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Activated Peroxygens for Remediation of Contaminated Soil and Groundwater

Ph.D. thesis

Submitted by

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to the Faculty of Engineering and Science, Aalborg University
for the degree of Doctor of Philosophy

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**ABSTRACT**

The present thesis consists of an extended summary of the subject “activated peroxygens for remediation of contaminated soil and groundwater” along with 5 papers describing part of the work carried out in the Ph.D. project.

Today soil and groundwater contamination is a widespread and challenging problem threatening groundwater resources throughout the world. In Europe alone more than 250,000 contaminated sites requiring some form of remediation have been identified. Since none of these sites are identical with regards to type of contaminant, geology, hydrogeology and geochemistry, several different remediation technologies have been developed and are still being refined by scientists and engineers. In the 1990’s the first reports on in situ chemical oxidation (ISCO) for remediation were published. These techniques involves introduction of chemical oxidants primarily permanganate, hydrogen peroxide, ozone or persulfate into the subsurface in order to transform contaminants into less harmful compounds.

The use of activated peroxygens (hydrogen peroxide and persulfate) for ISCO holds promise for rapid destruction of a wide range of dissolved, sorbed and non-aqueous phase liquid (NAPL) organic contaminants in soil and groundwater. These peroxygen ISCO technologies includes modified Fenton’s reagent (MFR) and activated sodium persulfate (ASP) as the most widely applied. In MFR, decomposition of hydrogen peroxide is catalyzed by soluble iron or naturally occurring subsurface minerals to produce reactive species including the hydroxyl radical, perhydroxyl radical and superoxide, providing an almost universal treatment mixture. In ASP, the peroxodisulfate anion needs to be activated by e.g. iron, heat, UV or alkaline pH to produce reactive oxygen species, primarily sulfate radicals. MFR and ASP are similar in many ways, but each technique has its advantages and disadvantages.

The present Ph.D. thesis deals with several aspects within the use of activated peroxygens for remediation of contaminated soil and groundwater. The Industrial Ph.D. project was carried out with Rambøll Danmark A/S and Aalborg University with involvement of several other companies and Danish authorities. The experimental work focused on testing the effectiveness of the technique towards organic contaminants, investigating the mobilization of metals during treatment and to determine the influence of chloride and carbonates on the processes. A major part of the project was based on laboratory and field tests involving the largest contaminated site in Denmark, Kærgård Plantation, which is also considered one of the most difficult remediation challenges in Scandinavia.
MFR was tested in laboratory tests and at five different fuel oil contaminated sites. The results demonstrated that residual free phase fuel oil could be degraded with MFR and site closure was obtained at three sites treated in full scale. In all cases the reactions were controllable with temperatures increasing no more than 10 °C. Significant effects on pH, oxidation reduction potential and dissolved oxygen were observed and persisted for more than 200 days after treatment when monitoring was stopped. Bacteria in the groundwater were reduced by 4 orders of magnitude, but started increasing significantly shortly after treatment.

MFR and ASP were compared in a bench scale study with contaminated soil and groundwater from Kærgård Plantation. Both oxidants were able to degrade residual free phase perchloroethylene (PCE) in soil slurry experiments and the most efficient activation of persulfate was obtained by MFR activation. Also both oxidants were stable in the presence of subsurface solids but their half-lives were significantly decreased when they were activated. The low buffered soil and groundwater resulted in significant pH changes from 5.7 to 1.0 for the ASP and 2.5 for the MFR. MFR activated persulfate could efficiently degrade aniline, pyridine, sulfonamides, barbiturates, petroleum hydrocarbons, benzene, toluene, trichloroethylene (TCE), and PCE in the aqueous phase.

Based on the laboratory tests, MFR was tested in pilot scale in Kærgård Plantation. Average soil concentrations of PCE were reduced from 3,100 mg/kg to 1,600 mg/kg with a total dose of 14 g H$_2$O$_2$/kg soil injected over 4 injection events. Similar degrees of destruction were obtained for TCE, toluene and benzene, although start concentrations were lower. After MFR pH was 2-3 in the treatment zones and redox potential was about +300 mV. These extreme conditions were stable for months, but by adding of a buffer (carbonate/hydrogen carbonate) and electron donor (Newman zone, emulsified soybean oil) conditions were rapidly and easily converted to conditions favorable for biological remediation with enhanced reductive dechlorination (ERD). Signs of reductive dechlorination were observed shortly after addition of electron donor and subsequent bioaugmentation the dechlorination rate increased significantly demonstrating that ERD with bioaugmentation as a second step in a treatment train after MFR in source zones is a promising remediation approach that warrant further exploration.

Metal mobilization was investigated in batch and column experiments as well as in field scale tests. Significant mobilization of metals from low buffered soils was demonstrated during treatment with activated peroxygens, e.g. lead concentrations 34,000 times above the quality criteria for groundwater were observed in the treatment area, but could not be found downgradient the treatment zone. Results with MFR indicated that low pH and the use of chelating agents for the iron catalyst could
only account for a small increase in metal concentrations. It is believed that the most significant processes causing the mobilization is redox reaction involving the reactive species generated in ASP and MFR and possible also formation of small organic acids as a result of oxidation that will chelate and mobilize metals.

Chloride and carbonates have the potential to impact pathway, kinetics, and efficiency of oxidation reactions both as radical scavengers and as metal complexing agents. Traditionally, it is assumed that they have an overall negative impact on the performance of activated peroxygens, but results from this study showed that enhanced reactivity was obtained with both chloride and carbonates when degrading the model compound p-nitrosodimethylaniline with heat and alkaline activated persulfate. It was also showed that the overall oxidation efficiency was unaffected for destruction of PCE with iron activated persulfate even though reaction rates decreased with increasing chloride concentration. It is not known if the enhanced effect is caused by direct attack of produced reactive chlorine and carbonate species or by catalysis of the propagation reactions resulting in more sulfate radicals. These results indicate that carbonate and chloride might play an important role in activated persulfate systems and should not strictly be considered as scavengers.

Overall, the findings from the project demonstrate the potential of aggressive ISCO technologies with activated peroxygens for treating complex contaminants mixture in source zones including NAPLs. There are still many unknown processes involved and reactions taking place in situ when these technologies are applied, but these years a lot of effort is put into understanding these in details, which is believed to increase the success rate for future full scale remediation with activated peroxygens.
SYNOPSIS

Denne Ph.d.-afhandling er opbygget som en sammenfatning af emnet ”Aktiverede peroxygener til oprensning af forurenet jord og grundvand” samt 5 artikler, som dækker en del af arbejdet udført i Ph.d.-projektet.

Forurening af jord og grundvand er i dag et omfattende problem som bl.a. truer grundvandsressourcer i hele verden. Alene i Europa er der på nuværende tidspunkt identifieret mere end 250.000 forurene lokale lokaliteter, hvor oprensning er påkrævet. Da ingen forurene lokale lokaliteter er ens mht. type af forurening, geologi, hydrogeologi og geokemi, er der udviklet en lang række forskellige biologiske, fysiske og kemiske oprensningsteknikker. I 1990’erne blev de første rapporter udgivet omkring in situ kemisk oxidation (ISCO) til oprensning af forurenet jord og grundvand. Disse teknikker fungerer alle ved at introducere kemiske oxidanter (primært permanganat, hydrogenperoxid, ozon eller persulfat) direkte til det forurenede område i jorden for at nedbryde forureningskomponenterne til uskadelige stoffer.


MFR blev afprøvet i laboratoriet og på 5 lokaliteter forurenet med fyringsolie. Testene viste, at MFR var i stand til at nedbryde residual fri fase fyringsolie og at reaktionerne i alle tilfælde var kontrollable med maksimale temperaturstigninger på 10 °C. Der blev observeret signifikante og vedblivende (>200 dage) effekter på pH, redox potentiale og opløst ilt i behandlingsområderne. Det blev desuden vist, at MFR reducerede antallet af bakterier i grundvandet med 4 størrelsesordener, men at antallet steg kraftigt igen efter MFR.

MFR og ASP blev sammenlignet i laboratoriestudier med kraftigt forurenet jord og grundvand fra Kærgård Plantage. Begge teknikker var i stand til at nedbryde residual fri fase tetraklorethylen (PCE) i slurrytests og baseret på disse tests blev den mest effektive aktivering af persulfat opnået ved at aktivere med MFR. Både hydrogenperoxid og persulfat var relativt stabile ved tilstedeværelsen af forurenet jord, men halveringstiden blev nedsat markant når oxidanterne blev aktiverede. Den lavere bufferkapacitet i jord og grundvand resulterede i et væsentligt fald i pH fra 5,7 til 1,0 for ASP og til 2,5 for MFR. MFR aktiveret persulfat kunne effektivt nedbryde både anilin, pyridin, sulfonamider, barbiturater, totalkulbrinter, benzen, toluen, triklorethylen (TCE) og PCE i vandfasen.

Baseret på laboratorietestene blev der udført et pilotforsøg med MFR i Kærgård Plantage. Her blev koncentrationer af PCE i jorden nedbragt fra 3.100 mg/kg til 1.600 mg/kg med en total dosis svarende til 14 g H₂O₂/kg jord injiceret over 4 injektionsrunder. Lignende nedbrydning blev observeret for TCE, benzen og toluen, dog var startkoncentrationerne her væsentligt lavere. Efter MFR var pH 2-3 og redox potentialet omkring +300 mV, og forholdene var stabile i måneder, men ved at tilsætte buffer (karbonat/bikarbonat) og en elektron donor (Newman zone, emulgeret sojabønne olie) kunne betingelserne hurtigt og nemt vendes til gunstige forhold for stimuleret reduktiv deklorering (SRD). Efter tilsætning af elektron donor blev der hurtigt observeret tegn på begyndende deklorering, og efter tilsætning af bakterier og yderligere elektrondonor steg nedbrydningshastigheden markant og meget høje koncentrationer af nedbrydningsproduktet cis-1,2-diklorethylen blev observeret. Dette viser, at SRD som andet trin i en oprensning efter anvendelse af aggressiv kemiske oxidation med aktiverede peroxygener er en lovende teknologi, som bør undersøges nærmere.

Metalmobilisering fra jord behandlet med aktiverede peroxygener blev undersøgt i batch, kolonne og feltforsøg. Der blev i alle tilfælde observeret en væsentlig mobilisering af metaller, når der blev anvendt jord og vand med lav bufferkapacitet. Bl.a. blev der måle koncentrationer af opløst bly 34.000 gange over grundvandskvalitetskriteriet i behandlingsområdet, men nedstrøms kunne metallerne ikke genfindes. Lav pH og anvendelsen af kompleks bundnede katalysatorer kunne kun
tilskrives en mindre del af mobiliseringen ved anvendelse af MFR. Resultaterne indikerer, at størstedelen skyldes en kombination af redox reaktioner evt. sammenholdt med tilstedeværelsen af små organiske syrer dannet ud fra oxidation af aromatiske forbindelser, som muligvis kan kompleksbinde metaller og dermed holde disse i oplosning.


Overordnet har resultaterne fra Ph.d.-projektet demonstreret potentialet for aktiverede peroxygener som aggressive teknologier til oprensning af komplekst og stærkt forurenet jord og grundvand. Der er stadig mange ukendte processer involveret i teknologierne og yderligere forskning skal være med til at fremme procesforståelsen for derved at øge sandsynligheden for flere succesfulde anvendelser i fuldska. 
PREFACE

This thesis is submitted in partial fulfillment of the requirements for the Ph.D. degree at Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Denmark. The Ph.D. project was carried out in the period May 2008 to April 2011 under the Industrial Ph.D. program and the work was partly funded by Rambøll Danmark A/S and the Danish Agency for Science, Technology and Innovation. The main supervisors were associate professor Erik G. Søgaard from CIChem research group, Section of Chemical Engineering, Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University and head of department Lars Mortensen and senior chief consultant Torben H. Jørgensen from Rambøll Danmark A/S.

Research under the Industrial Ph.D. program has to be business-oriented and hence the focus of this present project was the applied part of the investigated processes combined with some detailed investigation of selected issues. This also meant that much time was spend on designing pilot tests, establishing test-setup in the field, conducting extensive monitoring and writing report. This work has been very educating, but will not be included in the present thesis.

The present thesis is composed of 5 supporting papers and an extended summary of research conducted in this Ph.D. study. The summary highlights the most significant results achieved and relates the findings to the current state-of-the-art as well as introduces background knowledge on the investigated issues.
ACKNOWLEDGMENTS

I would like to thank Rambøll Danmark A/S, Aalborg University and the Danish Agency for Science, Technology and Innovation under the Ministry of Science, Technology and Innovation for granting me the opportunity to do this Industrial Ph.D. work. First of all, I would like to thank my supervisors at Rambøll Danmark A/S, head of department Lars Mortensen and senior chief consultant Torben H. Jørgensen, for help and guidance during the work and for the opportunity to participate in different exciting and innovative projects which resulted in essential practical and theoretical experience. I look forward to continue in this field of work. I would also like to thank all my good colleagues at the office in Vejle and especially Morten for helping with several practical matters during pilot tests.

At Aalborg University, Esbjerg, my main supervisor associate professor Erik G. Søgaard provided enthusiastic and committed guidance throughout the Ph.D. project and several projects during my bachelor and master study. Special thanks go to my friend and office mate Jens for helping with all possible matters including scientific discussions, reviewing manuscripts and this thesis, solving all sorts of problems, etc. for almost 9 years. It’s been a pleasure working with the CIChem group and Dorte, Linda, Vivi and Heidi provided valuable help with analytical and experimental work in the laboratories. Anne and Krzysztof performed interesting student projects which were of value for the Ph.D. project. Also professor Jan Skov Pedersen from Interdisciplinary Nanoscience Center, Aarhus University, was involved as a third party supervisor. I also had the pleasure of being involved in a Remtec project with Arno Rein, Kresten Ole Kusk and Poul L. Bjerg from the Technical University of Denmark.

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Finally, I would like to thank my friends and family for their encouragement and support of my work throughout the last three years. Special tanks go to to Karina for her patience and understanding during the final stages of this work and for taking loving care of our son Mads.

Esbjerg, May 2011, Lars Bennedsen
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LIST OF SUPPORTING PAPERS

I. Bennedsen, LR & Søgaard, EG, 'Simple Spectrophotometric Determination of Peroxygens in the Field during ISCO'. *Groundwater Monitoring and Remediation* (accepted 2011)


The papers are enclosed at the end of the thesis. Supporting papers will be referred to by their roman numbers, e.g., Paper II.

