and sorbed PCE, using the theoretical ratios and assuming complete PCE oxidation and 60% OC consumption (I, Hønning et al., 2007a). The tendency from the theoretical calculations have been demonstrated experimentally by Hønning et al. (II, 2007b) where the majority of the total MnO_4^- consumption originated from the reaction between MnO_4^- and the sediment with over 90% of the total MnO_4^- consumption. This corresponds well with other studies which have shown that the consumption of MnO_4^- to NOD reactions will be large in comparison to the oxidant demand exerted by reactions with the target contaminant (Drescher et al., 1998; Hood and Thomson, 2002; Hood et al., 2002; Mumford et al., 2005). Hence, the presence of dissolved PCE does not make a substantial impact on the total MnO_4^- consumption.

7.4. Oxidation of chlorinated solvents in low permeable media

Several field studies in low permeable media have shown a limited overall efficiency due to both the high oxidant demand and the inability to get MnO_4^- in good contact with the contaminant (Siegrist et al., 1999; Moes et al., 2000; McKay and Berini, 2002; Westergaard et al., 2004; McGuire et al., 2006). Complete removal of contamination with chlorinated solvents in low permeable geologic media, where groundwater flow preferentially occurs in higher permeability sand lenses or fractures, may be very difficult to achieve. This is especially true in cases where the contamination has diffused into the low permeable soil matrix (Johnson et al., 1989; Bedient et al., 1999).

Hønning et al. (II, 2007b) showed that MnO_4^- could diffuse into a clay matrix using the formation of MnO_2 and oxidation of OC as evidence (Figure 10, chapter 6). However the formation of MnO_2 could also be due to the oxidation of PCE and samples from the clay matrix demonstrated that PCE was oxidized by MnO_4^- in the areas where the inward diffusion of MnO_4^- had reached (referred to as the oxidation front in Figure 14).

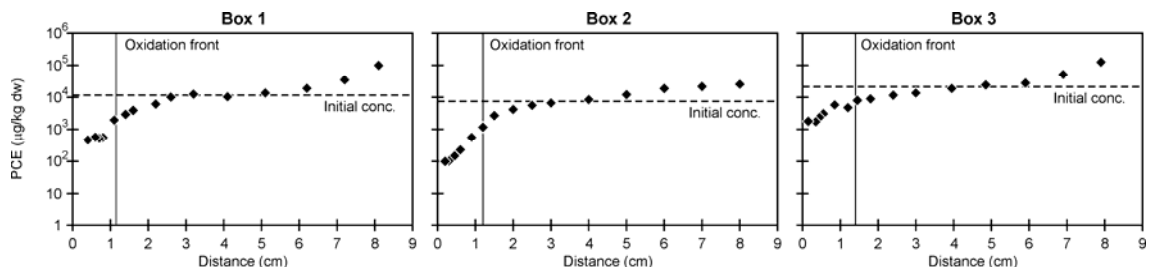


Figure 14. Concentration of PCE in a clay matrix after cessation of MnO_4^- flow. The dotted line, indicate the initial PCE concentration. Modified from Hønning et al. (II, 2007b).

The study by Hønning et al. (II, 2007b) showed that the concentration of PCE was affected beyond the front of the inward diffused MnO_4^- , but also that some PCE was present in the treated area suggesting that back diffusion of PCE had taken place. Back diffusion was also seen in core samples from a field observation (II, Hønning et al., 2007b), as illustrated in **Figure 15**.

