Catalyzed Calcium Peroxide as Treatment Technology for Organic Compound Contaminated Soil and Groundwater

Master's Thesis in Chemical Engineering

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STUDENT REPORT

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Preface

The present writing is a master's thesis named 'catalyzed calcium peroxide as treatment technology for organic contaminated soil and groundwater' made by Barend de Jong. This work serves the final work for the Master of Science (M.Sc.) degree in Chemical Engineering at Aalborg University Esbjerg. This work was written in the period from the 1st of October 2018 till the 7th of June 2019, under supervision of Jens Muff.

This thesis concerns technology development of calcium peroxide based in-situ chemical oxidation. The potential of this technology has been demonstrated in previous research, but requires more research, development and optimization.

Laboratory studies are carried out in order to optimize a variety of operating parameters of aqueous and soil systems. Contaminants used in this work are benzoic acid and perchloroethene. Column studies were performed in order to determine the behaviour of this oxidant in subsurface environments. All experimental work was carried out at Aalborg University in Esbjerg. Soil samples and groundwater samples were provided by Rambøll during an excursion to the Kærgård plantation.

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Abstract:

In this work, calcium peroxide has been used as a source of hydrogen peroxide for the development of the calcium peroxide advanced oxidation process. Calcium peroxide has been used to degrade a variety of contaminants in both aqueous and soil systems at neutral pH using chelated Fe(II) as catalyst. Benzoic acid (BA) was successfully degraded at neutral pH in aqueous system using citric acid (CiAc) and oxalic acid (OA) as chelating agents. The optimal ratio between oxidant and catalyst was found to be 1/1. 98% of the initial BA present in a soil slurry was degraded by using a 1/1 ratio between oxidant and catalyst and a 100/1 ratio between oxidant and contaminant. Heavily tetrachloroethene (PCE) contaminated soil has been successfully treated reaching up to 77% PCE removal by using calcium peroxide activated by Fe(II) chelated with OA. Column studies showed that calcium peroxide is able to release hydrogen peroxide effectively over a minimum of 8 hours. The operating flowrate did not have any influence on the hydrogen peroxide concentration measured at the outlet of the column. A decrease in temperature increases the total amount of hydrogen peroxide released.

List of abbreviations

List of abbreviations and their meaning

ISCO	In-situ chemical oxidation
CP	Calcium peroxide
HP	Hydrogen peroxide
OA	Oxalic acid
CiAc	Citric acid
CT	Carbontetrachloride
PCE	Tetrachloroethene
TCE	Trichloroethene
COC	Contaminant of concern
CCP	Catalyzed calcium peroxide
CHP	Catalyzed hydrogen peroxide
AOP	Advanceed oxidation process
EDDS	Ethylenediamine-N,N-disuccinic acid
EDTA	Ethylenediamineteraacetic acid
NTA	Nitrilotriacetic acid
ROS	Reactive oxygen species
SPC	Sodium percarbonate
APS	Activated persulfate
FA	Formic acid
CA	Chelating agent
NAPL	Non-aqueous phase liquid
DNAPL	Dense non-aqueous phase liquid
BA	Benzoic acid
HBA	Hydroxy-benzoic acid
ERD	Enhanced reductive dechlorination
NOM	Natural organic matter
IC	Ion chromatography
GW	Groundwater

Contents

1 Introduction **6**
- 1.1 State of the art research in calcium peroxide oxidation . . . 9
- 1.2 Aim of this Thesis . . . 12

2 Calcium peroxide based in-situ chemical oxidation **14**
- 2.1 Calcium peroxide . . . 14
- 2.2 Hydrogen peroxide and Fenton's chemistry . . . 15
- 2.3 Subsurface and contaminant properties . . . 21
  - 2.3.1 Contaminant properties . . . 22
  - 2.3.2 ISCO for remediation of DNAPLs . . . 23
  - 2.3.3 Scavenging . . . 24
  - 2.3.4 Natural organic matter . . . 26
  - 2.3.5 Kinetic data for common scavengers . . . 26
- 2.4 Kærgård plantation . . . 27
- 2.5 Chelating agents . . . 29

3 Experimental considerations **32**
- 3.1 I-A: Hydroxyl radical yield determination . . . 32
- 3.2 I-B: Influence of oxidant/catalyst ratio on benzoic acid degradation in drinking water . . . 33
- 3.3 II-A: Degradation of model contaminant in a soil slurry: batch experiments 34
- 3.4 II-B: Degradation of PCE contaminated soil: batch experiments . . . 34
- 3.5 III-A: Oxidant delivery and CP dissolution . . . 34
- 3.6 III-B: BA degradation in continuously operated column . . . 35
- 3.7 III-C: PCE degradation in continuously operated column . . . 35
- 3.8 Hydrogen peroxide analysis . . . 36
- 3.9 Chloride analysis . . . 37

4 Materials and methods **38**
- 4.1 Materials . . . 38
  - 4.1.1 Contaminants . . . 38
  - 4.1.2 Soils . . . 41
  - 4.1.3 Buffer solutions . . . 41
- 4.2 Analytical methods . . . 42