Full publication list can be found in section 9.
ABBREVIATIONS

AOP Advanced oxidation processes
ASP Activated sodium persulfate
Bgs Below ground surface
BTEX Benzene, toluene, ethylbenzene and xylenes
CHP Catalyzed hydrogen peroxide propagation
cis-DCE cis-1,2-Dichloroethylene
COC Contaminants of concern
DO Dissolved oxygen
DNAPL Dense non-aqueous phase liquids
ERD Enhanced reductive dechlorination
ISCO In situ chemical oxidation
m bgs Meters below ground surface
MFR Modified Fenton’s reagent
MFSP Modified Fenton’s activated sodium persulfate
MNA Monitored natural attenuation
NAPL Non-aqueous phase liquid
NOM Natural organic matter
ORP Oxidation reduction potential
PAH Polycyclic aromatic hydrocarbons
PCE Perchloroethylene
PCB Polychlorinated biphenyl
RNO p-nitrosodimethylaniline
ROI Radius of influence
TCE Trichloroethylene
TOD Total oxidant demand
TPH Total petroleum hydrocarbons
VC Vinyl chloride
1 INTRODUCTION

1.1 SOIL AND GROUNDWATER CONTAMINATION

Freshwater comprises only 3% of the all water on Earth and around 20% of this small fraction occurs as groundwater, which is a critical resource throughout the world because of its use as drinking water, for agricultural application, for irrigation of crops and for industrial activities. Groundwater serves as a significant source of drinking water ranging from 15% in Australia to 75% in Europe [1]. In Denmark close to 100% of the drinking water originates from groundwater.

Today soil and groundwater contamination is a widespread and challenging problem threatening groundwater resources throughout the world. The contamination originates from introduction of xenobiotic chemicals to the environment or from naturally occurring sources and the most common chemical contaminants found in the environment are petroleum hydrocarbons, solvents, coal tar, heavy metals and pesticides. An overview of contaminants affecting soil and groundwater in Europe is given in Figure 1-1. The contamination originates from a broad range of sources with landfills, above/underground storage tanks, septic systems, dry cleaners and industrial facilities being among the frequent sources, see more details in Figure 1-2.

FIGURE 1-1: OVERVIEW OF MAIN CONTAMINANTS AFFECTING SOIL AND GROUNDWATER IN EUROPE SHOWN AS PERCENTAGE OF CONTAMINATED SITES. DATA FROM [2].

<table>
<thead>
<tr>
<th>Country</th>
<th>Main Contaminants [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulgaria</td>
<td>Chlorinated Hydrocarbons, Mineral oil</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Chlorinated Hydrocarbons, Mineral oil, Polycyclic Aromatic Hydrocarbons (PAH)</td>
</tr>
<tr>
<td>Belgium</td>
<td>Chlorinated Hydrocarbons, Mineral oil, Polycyclic Aromatic Hydrocarbons (PAH)</td>
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<td>Sweden</td>
<td>Chlorinated Hydrocarbons, Mineral oil, Polycyclic Aromatic Hydrocarbons (PAH)</td>
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<td>Norway</td>
<td>Chlorinated Hydrocarbons, Mineral oil, Polycyclic Aromatic Hydrocarbons (PAH)</td>
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<td>Estonia</td>
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<td>Austria</td>
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<td>Denmark</td>
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<td>Italy</td>
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<tr>
<td>Czech Republic</td>
<td>Chlorinated Hydrocarbons, Mineral oil, Polycyclic Aromatic Hydrocarbons (PAH)</td>
</tr>
</tbody>
</table>
In North America and Western Europe most countries have a legal framework to identify and deal with these issues. In the United States alone there are estimated to be in excess of 200,000 sites requiring some form of remediation [3]. In Europe this number is approximately 250,000 sites in the European Environmental Agency (EEA) member countries and the number is expected to grow. Potentially polluting activities are estimated to have occurred at nearly 3 million sites in Europe (including the 250,000 sites already mentioned) and investigation is needed to establish whether remediation is required. If current investigation trends continue, the number of sites needing remediation will increase by 50% in 2025. By contrast, more than 80,000 sites have been cleaned up in the last 30 years in the countries where data on remediation is available [2]. In Denmark around 24,000 sites have been identified as definitely or potentially contaminated and remediation at 122 of these sites were in 2007 estimated to cost more than 10 million DKK each [4].

1.2 REMEDIATION TECHNOLOGIES

Contamination of the subsurface by persistent organic contaminants remains a significant problem, even after decades of research on remediation technologies [5, 6]. New types of remediation technologies and modifications of existing technologies are continuously developed by scientists and engineers. First approaches for remediation focused on excavation, pump-and-treat via activated carbon, bioremediation, and natural attenuation. In the 1990ties the first reports on in situ chemical oxidation
(ISCO) were published. An overview of the different types of remediation technologies divided into three major categories is presented in Figure 1-3.

![Diagram of Remediation Technologies](image)

**FIGURE 1-3: OVERVIEW OF REMEDIATION TECHNOLOGIES DIVIDED INTO THREE MAJOR CATEGORIES.**

Only the technologies listed under "Degradation" in Figure 1-3 will result in degradation of the hazardous contaminants and hence eliminate the toxicity and because of this, these technologies should be the preferred. In practice these treatment technologies are often complex to control and it is difficult to predict the outcome. Consequently, excavation and other low-tech methods are still the far most frequently applied remediation technologies. Very often remediation consists of a combination of containment, removal and degradation technologies.

No contaminated sites are identical with respect to type of contaminant, geology, hydrogeology and geochemistry and therefore, all the mentioned remediation technologies still play important roles. However, some contaminations are too complex to be remediated cost-effectively with the technologies available today, and therefore further improvements of existing techniques and development of new techniques are still needed. An important task in the present Ph.D. work was to gain a better understanding of the processes occurring in situ in the contaminated soil and
groundwater. One of the newer technologies attracting a lot of interest and possessing a great potential is ISCO.

1.3 IN SITU CHEMICAL OXIDATION (ISCO)

ISCO is a technology involving the introduction of chemical oxidants into the subsurface in order to transform contaminants into less harmful compounds. Hydrogen peroxide was the first chemical oxidant investigated and used for full scale treatment. Shortly after ozone and permanganate came into use. In the past few years persulfate, percarbonate and other peroxygens have provided more options.

The use of permanganate for ISCO is considered an almost fully developed technique, is relatively easy to apply compared to other oxidants and has been used at numerous sites with well-documented results. Hydrogen peroxide has also been deployed at a large number of sites. However, the use of this oxidant is much more complex because of the numerous reactive intermediates and mechanisms occurring in the subsurface, which makes the process difficult to control and predict in the field. Ozone has only been used in a much more limited number of applications. Persulfate has, during the last 5-10 years, been used in an increasing number of full scale remediation projects [7].

Since no sites are identical, site specific conditions regarding contaminant, geology, hydrogeology and geochemistry always have to be taken into consideration and evaluated in order to decide the remediation approach and technique to be used. This also means that there is no universal ISCO technique that will be useful at every site. ISCO for site remediation provides some advantages, but as most technologies; ISCO has limitations that should be recognized. When facing a remediation, it is important to screen if ISCO is an option for the site. Development of a comprehensive technology practices manual, including protocols and tools, to enable site-specific engineering of ISCO is almost finished [8].

1.4 RESEARCH OBJECTIVES

The Kærgård Plantation megasite provided the fundamental basis of the research presented in this thesis. This site represents one of the most difficult remediation challenges in Scandinavia and therefore regulatory agencies in Denmark are now in the process of evaluating remediation techniques for source area remediation at the site. As there is no precedent for treating this type of complex pharmaceutical waste mixture, containing sulfonamides, barbiturates, aniline, pyridine, chlorinated solvents, mercury, cyanide and several other contaminants, the feasibility of a variety of in situ remediation technologies are being evaluated, including biological, chemical, and
thermal techniques. This Ph.D. study focused on investigating the applicability of modified Fenton’s reagent (MFR) and activated sodium persulfate (ASP) through laboratory experiments and pilot tests at the site. Since the Ph.D. thesis was written as part of the Industrial Ph.D. program (50/50 division between a university and a private company), the research focused on the application (engineering) part of ISCO rather than the fundamental processes involved. The overall objectives of the research were to:

- Collect general knowledge through literature review, laboratory test and field test with MFR and ASP and disseminate this knowledge in order to obtain more understanding, acceptance and widespread use of the techniques in full scale focusing on Denmark
- Evaluate and compare the applicability of MFR and ASP to treat a complex mixture of pharmaceutical and other contaminants including residual free phase contamination (section 4)
- Investigate the extent of metal mobilization during ISCO (section 5) and
- Investigate the influence of carbonates and chloride on the oxidation processes (section 6)

More specific objectives for the above points will be reviewed in the relevant sections.

1.5 STRUCTURE AND CONTENT

The present thesis is organized as 5 journal papers together with an extended summary of research conducted in this Ph.D. study. The summary highlights the most significant results achieved and relates the findings to the current state-of-the-art. It is mainly based on results presented in paper I-V, but is supplemented with more extensive background knowledge on the fundamentals of ISCO and incorporates additional unpublished data from laboratory studies and field tests performed as part of the Ph.D. study at different test sites.
2 FUNDAMENTALS OF ISCO

In oxidative treatment systems, numerous reactions could potentially occur, including acid/base reactions, adsorption/desorption, dissolution, hydrolysis, ion exchange, oxidation/reduction, precipitation, etc. [9]. All of these reactions can make ISCO a challenging technique to apply in field scale. In the following sections chemical oxidation focusing on hydrogen peroxide and persulfate applied for soil and groundwater remediation are reviewed.

2.1 CHEMICAL OXIDATION

All of the ISCO technologies are based on the oxidative power of specific chemicals (oxidants) and the strength of the oxidants can be compared based on their standard reduction potential $E_0(V)$ as shown in Table 2-1. This potential is also known as the oxidation/reduction potential (ORP) and is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. The standard hydrogen electrode (SHE) is the reference from which all reduction potentials are measured and the potential of this electrode has therefore been defined as 0 V.

**TABLE 2-1: STANDARD REDUCTION POTENTIALS $E_0$ OF REACTIVE SPECIES INVOLVED IN ISCO.**

<table>
<thead>
<tr>
<th>Standard reduction potential ($E_0$)</th>
<th>Permanganate</th>
<th>Hydrogen Peroxide</th>
<th>Ozone</th>
<th>Persulfate</th>
<th>Other oxidants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>$\text{MnO}_4^- + 4\text{H}^+ + 3e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$</td>
<td>1.68 V</td>
<td>$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.78 V</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>$2\text{HO}^* + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>2.76 V</td>
<td>$\text{HO}_2^- + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.7 V</td>
<td>$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>$\text{HO}_2^- + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>2.76 V</td>
<td>$\text{HO}_2^- + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.7 V</td>
<td>$\text{HO}_2^- + 2\text{e}^- \rightarrow 3\text{OH}^-$</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>$2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2\text{O}$</td>
<td>-0.88 V</td>
<td>$\text{HO}_2^- + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.7 V</td>
<td>$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$</td>
</tr>
<tr>
<td>Ozone</td>
<td>$2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2\text{O}$</td>
<td>2.08 V</td>
<td>$\text{O}_3 + 2\text{H}^+ + 2e^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$</td>
<td>2.08 V</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Persulfate</td>
<td>$\text{HSO}_3^- + 2e^- + 2\text{H}^+ \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$</td>
<td>1.82 V</td>
<td>$\text{SO}_4^{2-} + e^- \rightarrow \text{SO}_4^{2-}$</td>
<td>2.6 V</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Persulfate</td>
<td>$\text{HSO}_3^- + 2e^- + 2\text{H}^+ \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$</td>
<td>1.82 V</td>
<td>$\text{HSO}_5^- + 2e^- \rightarrow \text{SO}_4^{2-}$</td>
<td>2.6 V</td>
<td>$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$</td>
</tr>
<tr>
<td>Persulfate</td>
<td>$\text{S}_2\text{O}_8^{2-} + 2e^- \rightarrow 2\text{SO}_4^{2-}$</td>
<td>2.01 V</td>
<td>$\text{SO}_4^{2-} + e^- \rightarrow \text{SO}_4^{2-}$</td>
<td>2.6 V</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Persulfate</td>
<td>$\text{S}_2\text{O}_8^{2-} + 2e^- \rightarrow 2\text{SO}_4^{2-}$</td>
<td>2.01 V</td>
<td>$\text{SO}_4^{2-} + e^- \rightarrow \text{SO}_4^{2-}$</td>
<td>2.6 V</td>
<td>$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$</td>
</tr>
<tr>
<td>Persulfate</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.23 V</td>
<td>$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$</td>
<td>1.36 V</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Persulfate</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.23 V</td>
<td>$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$</td>
<td>1.36 V</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

Even though the standard reduction potentials of the oxidants presented in Table 2-1 are high enough to oxidize most organic contaminants, these potentials do not indicate how the oxidants will perform under field conditions. Four major factors determine whether success will be obtained in the field; kinetics, thermodynamics, stoichiometry, and contact between oxidant and contamination. The reactions might be thermodynamically favorable based on standard reduction potentials, but under field
conditions, the reaction rates can be very slow since they are dependent on several variables such as temperature, pH, concentrations of reactants, catalyst, reaction by-products, natural organic matter (NOM), oxidant scavengers, etc. [3].

The present research focused on hydrogen peroxide and persulfate. Both oxidants have an oxygen-oxygen single bond (peroxy group) and therefore belong to the group of peroxygens. The oxygen atoms in the peroxy group are in oxidation state -1 and the oxygen-oxygen bond is unstable and splits easily into other reactive species. Several different forms of peroxygens exist, e.g. peroxides, persulfate, percarbonate, perborate, and perphosphate. It should be noted that permanganate and perchlorate are not peroxygens. In Table 2-2 an overview of some of the peroxygens used for ISCO and examples of suppliers with product names is given. When the term persulfate is used in this thesis it refers to peroxodisulfate.
TABLE 2-2: OVERVIEW OF PEROXYGENS USED FOR REMEDIATION.