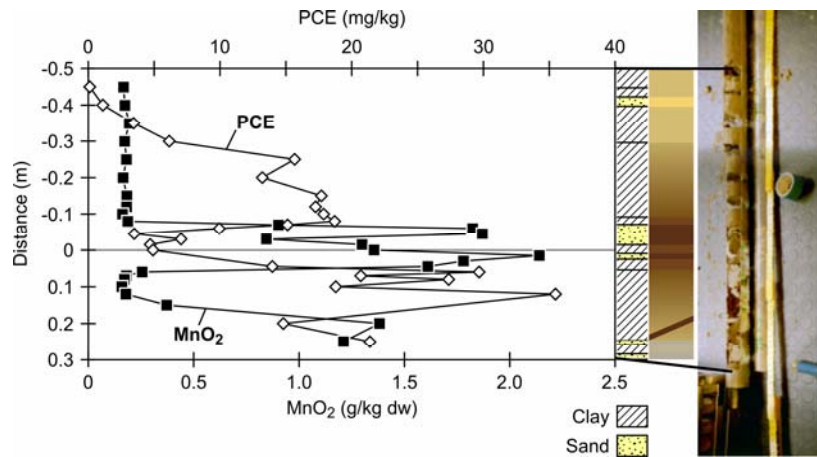


Figure 15. PCE and MnO_2 profiles for core samples from the reduced clayey till. Color and geological profiles are shown to the right. Modified from Hønning et al. (II, 2007b).

The illustrated profile shows an oxidation front going from the interbedded sand lenses out to the adjacent clayey till. High concentrations of PCE (30 mg/kg) are observed in the clayey till not affected by MnO_4^- and distinctly lower concentrations within the oxidation front (**Figure 15**). However PCE concentrations within the oxidation front were still relatively high, indicating rebound of PCE from the clayey till into the sand lens, similar to a study by (Chapman and Parker, 2005 that reported back diffusion of TCE from a clay silt aquitard into an aquifer.

8. Conclusions and perspectives

Groundwater contamination by chlorinated solvents, particularly PCE and TCE is widespread. The large extent of groundwater contamination with these compounds has led to use of various innovative remediation technologies. Application of ISCO using MnO_4^- has been proven effective in remediating contaminated sites although this is not always enough to reach regulatory goals.

The experience with applications of ISCO in low permeable media is limited as is the knowledge of the governing processes in these media. ISCO performance may be impaired by consumption of MnO_4^- from reaction with a variety of non-target sedimentary reductants such as organic matter and/or inorganic species associated with subsurface material. The consumption of MnO_4^- by the sedimentary reductants is referred to as the NOD and is expressed as the mass of oxidant consumed per mass of dry solid. The complexity of the system in low permeable sediments makes it difficult to predict the effectiveness of MnO_4^- oxidation. Therefore, field investigations and experimental work is essential to understand the relative importance of the transport and oxidation processes.

This thesis focused on the use of ISCO with MnO_4^- in clayey till with sand lenses contaminated with PCE. A broad array of experimental approaches has been used in order to examine the transport and oxidation processes during chemical oxidation and to evaluate the applicability of ISCO with MnO_4^- for the removal of PCE in heterogeneous low permeable media, involving both batch and two-dimensional box experiments, as well as core samples from a field investigation.

The main conclusions that can be drawn from this study are:

- 1) The long term consumption of MnO_4^- and oxidation of PCE can not be described by a single rate constant. In the first hours of reaction a first order reaction can be applied. The short term first order rate constants for consumption of MnO_4^- and oxidation of PCE are 0.05-0.5 hours⁻¹ and 0.5-4.5 hours⁻¹, respectively.
- 2) The sediment does not act as an instantaneous sink for MnO_4^- . The consumption of MnO_4^- by reaction with the sedimentary reductants is the result of several parallel reactions, during which the reaction between the contaminant and MnO_4^- also takes place. Dissolved PCE in concentrations up to 100 mg/l in the investigated sediments is not a significant factor in the measured MnO_4^- consumption, suggesting that the total oxidant demand (TOD) can be considered equivalent with the NOD for dissolved PCE. Hence, application of low MnO_4^- concentrations can cause partly oxidation of PCE, as the oxidant demand of the sediment does not need to be met fully before PCE is oxidized.