<table>
<thead>
<tr>
<th>Compound and supplier</th>
<th>Structure</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrogen peroxide</strong></td>
<td>( \text{H}_2\text{O}_2 )</td>
<td>Solid peroxide. Insoluble in water but will slowly release oxygen at their natural pH&gt;10: ( \text{MgO}_2 + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \frac{1}{2}\text{O}_2 ). Lower pH (below natural pH 10) ( \Rightarrow ) more ( \text{H}_2\text{O}_2 ) is produced. The active oxygen can be liberated within minutes in acid: ( \text{MgO}_2 + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2\text{O}_2 ).</td>
</tr>
<tr>
<td><strong>Magnesium peroxide</strong></td>
<td>( \text{MgO}_2 )</td>
<td>[\text{Cool-Ox}^\text{TM}, \text{DeepEarth Tec.}] [\text{ORC}^\text{®}, \text{Regenesis}] [\text{IXPER}^\text{® M}, \text{Solvay}] Solid oxide. Insoluble in water but will slowly release oxygen at their natural pH&gt;10: ( \text{MgO}_2 + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \frac{1}{2}\text{O}_2 ). Lower pH (below natural pH 10) ( \Rightarrow ) more ( \text{H}_2\text{O}_2 ) is produced. The active oxygen can be liberated within minutes in acid: ( \text{MgO}_2 + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2\text{O}_2 ).</td>
</tr>
<tr>
<td><strong>Calcium peroxide</strong></td>
<td>( \text{CaO}_2 )</td>
<td>Same as above</td>
</tr>
<tr>
<td><strong>Sodium peroxodisulfate</strong></td>
<td>( \text{Na}_2\text{S}_2\text{O}_8 )</td>
<td>[\text{Klozur}^\text{TM}, \text{FMC}] Same as above</td>
</tr>
<tr>
<td><strong>Potassium peroxymonosulfate</strong></td>
<td>( \text{KHSO}_5 )</td>
<td>[\text{Oxone}^\text{®}, \text{DuPont}] Same as above</td>
</tr>
<tr>
<td><strong>Percarbonate</strong></td>
<td>( \text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2 )</td>
<td>[\text{RegenOx}^\text{TM}, \text{Regenesis}] [\text{ENVIROFirst}^\text{TM}, \text{Solvay}] Despite the name, it is, in fact, a crystalline water-soluble chemical compound of sodium carbonate and hydrogen peroxide: ( 2(\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2) \rightarrow 2 \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2 ). Part of it reactivity might be attributed to the formation of “true” percarbonate [10]: ( \text{HCO}_3^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{HCO}_4^- + \text{H}_2\text{O} ).</td>
</tr>
</tbody>
</table>
2.2 **HYDROGEN PEROXIDE**

The use of hydrogen peroxide for soil and groundwater remediation is an extension of the advanced oxidation processes (AOP), which have been applied for years to treat different waste streams ex situ. Although hydrogen peroxide is a strong oxidant, with a standard reduction potential of 1.78 V (reaction 2.2) the rate of direct oxidation of most hazardous organics is too slow to be useful for remediation [6].

2.2.1 FENTON’S REAGENT

In order to produce more reactive oxidants, hydrogen peroxide needs to be activated. In 1894 H.J.H. Fenton discovered that addition of Fe(II) dramatically increased the oxidation rate of tartaric acid with hydrogen peroxide [11] and in 1934 it was proposed that production of hydroxyl radicals (OH•) caused this increased reactivity [12], according to the initiating reaction 2.13 known as the classical Fenton’s reaction. The Fenton’s reagent is defined as a procedure where dilute hydrogen peroxide is slowly added to a rapidly stirred, degassed Fe(II)-substrate [13]. This results in a near 1:1 conversion of hydrogen peroxide to hydroxyl radicals:

\[
H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^* + OH^- \quad (2.13)
\]

The hydroxyl radical is a short lived extremely reactive oxygen species with a high oxidation potential (2.76 V, reaction 2.3) that can rapidly degrade most organic contaminants. Hydroxyl radicals react with >95 % of contaminants of concern (COC) at near diffusion-controlled rates, i.e. \(k > 10^9 \text{ M}^{-1}\text{s}^{-1}\) [14, 15].

2.2.2 PROPAGATION AND TERMINATION REACTIONS

A classical Fenton’s system cannot be readily created in soil and groundwater since it is too difficult to maintain a well-mixed, low-concentration hydrogen peroxide system in the subsurface. In practice more concentrated solutions of hydrogen peroxide (often 2-12 %[6]) and varying types of catalyst are injected. This modified Fenton’s system is often referred to as catalyzed hydrogen peroxide propagation (CHP) or modified Fenton’s reagent (MFR). When these high concentrations are used, a series of propagation reactions starts, reaction 2.14-19:

\[
H_2O_2 + OH^* \rightarrow HO^*_2 + H_2O \quad (2.14)
\]

\[
HO^*_2 \rightleftharpoons O_2^- + H^+ \quad pK_a = 4.8 \quad (2.15)
\]

\[
HO^*_2 + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \quad (2.16)
\]

\[
RH + OH^* \rightarrow H_2O + R^* \rightarrow \text{further oxidation} \quad (2.17)
\]
Fundamentals of ISCO

\[ \begin{align*}
\text{R}^* + \text{H}_2\text{O}_2 & \rightarrow \text{ROH} + \text{OH}^* \\
\text{R}^* + \text{O}_2 & \rightarrow \text{ROO}^* \\
\text{H}_2\text{O}_2 & \rightleftharpoons \text{H}^+ + \text{HO}_2^- \quad \text{pK}_a = 11.62
\end{align*} \tag{2.18, 2.19, 2.20} \\

Chain propagating sequences generate perhydroxyl radicals (\(\text{HO}_2^*\)), superoxide radical anions (\(\text{O}_2^-\)), hydroperoxide anions (\(\text{HO}_2^-\)) and organic radicals (\(\text{R}^*\)). These propagation reactions become important when hydrogen peroxide concentrations are relatively high (>0.3M) [6]. Processes using these high concentrations are very different from the classical Fenton’s reagent because reactive species other than hydroxyl radicals are formed resulting in a wide range of reactivity. It should be noticed that although some of these reactive species (e.g., superoxide) are not very reactive in deionized water, their reactivity is significantly increased in systems that have solutes such as hydrogen peroxide, which provides a solvent effect (probably by changing its solvation shell), increasing the reactivity of superoxide [16]. Similar to the addition of solvents, it has been shown that the presence of surfaces in water-solid matrices also enhances the reactivity of superoxide in water, possibly by altering the superoxide solvation shell [17].

For years all contaminant destructions obtained with MFR was ascribed to hydroxyl radicals. It has now been demonstrated that other reactive species are involved in the processes and MFR can treat compounds such as carbon tetrachloride and chloroform that were previously considered untreated by MFR since these are unreactive with hydroxyl radicals. It was showed that a transient oxygen species other than the hydroxyl radical formed through MFR reactions was likely responsible for degradation [18, 19]. The species responsible for this destruction may be superoxide or hydroperoxide [6], both of which are produced by propagation reactions in MFR systems using relatively high concentrations of hydrogen peroxide. The propagation reactions are followed by termination reactions:

\[ \begin{align*}
\text{OH}^* + \text{Fe}^{2+} & \rightarrow \text{OH}^- + \text{Fe}^{3+} \\
2\text{OH}^* & \rightarrow \text{H}_2\text{O}_2 \\
\text{HO}_2^* + \text{Fe}^{3+} & \rightarrow \text{O}_2 + \text{Fe}^{2+} + \text{H}^+ \\
\text{HO}_2^- + \text{Fe}^{2+} & \rightarrow \text{HO}_2^- + \text{Fe}^{3+} \\
\text{R}^* + \text{OH}^* & \rightarrow \text{ROH} \\
\text{R}^* + \text{Fe}^{3+} & \rightarrow \text{R}^+ + \text{Fe}^{2+}
\end{align*} \tag{2.21, 2.22, 2.23, 2.24, 2.25, 2.26} \]
\[ R^* + Fe^{2+} \rightarrow R^- + Fe^{3+} \] (2.27)
\[ 2R^* \rightarrow R \cdot R \] (2.28)

2.2.3 Catalyst

The acidic properties of Fe(II) lower pH to 3-4 in classical Fenton’s system, when Fe(II) is added to deionized water. In soil and groundwater the effects of pH are more complicated since most of these systems possess a strong buffering capacity which will maintain pH neutral and result in iron precipitation and ineffective catalysis:

\[ Fe^{3+} + nOH^- \rightarrow amorphous iron oxide/hydroxides (precipitate) \] (2.29)

As an alternative to lowering pH in the entire treatment area to 2-4 with e.g. sulfuric acid, other methods have been used to catalyze the reaction in MFR. These include soluble iron [20-22], iron minerals [21, 23-28], and chelated iron [29-34].

For concentrations of hydrogen peroxide greater than 30mM (>1 g/l), which are often used for ISCO, iron (III) is a more effective catalyst compared to iron (II) and the reactions proceed through formation of superoxide/perhydroxyl radicals [20, 22]:

\[ H_2O_2 + Fe^{3+} + Fe-OOH^{2+} + H^+ \rightarrow Fe^{2+} + HO_2^- + H^+ \] (2.30)

The main advantages of using chelated catalysts are that the process can be conducted at neutral pH and that chelated iron may travel farther in the subsurface compared to soluble iron [6]. However, the dosage of oxidants has to be increased since MFR also oxidizes the chelating agents. It has been documented that contaminant oxidation can take place in MFR systems containing soil with naturally occurring iron oxides but no soluble iron catalyst [21]. Crystalline iron oxides like goethite are more effective catalyst compared to amorphous as ferrihydrite [25, 26, 35]. Also soluble manganese (II) and other transition metals can catalyze the Fenton’s reaction and the presence of manganese oxides (amorphous and crystalline) can catalyze the formation of reductants [36].

2.2.4 Decomposition and Transport

Besides all of the above mentioned reactions a large part of the hydrogen peroxide decomposes to molecular oxygen in contact with aquifer materials resulting in waste of oxidant when applied for ISCO:

\[ 2H_2O_2 \rightarrow 2H_2O + O_2 \] (2.31)

The successful application of hydrogen peroxide based ISCO is strongly limited by the instability of hydrogen peroxide [37, 38]. Several studies have evaluated the impact of
NOM and minerals on decomposition rates [5, 25, 27, 28, 35, 39-42]. Attempts have been done to minimize this decomposition by stabilization of hydrogen peroxide using stabilizing agents such as citrate, malonate, etc. [34, 39]. Stabilization is important in order to enhance transport of hydrogen peroxide and thereby create contact between oxidants and contaminants farther from the injection point. The one dimensional transport of hydrogen peroxide with dispersion and advection can be described as:

\[
\frac{\partial[H_2O_2]}{\partial t} = D \frac{\partial^2[H_2O_2]}{\partial x^2} - v \frac{\partial[H_2O_2]}{\partial x} - k_{obs}[H_2O_2] \quad (2.32)
\]

where \( t \) (s) is time, \( D \) (m\(^2\)/s) is the dispersion coefficient, \( x \) (m) is distance, \( v \) (m/s) is pore water velocity and \( k_{obs} \) (s\(^{-1}\)) is the rate of hydrogen peroxide decomposition/reaction. At steady state conditions and negligible dispersion the solution for the equation will be:

\[
x = -\frac{v}{k_{obs}} \ln \left( \frac{[H_2O_2]}{[H_2O_2]_0} \right) \quad (2.33)
\]

showing that transport distance is greatly dependent on decomposition/reaction and pore water velocity. If site specific stability data of hydrogen peroxide is collected it is possible to use these data to determine injection rates and injection point spacing. By rearranging equation 2.33, the radial flow from an injection well can be calculated:

\[
\frac{[H_2O_2]}{[H_2O_2]_0} = \exp \left( -\frac{k_{obs} \cdot R^2 \cdot \pi \cdot Z \cdot n}{Q} \right) \quad (2.34)
\]

where \( R \) (m) is the radial distance, \( Z \) (m) is the vertical injection interval, \( n \) is the porosity and \( Q \) (m\(^3\)/s) is the flow rate. Figure 2-1 shows an example of using equation 2.34 to calculate the radial distribution of hydrogen peroxide in a homogeneous soil. From the figure it is seen that higher injection rates can result in a greater radius of influence.
2.3 Persulfate

Persulfate (peroxodisulfate) salts dissociate in water to persulfate anions ($S_2O_8^{2-}$), which are strong oxidizing agents with an oxidation potential of 2.01 V [43], reaction 2.8. However, the kinetics involved in degrading many organic compounds is very slow [43]. To enhance the oxidation strength, persulfate needs to be activated in order to produce free sulfate radicals ($SO_4^{•-}$) with an oxidation potential of 2.6 V [44], reaction 2.10. As with hydroxyl radicals, these radicals are short lived and highly reactive. Sulfate radicals have a reported half-life of about 4 seconds at 40 °C [45]. The primary limitation of activated persulfate in ISCO is the minimal knowledge of its reaction pathways in the subsurface [46].

2.3.1 Activation

Activation of persulfate can be accomplished by heat [43, 47-49], metals [50, 51], or ultraviolet light [52]. These mechanisms are well described. However, in full scale ISCO applications more recent activation methods include strongly alkaline pH [14] or addition of hydrogen peroxide [53].

UV activation is obviously not an option for ISCO. Both UV and heat activation occurs via homolysis of the oxygen-oxygen bond [54], reaction 2.35. Thermal activation has been demonstrated at temperatures ranging from 35-130 °C [43, 47, 55-57] and the relation between temperature and reaction rate obeys the Arrhenius equation [47, 49, 58], equation 2.36, where $A$ is the pre-exponential factor, $E_a$ is the activation energy, $R$ is the universal gas constant and $T$ is the temperature.

\[
S_2O_8^{2-} \xrightarrow{\text{Heat or UV}} 2SO_4^{•-} \tag{2.35}
\]
\[ k = Ae^{-Ea/RT} \]  

(2.36)

Metal activation occurs via oxidation and reduction processes analogous to the Fenton’s reaction with electron donors including \( e^- \) from radiolysis of water [52] or low valent metal ions such as \( \text{Fe}^{2+} \) [51], reaction 2.37. Because of the similarities to Fenton’s chemistry, the knowledge about this activation technique and potential problems, such as the unwanted reaction 2.38, are well known. Chelating agents are often used to keep iron in solution [53, 59-61]. It has also been indicated that naturally occurring iron oxides [49, 62] and zero valent iron [63] can activate persulfate.

\[
\begin{align*}
S_2O_8^{2-} + \text{Fe}^{2+} & \rightarrow SO_4^{2-} + SO_4^{2-} + \text{Fe}^{3+} \quad (2.37) \\
SO_4^{2-} + \text{Fe}^{2+} & \rightarrow SO_2^{2-} + \text{Fe}^{3+} \quad (2.38)
\end{align*}
\]

Base is the most commonly used activator for persulfate in full scale ISCO [46]. Several mechanisms have been proposed for the alkaline activation [43, 50], but the mechanisms have not been evaluated and confirmed. A recent thorough study by Furman et al. [46] documented the reactions involved in base-catalyzed hydrolysis of persulfate to hydroperoxide anion and sulfate followed by the reduction of another persulfate molecule by hydroperoxide. Reduction by hydroperoxide cause decomposition of persulfate into a sulfate radical and sulfate anion, and hydroperoxide is oxidized to superoxide. Summing the proposed reactions yields the following net reaction 2.39 and under highly alkaline conditions, the sulfate radical reacts with hydroxide to form hydroxyl radicals according to reaction 2.40. Hence, the hydroxyl radical is likely the dominant radical available for organic oxidation using alkaline activated persulfate. Furthermore, at high pH, hydroxyl radicals themselves may dissociate into oxide radicals, reaction 2.41, which can impact their reactivity [14].

\[
\begin{align*}
2S_2O_8^{2-} + 2H_2O & \rightarrow 3SO_4^{2-} + SO_4^{2-} + O_2^{2-} + 4H^+ \quad (2.39) \\
SO_4^{2-} + OH^- & \rightarrow SO_2^{2-} + OH^* \quad (2.40) \\
OH^* & \rightleftharpoons O^{2-} + H^+ \quad pKa = 11.9 \quad (2.41)
\end{align*}
\]