- 3) Typical levels for the natural oxidant demand in Danish subsurface materials have been established. The NOD for sandy aquifer sediments are 0.5-2 g MnO_4^- /kg dw, 1-8 g MnO_4^- /kg dw for sandy till and 5-20 g MnO_4^- /kg dw for clayey till. However, the total MnO_4^- consumption increases with a higher initial MnO_4^- concentration for all sediment types, which implies that a fixed NOD value can not be assigned to any sediment.
- 4) Both organic and inorganic species contribute to the NOD. Organic carbon is found to be the primary reactive species with regards to the total MnO_4^- consumption in the reaction with the sediment. However, inorganic species such as Fe^{2+} can contribute to the consumption of MnO_4^- in some cases, dependent on the clay minerals present in the sediment.
- 5) Diffusion of MnO_4^- into low permeable media has been shown to take place. However, the rate of oxidant loss to NOD is large relative to the rate of diffusion of MnO_4^- into the clay, and hence retards the extent of oxidant penetration in clay media. The oxidation of PCE in the area treated by the inward diffusion of MnO_4^- has been demonstrated. However, a rebound or back diffusion of PCE is observed when MnO_4^- has been depleted.

In general, the experiments conducted and the literature reviewed suggests that *in situ* chemical oxidation is a feasible remediation technology in low permeable media, such as clayey till. However, there are several challenges if ISCO is to be applied in low permeable media, such as the high oxidant demand from the sediment, the possible permeability loss from formation of MnO_2 and CO_2 and the diffusion processes. The experimental results have underlined the necessity of shifting the focus from the contaminant to the contribution of the sedimentary reductants, as the NOD must be considered in the design of field scale remediation of sediments contaminated with chlorinated solvents. In this regard laboratory scale batch and column experiments should always be conducted with relevant MnO_4^- concentrations in order to quantify the MnO_4^- consumption in soil/water systems, especially in silty and clayey sediments which exert a high oxidant demand.

Even though the diffusion process have been shown to take place for both MnO_4^- and PCE, the findings have shown that it is difficult to quantify the oxidation of PCE in the low permeable media and especially to determine whether a decrease in the PCE concentration in the soil matrix is due to contaminant destruction or diffusion processes. In this context further investigations focusing on the quantification of oxidation of chlorinated solvents, for example by using isotope fractioning to document the fate of PCE or by modelling the oxidation process are recommended.

To make ISCO more effective in heterogeneous aquifers the focus should be on optimizing the contact between MnO_4^- and PCE. This could be done by taking advantage of the back diffusion of PCE into the oxidized clay and the sand, e.g. using an iterative oxidant loading approach with a low oxidant dose MnO_4^- , giving PCE time to diffuse out from the low permeable media. Another approach could be shortening the distance between sand lenses and fractures, thereby minimizing the diffusion distance required, e.g. by fracturing as a tool for opening or extending and enlarging existing fractures and introducing new fractures (Siegrist et al., 1999; Riis et al., 2006).

Successful remediation can be difficult to achieve with a single remediation technology, due to the nature of the contaminants or the complexity of the subsurface. Thus, recent research has focused on the sequential use of multiple remediation technologies; “treatment trains” (Roote, 2003) in connection with the application of ISCO (ITRC; 2005; USEPA, 2006). For example, the use of bioremediation after using chemical oxidation (Hrapovic et al., 2005; Palmroth et al., 2006) or thermal treatment (Friis et al., 2006). Studies have shown that suitable conditions for biological treatment can be present after oxidation with MnO_4^- (Balba et al., 2002; Hrapovic et al., 2006; Taege et al., 2006). Hence the advantages and prospects of using chemical oxidation as the first step in a treatment train should be investigated by further research.