Hydrogen peroxide has been shown to be able to activate persulfate even without addition of transition metal catalysts [53, 64]. The mechanisms involved is unknown, but it might be due to activation of hydrogen peroxide by naturally occurring metal oxides resulting in formation of radicals able to interact with persulfate to form sulfate radicals through propagation reactions. Another suggestion is that activation happens because of the heat generated through the exothermic hydrogen peroxide reactions [65].
It has also been demonstrated that ketones, primary alcohols and low carbon chain aldehydes can activate persulfate to generate reactive species [66]:

\[ S_2O_8^{2-} + RH \rightarrow SO_4^{2-} + R^* + H^+ + SO_4^{2-} \] (2.42)

### 2.3.2 Propagation and Termination Reactions

Once persulfate is activated via the initiating reactions, the sulfate radical can initiate a series of propagation and terminating reactions involving other radicals and oxidants [51, 54, 55, 67] including the reaction involving hydroxyl radicals described in section 2.2.2. Examples of these reactions are:

\[ SO_4^{2-} + H_2O \rightleftharpoons OH^* + H^+ + SO_4^{2-} \] (2.43)

\[ SO_4^{2-} + RH \rightarrow R^* + H^+ + SO_4^{2-} \] (2.44)

\[ R^* + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{2-} + R \] (2.45)

\[ H_2O_2 + S_2O_8^{2-} \rightarrow 2H^+ + 2SO_4^{2-} + O_2 \] (2.46)

\[ SO_4^{2-} + OH^* \rightarrow HSO_5^- \] (2.47)

\[ 2SO_4^{2-} \rightarrow S_2O_8^{2-} \] (2.48)

\[ 2OH^* \rightarrow H_2O_2 \] (2.49)

Because different reactive species are generated in activated persulfate systems, the kinetics can be complicated, but COC removal should be described with a pseudo first order rate constant, \( k_{obs} \) [54]:

\[ \frac{d[COC]}{dt} = -k_{obs}[COC] \] (2.50)

\[ k_{obs} = k'_{SO_4^{2-}}[SO_4^{2-}] + k'_{OH^*}[OH^*] + k'_{S_2O_8^{2-}}[S_2O_8^{2-}] + k'_{other}[other] \] (2.51)

Under most conditions the dominant term will be the one involving sulfate radicals [50, 55], but as shown in the previous section, the activation method, pH and possible other factors may affect the kinetics and types of reactive species generated and other terms in the rate equation 2.51 may be dominant. The type of reactive species generated also decides which contaminants can be degraded by activated persulfate.
Besides generating reactive species able to degrade contaminants, the application of persulfate can cause acidification of aquifers with low buffering capacity [48, 62][Paper III]. The low pH can potentially increase the mobilization of metals, see section 5. On the other hand, well buffered systems often contain high concentrations of carbonates that will act as radical scavengers [14, 15, 52] and thereby reduce the efficiency of the persulfate, see section 6. Decomposition and transport of persulfate is similar to what is described in section 2.2.4 for hydrogen peroxide.

One of the main advantages of persulfate is that persulfate can be present for relatively long time in the subsurface, but its fundamental chemistry in the subsurface is only now being elucidated.

### 2.4 Site Characteristics

Site characterization is a critical component of hazardous site remediation and should provide information that is required for conducting risk assessments and for designing and implementing remediation systems. It is often stated that the completion of thorough site characterization is the most important factor in the success of any remediation project. In recent years there have been many advances in site characterization, and technologies such as direct push technologies can result in valuable information acquired at a lower cost compared to traditional methods. In the following two sections some of the important parameters are outlined.

#### 2.4.1 Geology

Naturally occurring subsurface heterogeneities such as zones of high permeability as well as subsurface utility corridors and other anthropogenic subsurface disturbances, can act as preferential pathways and unpredictable flow patterns for the injected oxidant. If low permeability zones are present, it will be difficult to obtain contact between oxidant and contaminant present in these zones.

#### 2.4.2 Hydrogeology

Due to fast reaction rates of hydrogen peroxide in the subsurface, ground water flow rate and direction only have a minimum of impact on the oxidant transport. Depending on the activation techniques used for persulfate, this oxidant might be transported significantly from the injection point and will undergo advective and diffusive transport as described in section 2.2.4. The greater the hydraulic conductivity and hydraulic gradient of the aquifer, the farther the transport distance will be.

#### 2.4.3 Geochemistry

Some of the important geochemical parameters to characterize are redox conditions, pH, buffering capacity, iron concentration, alkalinity, temperature and NOM. Reduced
conditions favor the presence of soluble $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ that can activate hydrogen peroxide and persulfate. However, the reduced conditions are also a source of treatment inefficiency due to presence of reduced species that will consume oxidant, which is further described in section 2.7. pH is important, especially if iron activation is desired since this requires a low pH (or use of chelating agents). The natural buffering capacity of soils will in most cases possess significant acid neutralization capacity and thereby maintain pH neutral. To overcome this, large amounts of acid is needed to lower pH or base to obtain alkaline activation of persulfate. High alkalinity can result in scavenging of the radicals and high concentrations of NOM can potentially consume large amounts of oxidants.

2.4.4 Contaminants

Types, distribution, concentrations and presence of non-aqueous phase liquid (NAPL) contaminants are critical parameters to determine before ISCO is evaluated as a potential technology for remediation. Based on the characterization, oxidant type and dosage can be estimated. This characterization is also very important in order to evaluate the effectiveness of ISCO, since this should be done based on total mass and not dissolved phase evaluations, which would be inaccurate and misleading. This is because ISCO will alter the equilibrium partitioning of total mass distribution by converting sorbed and free phase mass to dissolved phase both during and for a period of time after the application of ISCO.

2.5 Contaminants Amenable

The reactive species generated when the peroxygens are activated determines which compounds can be degraded. For hydrogen peroxide it is mainly hydroxyl radicals and for persulfate mainly sulfate radicals. However, as shown in the previous sections other reactive species can be generated under specific condition and by applying specific activation methods.

The reaction mechanisms involved in oxidation of organic compounds by hydroxyl radicals and persulfate radicals can be significantly different. The sulfate radical prefers to remove electrons from the organic molecule thereby producing organic radicals (reaction 2.52) whereas the hydroxyl radical adds to unsaturated bonds of alkenes (or alkynes) or abstracts hydrogen from the C-H bonds (reaction 2.53) [66, 68, 69]. Example with the carboxylate ion:

$$CH_3CO_2^- + SO_4^{2-} \rightarrow CH_3CO_2^+ + SO_4^{2-} \rightarrow ^*CH_3 + CO_2 + SO_4^{2-} \quad (2.52)$$

$$CH_3CO_2^- + OH^* \rightarrow ^*CH_2CO_2^- + H_2O \quad (2.53)$$
Reactions with aromatic or heterocyclic compounds also differ since the sulfate radical reacts by an electron transfer mechanism to produce a radical cation, reaction 2.54, whereas the hydroxyl radical reacts via a mechanism analogous to an electrophilic substitution reaction [70] in which the attack on the aromatic ring results in the formation of the cyclohexadienyl radical [68], reaction 2.55:

\[
\text{(2.54)}
\]

\[
\text{(2.55)}
\]

The reaction rates between hydroxyl radicals and aromatic compounds are close to diffusion controlled [14], but because of the electrophilic substitution reactions, electron withdrawing substituents such as nitro (\(-\text{NO}_2\)) or carbonyl (\(\text{C}=\text{O}\)) will decrease reaction rates and electron donating substituents such as hydroxyl (\(-\text{OH}\)), amino (\(-\text{NH}_2\)) or alkoxy (\(-\text{OR}\)) will accelerate the reactions [70]. The presence of halogens in organic compounds has been shown to slow down the reaction rates for hydroxyl radicals [15] and this will possibly also apply for sulfate radicals [57].

Besides the hydroxyl radical and sulfate radicals other reactive species formed with MFR and ASP, such as superoxide, can significantly enhance degradation of recalcitrant organic contaminants.

It is important to notice that the reactive species generated in MFR and ASP will react with a wide range of different reactants present in the system besides the contaminant and to describe this, competition kinetics has to be applied.

Some general rules have been established in [71] for the reactivity of hydroxyl radical with organic contaminants:

\[ k \approx 10^{10} \text{ M}^{-1}\text{s}^{-1} \quad \text{Rate of diffusion} \]
\[ k > 10^9 \text{ M}^{-1}\text{s}^{-1} \quad \text{ISCO can be used} \]
\[ k < 10^8 \text{ M}^{-1}\text{s}^{-1} \quad \text{ISCO cannot be used} \]

Second order rate constants for the reactivity of contaminants with hydroxyl and sulfate radicals are listed in Table 2-3 and Table 2-4. Again it should be noticed that for example carbon tetrachloride which is unreactive with hydroxyl radical, is rapidly
degraded in MFR systems through reactions with superoxide in the presence of sufficient hydrogen peroxide to provide a solvent effect [16, 27, 72, 73].

### TABLE 2-3: SECOND ORDER RATE CONSTANTS FOR CONTAMINANTS AND HYDROXYL RADICALS. MODIFIED FROM [37]. SOURCES ARE [15, 74, 75].

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k_{\text{OH}}) (M(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,5-Trichlorophenoxy acetic acid</td>
<td>(4.0\times10^9)</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>(4.0\times10^9)</td>
</tr>
<tr>
<td>Benzene</td>
<td>(7.8\times10^8)</td>
</tr>
<tr>
<td>Toluene</td>
<td>(3.0\times10^9)</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>(2.9\times10^9)</td>
</tr>
<tr>
<td>2,4,6-Trinitrotoluene</td>
<td>(4.3\times10^8)</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons</td>
<td>(1.0\times10^{10})</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>(&lt;2\times10^6)</td>
</tr>
<tr>
<td>Chloroform</td>
<td>(\approx 5\times10^6)</td>
</tr>
<tr>
<td>Perchloroethylene (PCE)</td>
<td>(2.8\times10^9)</td>
</tr>
<tr>
<td>Trichloroethylene (TCE)</td>
<td>(4.0\times10^9)</td>
</tr>
<tr>
<td>2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)</td>
<td>(4.0\times10^9)</td>
</tr>
<tr>
<td>Methyl tert-butyl ether (MTBE)</td>
<td>((3.9\pm0.73)\times10^9)</td>
</tr>
</tbody>
</table>

### TABLE 2-4: SECOND ORDER RATE CONSTANTS FOR CONTAMINANTS AND SULFATE RADICALS. MODIFIED FROM [37]. SOURCES ARE [14, 52, 76]. MORE RATE CONSTANTS ARE FOUND IN [57].

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k_{\text{SO}_4}) (M(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>(1.0\times10^7)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>(4.3\times10^7)</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>(8.2\times10^7)</td>
</tr>
<tr>
<td>t-Butyl alcohol</td>
<td>(&lt;10^6)</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>(1.6\times10^8)</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>(3.2\times10^8)</td>
</tr>
<tr>
<td>Anisole</td>
<td>(4.9\times10^9)</td>
</tr>
<tr>
<td>Acetanilide</td>
<td>(3.6\times10^9)</td>
</tr>
<tr>
<td>Benzene</td>
<td>(3.0\times10^9)</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>(1.2\times10^9)</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>(&lt;10^9)</td>
</tr>
</tbody>
</table>

### 2.6 DESTRUCTION OF FREE PHASE CONTAMINANTS

A critical issue associated with hazardous waste sites is the potential presence of immiscible liquid contamination in the subsurface. These NAPLs become trapped in the pore space due to capillary forces and once present, they are difficult to remove and will serve as a long-term source of contamination as they dissolve into the groundwater under mass transfer controlled conditions. Since the rate limiting step in NAPL remediation is mostly dissolution, NAPLs can be present for decades even when treated actively with traditional pump-and-treat techniques [77, 78]. It has been
estimated that the cost to clean up dense non-aqueous phase liquid (DNAPL) contaminated sites in the US with traditional techniques could be $100 billion or more [79] and even though treatment of DNAPLs by traditional methods as pump and treat have been proven ineffective [80], this technique is still widely used at DNAPL sites [81]. This clearly suggests that development or implementation of existing and emerging effective source-depletion technologies is needed. Modeling and limited data suggest that even removal of more than 90% of the DNAPL source is not enough to reduce concentrations in groundwater [82]. The most prevalent types of DNAPLs are the halogenated organic solvents including TCE and PCE, but many sites are contaminated with other types of DNAPLs including coal tar and creosotes, polychlorinated biphenyl (PCBs) and pesticides.

Historically, ISCO has been rejected at sites with large amounts of DNAPL [83], but there is a theoretical basis and experimental results suggesting that DNAPL can be degraded by ISCO [84]. The relationship between contaminant phases, oxidant required and the processes limiting the treatment efficiency is presented in Figure 2-2.

![Figure 2-2: Relationship between contaminant phase, oxidant requirement and the limiting processes. From [9].](image)

The rate limiting step in treating NAPLs is the mass transfer of contaminant into the aqueous phase (dissolution), which can generally be modeled based on the stagnant film model utilizing a first-order linear driving force [85]:

\[
\frac{dc_{bulk}}{dt} = -k_{La}(c_{bulk} - c_{sat})
\]

(2.56)
Fundamentals of ISCO

describing the rate of change of aqueous concentration per time (g/m³/s), \( k_{La} \) is the NAPL dissolution rate (s⁻¹), \( c_{bulk} \) is the aqueous solute concentration (g/m³), and \( c_{sat} \) is the solubility of the solute (g/m³). The model is based on Fick’s law of diffusion:

\[
J_a = -D_m \frac{dc}{dz}
\]  

(2.57)

stating that the mass flux \( J_a \) (g/m²/s) is proportional to the concentration gradient at the surface (g/m⁴). The linear concentration gradient can be approximated by \( (c_{sat} - c_{bulk})/\delta \), where \( \delta \) (m) is the thickness of the film. The model is illustrated in Figure 2-3 and also shows the accelerated mass transfer occurring when oxidants are introduced to the system as suggested by [86]. The concentration gradient is increased by reactions in the aqueous phase and reactions within the diffusion film layer. All ISCO technologies (and other mass removal technologies) will increase mass transfer of soluble organic contaminants, but the treatment is not very efficient, since it is still limited by diffusion.

![Figure 2-3: Thin Film Model with ISCO. Adapted from [86].](image)

In recent years it has been demonstrated in several laboratory experiments that MFR can be used for destruction of NAPL and that contaminants are degraded more rapidly than they dissolved into the aqueous phase [18, 71, 72, 84, 85, 87-89]. By applying hydroxyl radical scavengers and reductant scavengers in experiments with MFR treatments of sorbed phase contaminant, it has been demonstrated that a reductive pathway in MFR is responsible for enhanced contaminant desorption [18]. The experiments suggest that treatment of NAPL with MFR occurs by an enhanced desorption caused by reductants followed by oxidation and reduction of the contaminants in the aqueous phase. For destruction of carbon tetrachloride DNAPL, superoxide is the reactive species in MFR [73].

Until very recently there was no documentation showing if ASP could enhance desorption and NAPL destruction. In 2009, laboratory tests showed that treatment of sorbed phase PCE by Fe(II)-citrate and alkaline activated persulfate was equal or less than the rates of gas-purge desorption indicating that enhanced treatment of the
sorbed contaminants did not occur in the ASP reactions [90]. However, in 2010 it was demonstrated that alkaline activated persulfate generates superoxide [46], reaction 2.39. This discovery may lead to ASP applications for enhanced NAPL treatment in the future, but further studies are needed to evaluate this.

Only few well documented field studies have demonstrated destruction of NAPL. In 1997 at the "Savannah river project" in South Carolina, MFR was demonstrated to reduce the mass of DNAPL chlorinated solvents from 269 kg to 17 kg (94% reduction) over 6 days of MFR treatment [91].

In the present Ph.D. study destruction of residual free phase PCE and petroleum hydrocarbons were investigated, see section 4.

2.7 Oxidant Demand

Proper design of a field-scale implementation of ISCO requires data on target contaminant levels as well as quantitative estimates of other oxidant sinks. There are a number of chemical and physical factors that contribute to the total oxidant demand (TOD) of a subsurface environment. These include [92]:

1. Dissolved, sorbed and free phase contaminant
2. Dissolved, sorbed and solid phase reduced minerals
3. Dissolved and sorbed phase NOM
4. Thermal and chemical decomposition

There are no accepted standard methods for conducting TOD tests and several methods have been reported in the literature. Overall, these are based on tests where varying ratios of oxidant mass to soil mass are prepared in separate vials and the oxidant consumption is monitored to describe the kinetics of the oxidation and the total consumption of oxidants after 48 or 72 hours. This approach works rather well for permanganate, and TOD test with persulfate are very similar to permanganate tests, whereas additional considerations have to be taken into account when using hydrogen peroxide, since this oxidant undergoes autocatalytic decomposition and also minerals can catalyze the decomposition resulting in an infinite oxidant demand. This is also partly true for persulfate and makes TOD measurements difficult for activated peroxygens.

2.8 Coupling ISCO with Biological Remediation

ISCO has traditionally been used as a standalone treatment technology, but in recent years ISCO is often used as integrated parts of sequential remediation systems, where ISCO is used to rapidly reduce high concentrations of contaminants or to destroy NAPL.
Typical ISCO is coupled with traditional mass transfer technologies and monitored natural attenuation (MNA).

Several laboratory tests and field tests have documented that it is extremely difficult for ISCO technologies to render a site biologically inactive, even in cases involving reductive dechlorination (anaerobic) bacteria \([93, 94]\). Post-treatment bacteria populations have been demonstrated to grow rapidly within short time after even the most aggressive treatments.

Applying bioremediation as a polishing step after ISCO can be an effective technology since ISCO in most cases is only cost-effective for bringing down concentrations to a certain level. For treating the lower concentrations after ISCO, bioremediation can be an effective technology, and has several advantages:

- High concentrations that might be toxic for microorganisms are reduced
- Non biodegradable compounds can be degraded by ISCO
- Some compounds will be more biodegradable after ISCO pretreatment due to partial oxidation \([95, 96]\)
- ISCO will increase the bioavailability of contaminants \([97, 98]\)
- ISCO will create an oxidized environment leaving oxygen for the aerobic microbial degradation \([99]\)
- Organic matter released from the soil particles as a result of ISCO can act as electron donor for some processes \([100]\)
- Increased temperatures after ISCO can enhance the bioavailability of contaminants \([101]\) and the microbial activity \([102]\)

Challenges:

- Oxidants are toxic to microorganisms \([103]\)
- Changes in water chemistry after ISCO: low or high pH
- Changes in water chemistry after ISCO: high sulfate concentrations after ASP

Results from \([56]\) suggest that ASP may be less damaging to microorganisms than MFR.

In the present Ph.D. study field tests were performed, where MFR was followed by MNA at one site and enhanced reductive dechlorination (ERD) at another site, see section 4.3.
3 KÆRGÅRD PLANTATION

Most of the Ph.D. study has been focusing on remediation of a very large contaminated site located in the Western part of Denmark, see Figure 3-1. The site located in Kærgård Plantation has a varying geology as well as a very complex contaminant mixture and distribution. It represents one of the most difficult remediation tasks in Scandinavia and is considered the largest contaminated site in Denmark. The present Ph.D. study was based on this project and most of the research was done related to this site involving laboratory tests with soil and groundwater from the site combined with extensive pilot testing at the site. In the remaining part of the present thesis the presented results and general issues will be based on this site and interesting topics will be dealt with in more details.

![Figure 3-1: The location of Kærgård Plantation in the Western part of Denmark. From [104].](image-url)
3.1 History

The contamination in Kærgård Plantation originates from disposal of about 286,000 m$^3$ of pharmaceutical wastewater that was legally discharged by the former Grindstedværk in 6 separate waste pits in the plantation from 1956-1973. These waste pits were located 400-800 m from the shore and after the disposal the pits were covered by sand. The wastewater originated from the plant’s production of vitamins and medicinal products, and it was transported to the site in tank trucks. The disposed wastewater was estimated to include [105]:

- 40,000 tons of inorganic salt
- 15,000 tons of organic acid salts
- 1,500 tons of sulfonamides, barbiturates, aniline, pyridine, phenols, benzene and toluene
- Lithium, mercury, cyanide, etc.

Chlorinated solvents are not included in the above estimate, but investigations from 2006 estimated that about 340 tons of chlorinated solvents and 230 tons of sulfonamides are present in Kærgård Plantage today [105]. Recently, 1160 different compounds were identified to have been produced or used at the former Grindstedværk [106]. Taken the huge amounts of discharged wastewater into consideration, numerous of these compounds as well as their degradation products may be present in Kærgård Plantation today.

The present Ph.D. study focused on remediation of waste pit 1.

3.2 Contamination

Soil and groundwater beneath the Kærgård Plantage megasite in Denmark is still extremely contaminated with a complex mixture of pharmaceutical wastes, including sulfonamides, barbiturates, aniline, pyridine, chlorinated solvents (DNAPL), benzene, toluene, mercury, cyanide and several other compounds. From the waste pits located just above or at the groundwater table, the contaminants have been transported to the soil and groundwater underneath the pits and a continuous significant transport to the sea is still occurring with an estimated flux of sulfonamides to the ocean of 4000 kg/year [105]. The result is a contaminated area of about 500,000 m$^2$ and discharge into the sea at an 800 m stretch of the coast. Because of the contamination, swimming in the ocean became prohibited in 1964 and this still applies. In 2002, signs were put up in the area advising against staying in the area and getting in contact with the sand and water.
Investigations of the contamination were initiated in the 1980’s and the site is still being investigated to collect more knowledge on the distribution, spreading and composition of the contamination and thereby improve risk assessments and increase the basis for decision concerning a possible remediation. Overall, it can be concluded that the majority of the mass of the hydrophobic compounds (total petroleum hydrocarbons (TPH), chlorinated solvents, metals, etc.) are present in the waste pits, whereas the more water soluble compounds (aniline, barbiturates, sulfonamides, etc.) are present in the widespread plume area. The distribution and total masses will not be dealt with in the present thesis, but an example showing the masses of chlorinated solvents and TPHs in the waste pits is presented in Figure 3-2 to provide some idea of the huge amounts of contaminants present at the site. More details can be found in [105].

A conceptual model showing the spreading of contaminants from the waste pits is presented in Figure 3-3. From this model it is seen that DNAPL has penetrated the sand/gravel layer (layer 2) and the fine grained sand/silt layer (layer 3) all the way down to an impermeable silt/clay layer (layer 4). Today, residual DNAPL is still present in this area and continues to result in a significant contaminant flux towards the beach and the sea. The DNAPL is mainly present in the top and bottom of layer 2 and in layer 3, which is due to a higher hydraulic conductivity in the middle of layer 2 causing a more significant leaching of the chemicals present.
A more detailed conceptual model for waste pit 1 is presented in Figure 3-4, indicating the location of the waste pit (excavated in 2008) and the assumed presence of residual DNAPL PCE beneath the pit. Typical contaminant concentrations in water and soil as well as estimated mass fluxes of contaminants leaving the pit area are inserted in the model. As clarified in later sections, the Ph.D. work (laboratory and pilot tests) was carried out with water and soil from layer 2 with focus on the top of layer 2 (layer 2.1).
3.3 REMEDIATION

In 2007, a working group with the purpose of giving recommendations to a phase 1 for the future work in Kærgård Plantation was appointed by the Minister of Environment and the chairman of the regional council. The aim was to improve conditions for staying on the beach and in the dynes. The recommendations were divided into three:

1) Excavation of highly contaminated soil in pit 1 and 2 (2008-2009)
2) Test, selection, and design of remediation technique for contamination located below the groundwater table (2009-2011)
   a) Laboratory experiments
      i) Chemical - MFR
      ii) Chemical - ASP
      iii) Thermal – Steam
      iv) Biological – ERD
   b) Pilot tests
3) Full scale treatment of contamination in pit 1 and 2 (2011-?)

The excavation was finished in 2009 and the work now focuses on finding a technique or combination of techniques to treat the contamination present under the groundwater table. As there was no precedent for treating this type of mixture, the feasibility of a variety of in situ remediation technologies are being evaluated in bench tests at this stage, including biological, chemical, and thermal techniques. The results presented in this thesis will focus on laboratory experiments with MFR and ASP followed by pilot tests with MFR combined with ERD in waste pit 1 at the site. Based on the obtained results from the bench and pilot tests a full scale remediation technique will be chosen and designed. Full scale remediation is expected to start up during 2011.
4 **Bench and Pilot Tests**

Even though ISCO has been used at thousands of sites throughout the world and several peer reviewed papers describe the involved processes, there is still a lack of published, well documented field applications to back up the results observed in laboratories. In the present Ph.D. study, MFR was tested at six different contaminated sites in Denmark as described in Table 4-1. To the author’s knowledge, this is more than a doubling of the number of field MFR applications in Denmark. Back in 2000, three full scale tests were made in Denmark, but results were ambiguous and no clear conclusion could be drawn [107]. This thesis will focus on results from Kærgård Plantation, but also results from site A, B and C will be included. Site D and E will not be discussed, see Table 4-1. Sites A-E were all contaminated with fuel oil and the geology mainly consisted of sand. The purposes of the remediation at the sites were different and included direct oxidation of the contaminants, enhanced desorption in recirculation systems and stimulation of aerobic biological degradation.

**TABLE 4-1: SITES WHERE MFR WAS TESTED AS PART OF THE PH.D. PROJECT. AMOUNTS OF H₂O₂ ARE BASED ON 100% H₂O₂.**

<table>
<thead>
<tr>
<th>Site</th>
<th>Bench</th>
<th>Pilot</th>
<th>Full scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kærgård Plantation</td>
<td>126 batch and column</td>
<td>3.500 kg H₂O₂ + chelated Fe</td>
<td>-</td>
</tr>
<tr>
<td>Site A</td>
<td>37 batch tests</td>
<td>-</td>
<td>840 kg H₂O₂</td>
</tr>
<tr>
<td>Site B</td>
<td>39 batch tests</td>
<td>-</td>
<td>1.960 kg H₂O₂ + H₂SO₄</td>
</tr>
<tr>
<td>Site C</td>
<td>21 batch and column</td>
<td>140 kg H₂O₂</td>
<td>-</td>
</tr>
<tr>
<td>Site D</td>
<td>-</td>
<td>-</td>
<td>210 kg H₂O₂</td>
</tr>
<tr>
<td>Site E</td>
<td>-</td>
<td>10 kg H₂O₂</td>
<td>-</td>
</tr>
</tbody>
</table>

The objectives of the work presented in this section were to collect knowledge on the performance of MFR and ASP, and evaluate if the processes were applicable for treating fuel oil contaminated sites and more complex contaminants mixtures including the ability to destroy NAPL. This was done by:

- Batch and pilot tests with MFR (site A-E, [unpublished data])
- Batch test with MFR and ASP (Kærgård, [paper III])
- Pilot test with MFR followed by ERD (Kærgård, [paper IV])

Specific purposes are described in the following sections summarizing the results obtained.

As an introductory remark, it should be noticed that the sandy soils from the sites were different. One of the main parameters varying from site to site and causing different results in the bench and pilot tests was buffering capacity of the soil. To exemplify this, data from titrations of 10 g of soil from different sites with acid is presented in Figure...
4-1. It is clearly seen that the sand at site A and the sand from Kærgård Plantation possessed almost no buffering capacity, since titrations curves for these soils were almost identical to titration of demineralized water. It is believed that the large amounts of acids deposited at the site dissolved and removed carbonates.

**FIGURE 4-1: PH IN SOILS USED FOR BENCH AND PILOT TESTS AS A FUNCTION OF ACID ADDED [UNPUBLISHED DATA].**

4.1 **FUEL OIL CONTAMINATED SITES - MFR (BENCH AND PILOT)**

This section will focus on unpublished results from site B and include a few examples from site A and C. Description of the sites or the test setups will not be provided in details and only selected interesting results will be presented. For all sites, treatability soil slurry batch tests were conducted at 20°C in 1000 ml glass reactors with homogenized site soil and tap water to document if the relative high concentrations of residual free phase fuel oil could be degraded, some of these results are presented in Table 4-2. Reactors received 0, 1, 2 or 3 additions of reagents. It is seen that 4-94% removal was obtained compared to control reactors receiving no treatment. In general multiple treatments increased removal and also multiple additions of lower oxidant concentrations were more favorable compared to higher concentrations added in a single event. Surprisingly, treatment with only hydrogen peroxide and no acidification or addition of catalyst seems to be very effective for treating the fuel oil, which is ascribed to the high concentrations of iron in the soils (up to 9-10.000 mg/kg). The results demonstrate that residual free phase fuel oil can be degraded with MFR.
Bench and pilot tests

### TABLE 4-2: TREATABILITY TESTS WITH SOIL FROM SITE A-C SHOWING DEGRADATION OF TOTAL PETROLEUM HYDROCARBONS (TPH) IN THE SOILS USING DIFFERENT COMBINATION OF ACID, IRON AND HYDROGEN PEROXIDE. “-" NOT ADDED [UNPUBLISHED DATA].