9. References

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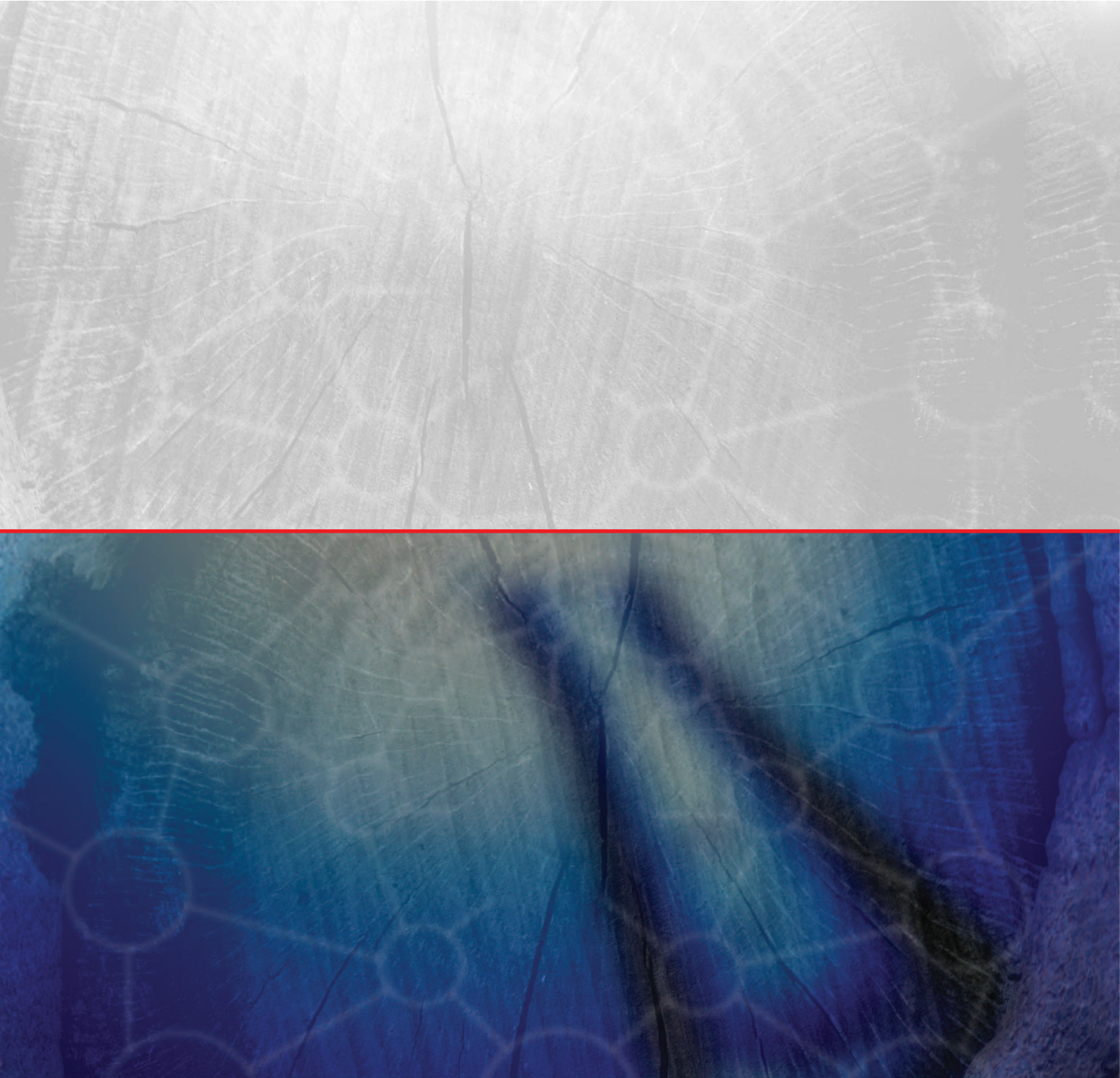
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Appendices

- I **Hønning, J.**, Broholm, M.M., Bjerg, P.L. Quantification of potassium permanganate consumption and PCE oxidation in subsurface materials. *Journal of Contaminant Hydrology, Vol. 90, pp. 221-239.*

- II **Hønning, J.**, Broholm, M.M., Bjerg, P.L. The role of diffusion in chemical oxidation of PCE-contaminated clayey till with interbedded sand lenses. *Submitted manuscript.*

- III **Hønning, J.**, Bender Koch, C., Bjerg, P.L. The role of Fe(II) in layer silicates on the consumption of MnO_4^- by subsurface materials during chemical oxidation. *Manuscript.*

A microscopic image of plant tissue, showing a network of veins and circular structures. A red horizontal line is drawn across the middle of the image.

Institute of Environment & Resources

Technical University of Denmark
Bygningstorvet, Building 115
DK-2800 Kgs. Lyngby

Phone: +45 4525 1600
Fax: +45 4593 2850
e-mail: reception@er.dtu.dk

Please visit our website www.er.dtu.dk

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