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil [g]</th>
<th>Water [ml]</th>
<th>H$_2$SO$_4$ [mM]</th>
<th>Citric acid [mM]</th>
<th>FeSO$_4$ [mM]</th>
<th>H$_2$O$_2$ [%]</th>
<th>TPH [mg/kg]</th>
<th>Time Days</th>
<th>Reduction %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>300</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4,100</td>
<td>8</td>
<td>Control</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.25</td>
<td>1,900</td>
<td>8</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3*5.25</td>
<td>1,400</td>
<td>8</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>200</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>5.25</td>
<td>2,100</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>200</td>
<td>50</td>
<td>-</td>
<td>1.8</td>
<td>3*5.25</td>
<td>550</td>
<td>8</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>200</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>5.25</td>
<td>1,900</td>
<td>8</td>
<td>54</td>
</tr>
<tr>
<td>B</td>
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<td>2,300</td>
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<td></td>
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<td>-</td>
<td>1.1</td>
<td>9.8</td>
<td>1,600</td>
<td>13</td>
<td>30</td>
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<tr>
<td></td>
<td>750</td>
<td>500</td>
<td>to pH 3</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>9.8</td>
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<tr>
<td>C</td>
<td>250</td>
<td>800</td>
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<td>800</td>
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<td>7</td>
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</tr>
<tr>
<td></td>
<td>250</td>
<td>800</td>
<td>to pH 3</td>
<td>-</td>
<td>-</td>
<td>8.8</td>
<td>890</td>
<td>7</td>
<td>77</td>
</tr>
</tbody>
</table>

To better understand the processes, the stability of hydrogen peroxide measured as the concentration over time was determined in the presence of contaminated sand from site B. Different combinations of acids and catalyst were tested in batch reactors and the concentration of hydrogen peroxide was measured over time. The results fitted to a first order decomposition are presented in Figure 4-2 and shows great effects since half-lives of hydrogen peroxide were 7-12 hours, when no acid was added, and increased to 70-250 hours, when acid was added. This shows the expected trend and Watts et al. 2007 observed a lowering of the decomposition rate of hydrogen peroxide by up to a factor 50 using citrate (with no catalyst added) cause by the processes explained in section 6.1, with minimal effects on superoxide and hydroxyl radical production [39]. The observed results cannot be transferred directly to be valid in field mainly because of the high ratio of water to soil (5g soil to 50 ml water) used in this lab test.
After termination of the bench tests in the laboratory, pilot test or full scale treatments were conducted at the sites. A large amount of data was collected, but in this thesis only monitoring results from selected wells at site B will be presented, see Figure 4-3. The results showed a significant effect on pH, oxidation reduction potential (ORP), dissolved oxygen (DO), temperature and conductivity in the treatment area (red lines) and a limited effects in monitoring wells placed upgradient and downgradient the treatment area (blue lines). Monitoring was continued almost 200 days after MFR injections and it is seen that pH, ORP and DO remains significantly impacted and only recovers very slowly. The number of viable bacteria and fungi in the groundwater was also monitored (as colony forming units, CFU, on agar plates). These results indicated that bacteria were affected by MFR, but will return after treatment as described in section 2.8. At site B, bacteria recovered after MFR despite the low pH. Based on the very high concentrations of oxygen (>20 mg/l) remaining almost 200 days after MFR injections there is a large potential, especially in the fringe of the treatment area, for microbiological aerobic degradation following MFR.
As a result of the full scale MFR treatment during the present Ph.D. study at site A, B and D, site closure was obtained at all three sites, demonstrating that the technique can be used at residual free phase fuel oil contaminated sites.
4.2 KÆRGÅRD PLANTATION - MFR AND ASP (BENCH)

As a part of selecting and designing a remediation approach for contamination located below the ground water table in waste pit 1 and 2 in Kærgård Plantation, bench scale tests with MFR and ASP were conducted. The overall objective of the laboratory tests was to determine the optimal treatment strategy for pilot tests using MFR and ASP and the specific objectives for the laboratory tests were to:

- Estimate the buffering capacity of the soil.
- Determine best suited activation method for persulfate.
- Determine the stability of the hydrogen peroxide and persulfate in presence of subsurface solids.
- Determine oxidation effectiveness towards chlorinated solvents, BTEX (benzene, toluene, ethylbenzene, and xylenes), barbiturates, sulfonamides, aniline, and pyridine.
- Evaluate the potential for mobilizing cyanide, mercury, and other metals during treatment, see section 5.
- Evaluate potential by-product formation.

The main results are described in paper III and all results will be published during 2011 by the Region of Southern Denmark. All oxidant measurements were performed with the method proposed in paper I. Some of the interesting findings will be reviewed in this section.

Because of a very low buffering capacity of the soil and groundwater from Kærgård Plantation, pH dropped to below 2 in all tests and all the way down to 1, when high dosages of persulfate were used. As described in section 2.3.1 there are different methods to activate persulfate. To determine the optimal methods for the Kærgård Plantation matrix, four different methods were tested and the results from closed batch reactors based on PCE degradation in soil slurries are presented in Figure 4-4. All activation methods worked, but surprisingly, the natural activation (no activation) was more effective (75% PCE removal) compared to the alkaline activation, which was only able to oxidize 49% of the PCE. The most effective removal of contaminants was obtained when MFR (H₂O₂ and chelated iron) was added to activate persulfate; this will be referred to as MFSP. MFR will activate sodium persulfate via two mechanisms – heat activation resulting from the exothermic nature of the MFR (modified Fenton’s activated sodium persulfate), and chelated iron activation. Furthermore, the effervescence via decomposition of hydrogen peroxide to oxygen and the heat generated by the MFR are expected to promote the rates of desorption of adsorbed contaminants and the dissolution of NAPL contaminants, increasing their availability for concurrent aqueous phase oxidation and subsequent polishing treatment by persulfate [90]. Based on these considerations and given the aggressive treatment...
goals at Kærgård Plantation, it was decided to continue with MFSP for further experiments to combine the strengths of MFR and ASP.

**FIGURE 4-4:** LEFT: TOTAL AMOUNT OF PCE IN THE REACTORS (SOIL, WATER, AND AIR) AFTER 9 DAYS OF REACTION COMPARED TO BASELINE (DAY 0) AND CONTROL (DAY 9) AS A FUNCTION OF ACTIVATION METHOD. RESIDUAL OXIDANT PRESENT IN THE REACTORS AFTER 9 DAYS IS ALSO PRESENTED [PAPER III]. RIGHT: TOTAL AMOUNT OF PCE IN THE REACTORS AFTER REACTION WITH DIFFERENT CONCENTRATIONS OF MFR –ONLY AND MFSP [PAPER III].

After having determined the activation technique for persulfate, the MFR-only and MFSP could be compared by setting up soil slurry batch reactors and treat these with different dosages of MFR-only (5, 15, 25 g H₂O₂/kg soil) and MFSP (5, 15, 25 g Na₂S₂O₈/kg soil + 1, 6, 11 g H₂O₂/kg soil for activation). Some of the results are presented in Figure 4-4 and MFR-only and MFSP were proven to be effective with 98% and 89% degradation of PCE respectively.

The degradation of several other contaminants present in the water phase by MFSP was also investigated with two different dosages of persulfate (21 and 83 mM S₂O₈²⁻) activated by MFR (63 and 315 mM H₂O₂ and 1.8 mM chelated Fe). The results presented in Figure 4-4 clearly demonstrate that MFSP was able to degrade the wide range of contaminants present in the groundwater. For all of the organic nitrogen compounds, sulfonamides and barbiturates, the removal was greater than 99.9% or to below detection limit (0.02-0.1 µg/l) with the high oxidant dose except for sulfanilic acid, which was reduced by 96%. This also makes sulfanilic acid, the medicinal compound, found in the highest concentration (2.1 µg/l) after treatment. The petroleum hydrocarbons were also degraded, but long carbon chains (C₂₅-C₄₀) seem more difficult to degrade compared to the smaller molecules (C₅-C₁₀). BTEX were also easily degraded and the high dosage also degraded the chlorinated ethenes completely. Similar test with groundwater from Kærgård Plantation for MFR-only were
Bench and pilot tests

conducted in 2006 by ISOTEC and showed similar results [108, 109] and there is no doubt that the MFR chemistry when used to activate persulfate plays an important and probably superior role compared to persulfate. No other studies concerning ISCO for remediation of these pharmaceutical exists in the peer reviewed literature.

The presented data and other test results showed that MFR and MFSP were comparable in many ways. Overall, both techniques and the dosages applied have proven to be effective towards the contaminants in Kærgård Plantation. Reaction rates, heat and gas production were controlled and acceptable in all experiments. Some differences were demonstrated. Compared to MFR-only, the MFSP reaction (oxidant consumption) was faster, resulted in lower pH, and produced less gas. As a result of the different activation mechanisms included in the MFSP, this technique will potentially be able to treat a wider range of contaminants. On the other hand, MFSP will be more expensive to apply in the field and leave high concentrations of residual sulfate and acidity in the groundwater after treatment. On this basis, it was decided to test MFR-only in a field pilot study, where ERD was to be included as a polishing step.

4.3 KÆRGÅRD PLANTATION – MFR FOLLOWED BY ERD (PILOT)

The objective of the proposed remedial action for Kærgård Plantage was to significantly reduce the concentrations of COCs, including DNAPL PCE, in soil and groundwater. More specifically, the objectives of the pilot test were to demonstrate the effectiveness of MFR followed by ERD as a polishing step towards the COCs within
a test cell and to collect design data for the full-scale remedial design. The following were to be clarified by this pilot test:

- Quantify the effect of the treatment
- Determine the radius of influence (ROI)
- Determine the consumption of oxidant and catalyst
- Determine the stability of oxidant
- Evaluate different injection techniques
- Determine the number of injection events to achieve clean-up goals
- Determine how heat and gas formation can be controlled and managed
- Evaluate extent of potential metal and cyanide mobilization out of the treatment zone
- Determine optimal injection pressure and flow
- Determine if clean soil above the treatment area is re-contaminated
- Determine the effectiveness of MFR for destruction of BTEX and chlorinated ethenes
- Demonstrate whether reducing and pH neutral conditions can be reestablished after MFR injection and, if so, determine the timeframe to achieve these conditions
- Demonstrate whether it is possible to achieve reductive dechlorination of PCE to ethene after MFR injection.

Some of the main results from the pilot test are described in details in paper IV and will be summed up in this section and supplemented with some additional data from the test. All results from the pilot test will be published by Region of Southern Denmark during 2011.

The site is described in detail in section 3 and the pilot test setup is illustrated in Figure 4-6. A total of 5 nested injection wells screened separately through Layer 2.1 and 2.2 were utilized for the pilot test. Monitoring results from only two central wells (M3 and M4) and a well (M105) placed 2.5 m down-gradient from the nearest injection well are included in this thesis. To accomplish the objectives, a number of injections were made in the two layers, see Table 4-3.
FIGURE 4-6: LEFT: SITE PLAN SHOWING THE TEST SETUP WITH ASSUMED 1.5 M ROI OF INJECTION WELLS. RIGHT: A CONCEPTUAL MODEL SHOWING THE GEOLOGY, HYDROGEOLOGY, AND DEGREE OF CONTAMINATION AS A FUNCTION OF DEPTH AS WELL AS CONSTRUCTION OF WELLS AND THE TWO TREATMENT ZONES, LAYER 2.1 AND 2.2. THE FIGURES ARE NOT TO SCALE.

TABLE 4-3: INJECTED VOLUMES OF REAGENTS IN THE TWO TREATMENT ZONES. ALL VOLUMES WERE DISTRIBUTED EQUALLY IN THE INJECTION WELLS.

<table>
<thead>
<tr>
<th>Day</th>
<th>Layer 2.1 (3-6 m bgs)</th>
<th>Layer 2.2 (7-9 m bgs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>MFR: 5,550 liter</td>
<td>MFR: 6,450 liter</td>
</tr>
<tr>
<td>56</td>
<td>MFR: 7,200 liter</td>
<td>MFR: 4,800 liter</td>
</tr>
<tr>
<td>104</td>
<td>MFR: 9,000 liter</td>
<td>-</td>
</tr>
<tr>
<td>146</td>
<td>MFR: 9,000 liter</td>
<td>-</td>
</tr>
<tr>
<td>157</td>
<td>-</td>
<td>Buffer: 62 kg NaHCO₃ and 100 kg Na₂CO₃ diluted to 10,000 liter</td>
</tr>
<tr>
<td>161</td>
<td>-</td>
<td>Donor: 675 liter Newman zone diluted to 18,000 liter</td>
</tr>
<tr>
<td>225</td>
<td>-</td>
<td>Buffer+donor: 18 kg NaHCO₃ and 450 liter Newman zone diluted to 18,000 liter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bacteria: 5 liter KB1®</td>
</tr>
</tbody>
</table>
Photos from the pilot test showing the setup of mixing tanks, pumps, well heads etc. are seen in Figure 4-7.
Before, during and after MFR injections, water samples were collected from all of the monitoring wells. The changes in pH and ORP over time in a few selected wells is presented in Figure 4-8 and as indicated by the laboratory tests, pH dropped significantly as a result of the MFR injections due to low buffering capacity and presumably formation of carboxylic acids as no strong acids were utilized as part of MFR. Both pH and ORP were expected to rebound quickly because of a relative high influx of reduced groundwater with a neutral pH, but this did not happen and therefore it was necessary to neutralize pH by addition of buffer and create reducing conditions by addition of an electron donor into layer 2.2, where ERD was to be applied. These injections quickly resulted in conditions favorable for ERD (ORP < -50 mV, pH 6.5-8.2).

Several other parameters were monitored in the wells; temperature, water level, dissolved iron, DO, conductivity, chloride, and formation of hydroxyl radicals (ability of groundwater samples to decolorize methylene blue [110]). All parameters indicated a ROI of minimum 1.5 m (data not shown). Soil samples collected before and after
Bench and pilot tests

treatment, see Figure 4-9, were used to document if contaminant levels were reduced. Based on average results, the concentration of residual free phase PCE in layer 2.1 was reduced from 3,100 mg/kg to 1,600 mg/kg with a hydrogen peroxide dosage of 14 g/kg soil and in layer 2.2 the concentration of PCE was reduced from 160 mg/kg to 1 mg/kg with a dosage of 8 g/kg soil. In layer 2.1, the concentration decreased in the treatment area corresponding to destruction of about 290 kg out of 600 kg PCE [paper IV]. Also the color of the soil changed after treatment from completely black to a white/yellow color, which presumable was due to oxidation of reduced sulfur compounds.

High contaminant concentrations in the soil were removed in layer 2.2 and ERD was applied as described in Table 4-3. Even though pH and redox conditions had been extreme for month, concentration of the degradation product cis-dichloroethylene (cis-DCE) was observed to increase to almost a factor 40 above baseline concentrations before MFR only one month after the first donor addition (Newman zone, emulsified soybean oil) indicating biological activity. Monitoring 15 days after bioaugmentation with KB1<sup>®</sup> culture showed concentration of 52,000 µg/l (factor 430 above baseline concentration) and small increases in vinyl chloride (VC) and ethene [paper IV]. The KB-1<sup>®</sup> culture is a natural microbial culture used to introduce Dehalococcoides bacteria, since these are the only known organisms capable of dechlorinating PCE all the way to non-toxic ethene. The project is ongoing and the bioaugmentation with KB1<sup>®</sup> at day 225 will hopefully take the dechlorination all the way to ethene over time. Monitoring is still performed at the site to document if ethene production can be observed.
4.4 IMPLICATIONS AND PERSPECTIVES

ISCO with MFR or ASP have only been tested at very few sites in Denmark, and during this Ph.D. study extensive field work with MFR at six different sites in Denmark provided more information and hopefully more accept of the technique as a safe (if handled correct) and effective technique for source zone treatment of both fuel oil and chlorinated solvents including NAPL contamination and most other organic contaminants. It was also showed that MFR and MFSP both were able to treat a wide range of different compounds in groundwater including different pharmaceuticals. Until recently, ISCO with aggressive methods (MFR and ASP) were not very accepted in Denmark compared to e.g. North America, but it seems as if this is slowly changing and ASP is currently being tested by others at a few sites in Denmark. In the future, aggressive ISCO technologies will be a supplement or alternative to traditional techniques and can be used as part of a sequential treatment strategy. Especially, ISCO followed by bioremediation will most likely be an attractive cost-effective combination. There are still many unknown processes involved and reactions taking place in situ when these technologies are applied, but these years a lot of effort is put into understanding these in details and thereby be able to control the reactions and predict the applicability of the techniques. However, it is still essential to conduct bench and pilot studies to collect important design data for full scale applications.
5 METAL MOBILIZATION

The coexisting occurrence of organic contaminants and heavy metals in soil is a significant factor complicating remediation of contaminated sites, as the enhanced desorption of organic contaminants by the MFR and ASP reactions may lead to mobilization of heavy metals [111, 112]. Mobilization can potentially be caused by changes in pH, changes in redox conditions, degradation of NOM, or the use of chelating agents.

In soils and groundwater the effects of pH during ISCO can be complicated since most of these systems possess a strong buffering capacity that will maintain pH neutral and result in iron precipitation and ineffective catalysis. As an alternative to lowering pH in the entire treatment area to 2-4 with e.g. sulfuric acid, which was the traditional custom practice, many other methods have been used to activate hydrogen peroxide and persulfate. These include soluble iron (Fe$^{2+}$ and Fe$^{3+}$) [20-22], iron minerals [21, 23-28], and chelated iron [29-34].

The main advantages of using chelates as catalysts are that the process can be conducted at neutral pH and that chelates may travel farther in the subsurface compared to soluble iron [6]. However, the dosage of oxidants has to be increased, since MFR or ASP will also oxidize the chelating agents that are typically organic compounds. Studies have shown that the widespread used chelating agents for consumer products and industrial processes combined with poor biodegradability of these chemicals have lead to accumulation of chelating agents in the environment and ethylenediaminetetraacetic acid (EDTA) is now among the highest concentrated anthropogenic compounds in European surface waters [113]. Chelating agents may enhance the mobility and transport of heavy metals once released into the environment and high concentrations are also able to remobilize metals out of soils [114].

The objective in this work was to investigate the mobilization of different metals from natural soils treated with MFR and MFSP. This was done by:

- Batch tests with MFR (Kærgård soil, [paper II])
- Column studies with MFR and MFSP (Kærgård soil, [paper III])
- Pilot tests with MFR (Kærgård, [paper II]) + (Site A+B, [unpublished])

Specific purposes are described in the following sections summarizing the results obtained. Before the results are described, the existing knowledge on metal mobilization and the chemistry of chelating agents will be reviewed in order to understand the mechanisms causing the mobilization.
5.1 EXISTING KNOWLEDGE

Only few studies have investigated metal mobilization during treatment of contaminated soils with MFR. In the first study from 2005 [111] mobilization of Cd, Cu, Pb, Ni, and Zn during MFR treatment was investigated employing kaolinite as a model sorbent. Using soluble Fe(III) as catalyst at pH 3 resulted in displacement of Cd, Cu and Zn and using Fe(III)-NTA as catalyst at pH 6 resulted in displacement of Cd, Cu, Pb and Zn. Also the concentrations of the metals released into the aqueous phase were higher in the Fe(III)–NTA catalyzed systems. The observed differences were suggested to have been mediated by transient oxygen species, such as superoxide, which may reduce sorbed metals and facilitate their release. In the second study from 2008 [112] the release of Pb was investigated during treatment of soil with MFR using the same catalysts as in the first study, only pH was changed from 6 to 7. At pH 3, Pb release was minimal and at pH 7 no Pb was released. When hydroxyl radicals were scavenged from the reactions by adding isopropanol, leaving superoxide as the primary reactant, Pb desorption increased significantly. Again it was suggested that superoxide played a role in Pb desorption.

Chelating agents can participate in different processes, where the most important related to potential metal mobilization during ISCO are metal exchange in solution, adsorption to mineral surfaces, dissolution of minerals, remobilization of adsorbed metals, degradation by oxidation, and redox reactions involving the coordinated metal ion. Equilibrium of metal exchange is determined by stability constants. However, it is very important to include knowledge on kinetics, since ligands containing multiple bonding groups such as EDTA is often kinetically hindered in its reaction [115], and especially the reactions involving Fe(III)-EDTA that have shown to be a catalyst for MFR [31] are very slow [116], and half-life of Fe(III)-EDTA, when exchanging with Zn$^{2+}$, has been shown to be about 20 days in natural waters [117]:

$$Fe(III)\cdot EDTA^- + Zn^{2+} \rightarrow Zn(II)\cdot EDTA^{2-} + Fe^{3+}_{(precipitates)} \quad (5.1)$$

Sorption of metals change significantly when chelating agents are used, which is illustrated in Figure 5-1. Most interesting is the fact that metals in general show increasing adsorption at increasing pH, while the opposite is true for chelated metals. This means that chelating agents are able to immobilize metals through adsorption, not at high pH, but especially at low pH. However, this is mostly true for low concentrations of chelating agents, whereas high concentrations used for technical purposes such as ISCO in many cases will decrease adsorption by forming dissolved complexes [115].
Remobilization of adsorbed metals can be accomplished by chelating agents, which is a process that have been used for years for characterizing bioavailability [118], for extraction of heavy metals from contaminated soils [119-125] and to enhance phytoextraction of heavy metals from contaminated soils [126-128]. These fields of application indirectly suggest that using chelating agents for ISCO may increase metal mobilization. In addition, the chelating agents can enhance dissolution of minerals via ligand exchange reactions [129].

5.2 Batch Study

As shown in section 4, the buffering capacity of the Kærgård Plantation soil was very low and the ISCO treatment resulted in significant pH changes. To learn more about potential metal mobilization a batch study with soil from Kærgård Plantation was performed to investigate influence of chelating agents, pH and oxidation/reduction processes on metal mobilization. The study is described in details in paper II. Ten different reactors with soil and water were used, all in duplicate. The study included a control reactor with water (#1), a reactor with H_2O_2 (#2), a reactor with H_2O_2 and Fe^{2+} (#3), reactors with chelated Fe^{2+} using EDTA, citrate and pyrophosphate (#4-6), reactors with H_2O_2 and chelated Fe^{2+} (#7-9), and finally a control reactor where pH was lowered with sulfuric acid (#10). pH was significantly affected in all reactors containing hydrogen peroxide, as shown in Figure 5-2.
The low pH could increase mobilization, but as showed in Figure 5-3, metal mobilization in the pH control reactor (#10) was only slightly above the concentrations in the water control (#1) for most of the investigated metals. It is also seen that the chelated iron catalyst (#4-6) itself do not increase the mobilization. A high degree of mobilization was observed in all reactors containing hydrogen peroxide (#2,3,7-9) and for As, Cu, Pb and Zn up to 38-129% of the metals analyzed in the soil were mobilized to the aqueous phase. Results above 100% mobilization is caused by a standard deviation in the analysis results of the soil samples of up to 30% because of the heterogeneous nature of the samples. Less than 0.5% of Ni was mobilized. One suggestion is that the increased mobilization observed, when hydrogen peroxide is present, is caused by superoxide that has the potential to rapidly reduce and mobilize transition metals [130] which is in accordance to suggestions from Monahan, Tell and Watts, 2005 [111]. Another suggestion for the increased mobilization in the presence of H₂O₂ is the fact that oxalic acid and other small carboxylic acids are produced when aromatic rings are oxidized by hydroxyl radicals [131]. Aromatic structures are abundant in soil organic matter. These acids can strongly chelate some metal cations. The two suggestions along with the acidity, might explain the observed mobilization.
FIGURE 5-3: AVERAGE METAL CONCENTRATIONS IN REACTORS AFTER 5 HOURS AND 7 DAYS OF REACTION. NOTE THE DIFFERENT SCALES. THE HIGHEST DEGREE OF MOBILIZATION COMPARED TO A MAXIMAL THEORETICAL MOBILIZATION (CORRESPONDING TO 100% MOBILIZATION OF THE METALS ANALYZED IN THE SOIL) IS SHOWN FOR EACH METAL EXCEPT Fe [PAPER II].

Soil from site B was also tested in an identical study [paper II], but the results are not reviewed in this summary. Generally, the mobilization and pH effects were insignificant with soil B.

5.3 COLUMN STUDY

Results from the batch test were further evaluated by column studies, described in details in paper III. Columns were filled with 700 g Kærgård soil and demineralized water was flushed through the columns until stable conditions (pH and metals) were measured in the outlet. At this point flushing with MFSP or MFR-only was started at a
flow rate of 7-10 ml/h. Chelated iron catalysts from ISOTEC was used for the tests. Concentrations of As, Cu, Pb, Zn, Cr and Hg measured in the outlet over time are presented in Figure 5-4. The results clearly showed that mobilization occurred immediately after addition of MFSP or MFR-only to the columns. Concentrations reached levels at or above the concentrations observed in the batch study and then started to decrease as a function of time (or pore volumes exchanged). Hg was included in the analysis, but could not be observed at any time. However, Cr was mobilized in concentrations up to about 120 and 75 µg/l for MFSP and MFR-only respectively. Cr and to a lesser extent Pb, were released over a longer period of time compared to the other metals indicating that As, Cu and Zn were more easily mobilized compared to Cr and Pb. This also corresponds to the results from the batch tests in section 5.2, where a larger parts of As, Cu and Zn were mobilized compared to Pb. As(III) and As(V) form oxyanions complexes and thereby differ from the other metals investigated. pH was about 1.8 and 2.3, respectively, in the outlets of the MFSP and MFR-only reactor during oxidant addition.

![Figure 5-4: Concentrations of Metals in the Outlet of the Columns Treated with MFSP (a) and MFR-Only (b) [Paper III].](image)

### 5.4 Field Tests

Based on the results obtained in the laboratory batch and column studies, monitoring in the field during MFR pilot and full scale treatments was performed. At the Kærgård Plantation MFR pilot project, metals were monitored in the treatment area, 2.5 m downgradient the nearest injection well and 25 m downgradient. The results are presented in Table 5-1, from where it is seen that metals were mobilized in concentrations even higher than those measured in the bench scale tests. Again it was especially Cu and Pb measured in concentrations up to 52 and 34 mg/l in the treatment area and 14 and 28 mg/l 2.5 m downgradient the injection wells. No metals above background concentrations were observed 25 m downgradient. Except from the
very high concentrations of metals, these trends are typical for ISCO, where metals are released in the treatment area, but precipitates when transported outside the reactive zone.

**TABLE 5-1: RESULTS IN MG/L FROM PILOT STUDY AT KÆRGÅRD PLANTATION. A TOTAL OF FOUR MFR INJECTION EVENTS WERE PERFORMED AFTER 7, 63, 111, 153 DAYS AS DESCRIBED IN SECTION 4.3. "N.A." NOT ANALYZED [PAPER IV].**

<table>
<thead>
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<th>Time (days)</th>
<th>0</th>
<th>29</th>
<th>79</th>
<th>135</th>
<th>175</th>
<th>247</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Center of treatment area</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>5.78</td>
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<td>2.65</td>
<td>2.41</td>
<td>2.26</td>
<td>2.64</td>
</tr>
<tr>
<td>Pb</td>
<td>2.20</td>
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<td>9.47</td>
<td>8.60</td>
<td>2.40</td>
</tr>
<tr>
<td>Cu</td>
<td>1.40</td>
<td>16.00</td>
<td>33.70</td>
<td>28.20</td>
<td>12.00</td>
<td>1.60</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td>0.35</td>
<td>0.25</td>
<td>0.14</td>
<td>0.14</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>16.00</td>
<td>63.00</td>
<td>60.00</td>
<td>130.00</td>
<td>64.60</td>
<td>26.00</td>
</tr>
<tr>
<td>Mn</td>
<td>0.66</td>
<td>1.80</td>
<td>1.70</td>
<td>3.90</td>
<td>1.38</td>
<td>0.40</td>
</tr>
<tr>
<td><strong>2.5 m downgradient the nearest injection well</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>5.04</td>
<td>2.54</td>
<td>2.61</td>
<td>2.43</td>
<td>2.86</td>
<td>3.44</td>
</tr>
<tr>
<td>Pb</td>
<td>0.03</td>
<td>14.00</td>
<td>n.a.</td>
<td>9.50</td>
<td>5.31</td>
<td>n.a.</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
<td>21.00</td>
<td>n.a.</td>
<td>28.10</td>
<td>11.80</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td>0.21</td>
<td>n.a.</td>
<td>0.14</td>
<td>0.19</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fe</td>
<td>12.00</td>
<td>71.00</td>
<td>n.a.</td>
<td>160.00</td>
<td>62.80</td>
<td>n.a.</td>
</tr>
<tr>
<td>Mn</td>
<td>0.70</td>
<td>2.60</td>
<td>n.a.</td>
<td>4.40</td>
<td>1.37</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Metal mobilization was also monitored at site A and B before, during and after MFR applications. Both treatments were performed with hydrogen peroxide and sulfuric acid to lower pH. No catalyst was added. The results are listed in Table 5-2 from where it is seen that sufficient Fe up to 86 and 160 mg/l was released from the sand to catalyze the MFR reactions. At site A, Cu, Fe, Mn, Ni, Zn and Mg were mobilized in concentrations above 1 mg/l, but all metal concentrations decreased to background levels in the following monitoring events except for Fe and Mn in one well, where pH remained low. No release or transport of metals to the monitoring wells 1 m from the treatment area was observed. The same trend was observed at site B, but no long term monitoring data exists to document if released metals precipitated, when conditions returned to conditions before injections.
5.5 Implications and Perspectives

Results reviewed in this section and paper II+III indicate that metals are mobilized during MFR (and MFSP) applications, but precipitates again when pH and redox conditions are neutralized outside the treatment area. Lowering of pH will cause some mobilization, but the most significant release is caused by reactions based on hydrogen peroxide, and according to the suggestions in the peer reviewed literature, reductants as superoxide plays an important role. But also formation of e.g. oxalic acids as a result.
of oxidation reactions might cause increased mobilization. Even though chelating agents are used to mobilize metals, it seems as if they do not significantly impact the release, when used to chelate Fe catalyst in ISCO. Only few studies have dealt with this issue and more research within this area is needed in order to fully understand the processes and thereby minimize mobilization in future ISCO applications. However, the problem might not be very significant, especially not in well buffered soils.
6 SCAVENGING

Radicals produced in oxidations systems react rapidly with other chemical species in solution at near diffusion controlled rates [14, 15, 52]. Besides contaminant degradation these reactions include non-productive reactions with other compounds and radicals resulting in reduced reaction efficiency and effectiveness, often referred to as scavenging reactions. In this section the processes of radical scavenging are reviewed with focus on carbonates and chloride. As an example, high concentrations up to 4,600 mg/l (130 mM) of chloride and 6,900 mg/l (113 mM) hydrogen carbonate have been observed in the source zone in Kærgård Plantation. Also very high concentration of chloride can occur when DNAPL chlorinated solvents are treated with ISCO.

The objective in this work was to investigate scavenging from chloride and carbonates in different ASP systems. This was done by:

- Batch tests with heat activated persulfate [paper V]
- Batch test with alkaline activated persulfate [paper V]
- Batch test with iron activated persulfate [paper V]

Specific objectives are described in the following sections summarizing the results obtained. Before the results are described, the existing knowledge on radical scavenging will be reviewed in order to understand the mechanisms causing the scavenging.

6.1 EXISTING KNOWLEDGE

Scavenger ions are one of the most common factors limiting the oxidation efficiency. Especially chloride and hydrogen carbonate/carbonate have the potential to impact pathways, kinetics, and efficiency of oxidation reactions both as radical scavengers and as metal complexing agents [25, 41, 132, 133]. Also, phosphate is often added to stabilize hydrogen peroxide, since phosphate is believed to adsorb to and inactivate catalytic and scavenging sites on e.g. iron oxides. Through addition of phosphate, oxidation efficiency can be enhanced and oxidant decomposition reduced significantly, which is assumed to be through reduction of surface scavenging sites in the soil [134]. Carbonates and chloride can act in the same way and form aqueous complexes or solid precipitates with metals or mineral surfaces [25, 41]. In the peer reviewed literature, experiments with MFR showed that these complexation processes are decreasing both the rate of contaminants degradation, oxidant decomposition and the overall oxidation efficiency [41, 132, 133, 135], whereas others have shown that the overall efficiency was not decreased even though the reaction rates for degradation of contaminants
were decreased [25]. Carbonates have also been shown to reduce rates of contaminant degradation as well as oxidant decomposition rates for ASP [47, 55, 136]. The adverse impact of the carbonates in ASP increases with increasing pH [55, 136].

Besides the complexation processes, chloride and carbonates can also form radicals on their own via reaction with the reactive species in MFR and ASP systems [14, 44, 136-139]:

\[
\begin{align*}
OH^+ + HCO_3^- &\rightarrow OH^- + HCO_3^* \\
OH^+ + CO_3^{2-} &\rightarrow OH^- + CO_3^{*} \\
OH^+ + Cl^- &\rightarrow ClHO^* \\
SO_4^{2-} + CO_3^{2-} &\rightarrow SO_4^{2-} + CO_3^{*} \\
SO_4^{2-} + HCO_3^- &\rightarrow SO_4^{2-} + HCO_3^* \\
SO_4^{2-} + Cl^- &\rightarrow SO_4^{2-} + Cl^* 
\end{align*}
\]

The formed carbonate and chloride radicals can react further [139]. The chloride radicals:

\[
\begin{align*}
ClHO^* &+ H^+ \rightarrow Cl^* + H_2O \\
Cl^* + Cl^- &\rightarrow Cl_2^- \\
2Cl_2^- &\rightarrow 2Cl^- + Cl_2 \\
Cl_2^- + H_2O &\rightarrow ClHO^*^- + H^+ + Cl^- 
\end{align*}
\]

The carbonate ions and radicals [138]:

\[
\begin{align*}
HCO_3^* &\equiv CO_3^{2-} + H^+ ; pK_a = 9.5 \\
HCO_3^- &\equiv CO_3^{2-} + H^+ ; pK_a = 10.45 \\
H_2CO_3 &\equiv HCO_3^- + H^+ ; pK_a = 6.33 
\end{align*}
\]

However, the reactivity of these radicals with organic contaminants or participation in chain propagation reactions are not widely investigated or well understood. It is traditionally assumed that they have an overall negative impact on the performance [47, 136]. The carbonate radical (CO_3^{*}) generated by reaction 6.2 was reported to yield reduction potential (CO_3^{*}, H^*/HCO_3^-) of 1.63 V at pH 8.4 [138] and it has been shown to be strong enough to degrade PAH's [140]. Based on these findings, carbonate
radicals might play an important role and should not strictly be considered a scavenger. It has also been suggested that the chloride radicals can participate in propagation reactions with oxidant and thereby not be entirely unproductive [141] and that the dichloride radical catalyzes perhydroxyl radical formation from hydrogen peroxide and the propagation reaction [137].

The concentration of chloride needed to decrease oxidation efficiency of heat activated persulfate at 130°C, was shown to be more than 20 mM Cl⁻ [142], and other studies with persulfate at 20°C at neutral pH showed that only chloride levels above 200 mM affected the degradation of TCE and that hydrogen carbonate up to 9.2 mM had no influence [136].

High concentrations (>100 mM) of chloride have also been reported to result in formation of halogenated by-products [142] and even hexachloroethane has been observed to be formed during treatment of PCE as a results of the reactive chloride species [54].

It is worth noticing that because hydrogen peroxide is generally present at high concentrations in MFR systems and has a moderate rate constant for reaction with hydroxyl radicals \(2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}\) [14], reaction 2.14, hydrogen peroxide is itself a primary source of inefficiency in MFR systems [143]. Also chelating agents used for keeping catalyst in solution represents a sink for the radicals [144] and the catalyst itself might consume significant amounts of radicals [62].

6.2 Experimental results with RNO

The organic dye p-nitrosodimethylaniline (RNO) was used as a model compound, since it is easily detectable by measuring absorbance at 440 nm, thermally stable [paper V], stable at high pH [145], and it is bleached by oxidation with hydroxyl radicals [146], sulfate radicals [147], and other strong oxidants [148]. It is not reactive with singlet oxygen, superoxide anions or other peroxygens [149-151].

The effects of chloride and carbonates were investigated for heat activated persulfate at 65°C at neutral pH, for alkaline activated persulfate at pH 12.4 and for chelated iron activated persulfate at neutral pH. Initial concentrations of persulfate and RNO were 5 mM and 0.05 mM respectively. Some results are presented in Figure 6-1.
FIGURE 6-1: EFFECTS OF CHLORIDE AND HYDROGEN CARBONATE/CARBONATE ON BLEACHING OF RNO BY HEAT ACTIVATION AT 65˚C, ALKALINE ACTIVATION AT PH 12.4 AND CHELATED IRON ACTIVATION OF PERSULFATE. MODIFIED FROM [PAPER V].

Heat activated persulfate was not affected by hydrogen carbonate based on RNO bleaching, but chloride significantly affected the bleaching by enhancing the initial reaction rate. However, when the concentration of RNO was decreased during the run, high (200-400 mM) and low (1mM) concentrations of chloride seemed to inhibit the bleaching reaction compared to the control. Only the chloride concentrations of 10 mM enhanced the bleaching over the entire 60 minutes reaction period. Less than 5% of the persulfate was consumed after 60 min.

Alkaline activated persulfate at pH 12.4 was affected by the presence of carbonate that enhanced the bleaching rate significantly. Chloride, in all the tested concentrations 1-400 mM, also enhanced the bleaching of RNO compared to control reactors containing no chloride. Less than 5% of the persulfate was consumed after 240 min.

Chelated iron activated persulfate was not affected significantly by chloride or hydrogen carbonate. This activation mechanism caused the fastest bleaching of RNO with a very rapid initial reaction rate resulting in 50% bleaching within seconds. This was also the only activation mechanism consuming measurable amounts of persulfate since about 25% of the persulfate reacted within the first 2 minutes and about 30% after 60 min.

Chloride and carbonates are generally assumed to have an overall negative impact on the performance in ISCO because of scavenging of hydroxyl and sulfate radicals, but the results presented in Figure 6-1 indicate that chloride and carbonates may have some positive effects enhancing oxidation reactions. From these results it was not evident if chlorine and carbonate species produced according to reactions 6.1-10 are directly involved in degradation of the target compounds or if they participate in propagation reactions with persulfate causing more sulfate radicals to be produced.
6.3 EXPERIMENTAL RESULTS WITH PCE

A test similar to the RNO test was conducted to investigate PCE destruction by chelated iron activated persulfate at ambient temperature with molar concentrations of \( \text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{citric acid/PCE} \) of 4/2/0.4/0.2 mM. No effects were observed in the RNO tests at neutral pH, but in these PCE tests no phosphate buffer was used and pH was therefore 2.5-2.6 in all tests. The results showed as degraded PCE and the consumed persulfate are presented in Figure 6-2. The conclusion from these results was that increased chloride concentration decreased the rate of oxidation, but the overall oxidation efficiency was not affected.

![FIGURE 6-2: DEGRADATION OF PCE BY CHELATED IRON ACTIVATED PERSULFATE AS A FUNCTION OF CHLORIDE CONCENTRATION AFTER 60 MINUTES OF REACTION. CONSUMPTION OF PERSULFATE IS ALSO SHOWN [PAPER V].](image)

6.4 IMPLICATIONS AND PERSPECTIVES

Reviewing the various processes involved in scavenging of radicals related to MFR and ASP reveals a system with numerous parameters to be optimized involving oxidant concentration, catalyst concentrations, use of chelating agents, naturally occurring ions, natural organic matter, unknown processes etc. In well known laboratory systems it might be possible to optimize these processes to minimize scavenging, but most studies only focused on optimizing a single parameter, e.g. oxidant/catalyst ratio. When taking all aspects into account it is always a question of compromises since changing one parameter to enhance a process in most cases will interfere with another process. When applying MFR or ASP for full scale treatments more unknowns are introduced and optimization becomes more difficult and relies in great extent on experience from similar sites and rule of thumbs.
As showed from the results presented in this section, the effects of scavenger ions are not fully understood or consistent for different activation mechanisms. Further research may improve the understanding of the role of chloride and carbonate radicals in oxidation systems, and potentially allow for optimization of process chemistry that would minimize their negative impacts and maybe even enhance their potential positive aspects.
7 CONCLUSIONS

Today soil and groundwater contamination is a widespread and challenging problem threatening groundwater resources throughout the world. As with all other technologies, ISCO with activated peroxygens is not a universal solution solving all the problems, but the technologies are important supplements to the tool box of remediation technologies available. In particular these techniques are suited for permeable geology, complex contaminant mixtures, toxic contaminants or high concentrations of contaminants including NAPLs.

Some of the most significant specific conclusions drawn from the research presented in this thesis are:

- Fast and robust spectrophotometric quantitative determination of persulfate and hydrogen peroxide can be performed in the field by measuring the yellow color developed from oxidation of iodide to iodine.
- MFR can degrade >1000 mg/kg levels of fuel oil and PCE in soils.
- MFR and ASP reactions can be controlled. The oxidants are relatively stable in presence of contaminated soil and groundwater and observed temperature increases during MFR treatments were only 5-10 °C.
- pH in low buffered soil treated with MFR or ASP can decrease to 1-2.
- MFSP can efficiently degrade aniline, pyridine, sulfonamides, barbiturates, petroleum hydrocarbons, BTEX, PCE, and TCE in the aqueous phase.
- ERD can be used as a second step in a treatment train in source zones after aggressive ISCO with MFR. Redox and pH conditions needs to be changed by injecting buffer and electron donor.
- MFR and MFSP can cause mobilization of metals (Cu, Pb, Fe, As, Mn, Ni, Zn, Mg) in the treatment area, but these are most likely precipitated when leaving the treatment area. Cyanide and Hg were not mobilized. Results indicate that low pH and chelating agents cause some of the mobilization, but the most significant mobilization is caused by redox reaction.
- Chloride and carbonates should not be strictly considered as scavengers in ASP systems. For some contaminants they may enhance oxidation rates and for other they may decrease reaction rates, but not affect the overall oxidation efficiency.
8 PERSPECTIVES AND FUTURE RESEARCH

Recent advantages in the use of activated peroxygens show that the involved processes are complex and still not fully understood. The techniques are widely used in full scale to treat contaminated soil and groundwater, but to increase the chances for successful ISCO application with activated peroxygen more knowledge is needed. Further research within the following areas will help improve the understanding of ISCO with activated peroxygen:

- In general more published well documented field applications are needed to support and validate the observation from small scale laboratory tests.
- MFR has been investigated in most details and hence more research on persulfate is needed, e.g. knowledge on activation mechanisms and interactions with subsurface soils.
- Optimization of coupled ISCO and bioremediation and other combinations.
- Mobilization of metals are still very often questioned when ISCO is applied, and more studies investigating the transport and fate of the mobilized metals are needed. Most research suggests that metals are precipitated outside of the treatment area, but well documented field tests could elucidate this issue.
- Is it possible to enhance the positive aspects of chloride and carbonates in ISCO? Which contaminants can be degraded by carbonate or chloride radicals? Can the ions catalyze the propagation reactions?
- Development of decision and design tools that incorporate process conditions specific to both the site and the contaminants to enable site-specific engineering of ISCO.

The application of activated peroxygens in combination with other technologies as treatment trains [152] of direct coupling of e.g. surfactants/co-solvents with ISCO to enhance NAPL removal [153] attracts increasingly attention and holds promise for enhanced treatment of contaminated soil and groundwater in the future when the involved complex processes are more understood and optimized.
9 FULL PUBLICATION LIST

9.1 PAPERS

Bennedsen, LR & Søgaard, EG, 'Simple Spectrophotometric Determination of Peroxygens in Field during ISCO', *Groundwater monitoring and remediation* (accepted 2011)


Kusk, KO, Rein, A, Bennedsen, LR, Christophersen, M, Durant, N, Jørgensen, TB, Rügge, K & Bjerg, PL, 'Use of toxicity assays for evaluating the effectiveness of groundwater remediation with modified Fenton’s reagent' (in preparation)


9.2 CONFERENCES - ORAL PRESENTATION


9.3 CONFERENCES - POSTER PRESENTATIONS

Bennedsen, LR, Søgaard, EG & Mortensen, L, 2009, 'Carbonate and Chloride Scavenging in $S_2O_8^{2-}$/Fe$^{2+}$/Citric Acid Oxidation of PCE', AOP5 - 5th IWA Specialist Conference - Oxidation Technologies for Water and Wastewater Treatment, Berlin, Germany.


Bennedsen, LR, Søgaard, EG & Mortensen, L, 2008, 'Test Concept for Advanced Oxidation Techniques', Oxidation & Reduction Technologies for In-Situ Treatment of Soil and Groundwater, San Diego, USA.
10 REFERENCES


[106] NIRAS, Redegørelse over anvendte kemikalier på Grindstedværket og deres potentielle trussel i forhold til miljøet, Region of Southern Denmark (2009).