4.2.1 Hydrogen peroxide analysis 42
4.2.2 Benzoic acid analysis 42
4.2.3 Chloride analysis 43
4.3 Experimental methods 43
4.3.1 I-A: Hydroxyl radical yield determination 43
4.3.2 I-B: Influence of oxidant/catalyst ratio on BA degradation in drinking water 44
4.3.3 II-A: Degradation of model contaminant in a soil slurry: batch experiments 45
4.3.4 II-B: Degradation of PCE contaminated soil: batch experiments . . 47
4.3.5 III: Continuous operated column studies 49
4.3.6 III-A: Oxidant delivery and CP dissolution 50
4.3.7 III-B: BA degradation in continuously operated column 50

5 Results and Discussion **52**
5.1 I-A: Hydroxyl radical determination 52
5.2 I-B: BA degradation in drinking water 55
5.2.1 Comparison of chelating agents 56
5.2.2 Influence of molar ratio 56
5.3 II-A: Soil slurry experiments with model contaminant 60
5.4 II-B: Soil slurry experiments with PCE contamination 63
5.5 III: Continuously operated column studies 69
5.5.1 III-A: Oxidant delivery and CP dissolution 70
5.5.2 III-B: Degradation of BA in continuously operated column 76
5.6 Summary and implications for CCP technology development 77

6 Conclusions **79**

7 Recommendations for future work **81**

Bibliography **83**

8 Appendices **89**
8.1 Appendix A: HP analysis calibration data 89
8.2 Appendix B: Model soil pore volume data 89
8.3 Appendix C: Pump calibration 90
8.4 Appendix D: Kærgård plantation soil data 90

1. Introduction

Environmental pollution can be considered as the accumulation of contaminants harmful to environment, human health or both. Common pollutants (among other) are for instance: gasoline/fuel oil, aromatic hydrocarbons, other organic compounds like alcohols, ethers and ketones, chlorinated organic solvents and (heavy) metals. These type of contaminants can have a variety of hazardous properties to human well being and the environment. They can be endocrine-disruptive, carcinogenic, toxic and may posses mutagenic properties giving rise to the need for the development of technologies able to remove these contaminants in order to limit their harmful effects. [1]

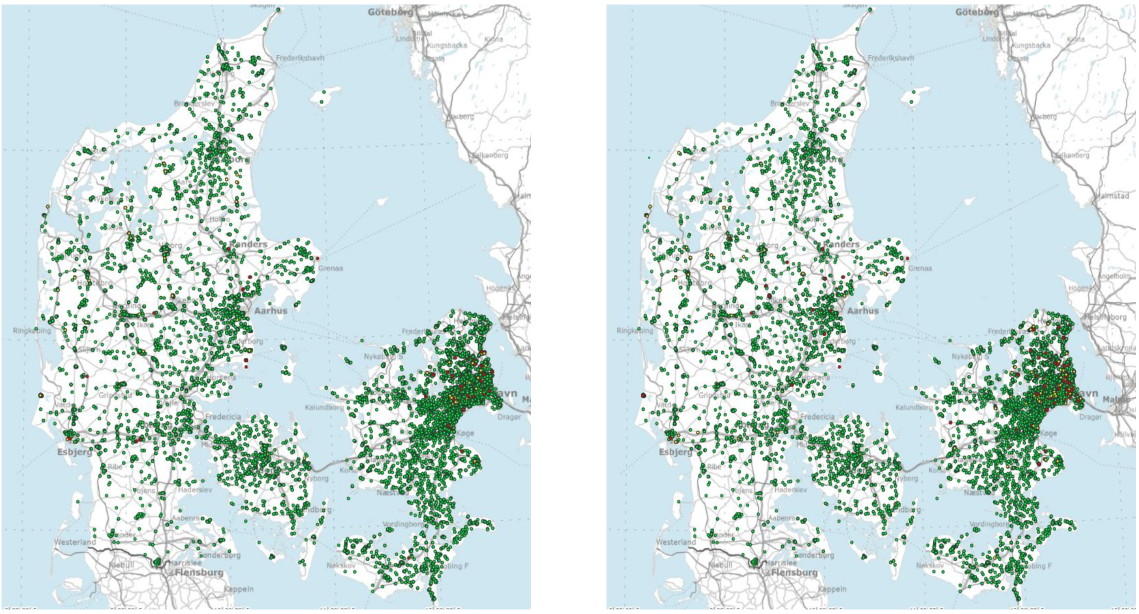
This work will focus on the technology development of soil and groundwater remediation of contaminants which are often encountered in the polluted soil and groundwater: organic compounds. Attention will also be placed on a prevalent challenge in groundwater and soil remediation: chlorinated solvent contaminated soil and groundwater [2, 3]. The term chlorinated solvents contains a wide range of compounds including chlorinated ethanes, ethenes, ethers and aromatic compounds. However, this project will focus on two of the most common ones encountered in polluted areas: trichloroethene (TCE) and tetrachloroethene, or as it is most commonly referred to: perchloroethene (PCE) [4]. Because of their low flammability, low reactivity, simplicity of evaporation and high dissolving capacity these solvents were utilized in a vast range of industrial applications in the 20th century including dry-cleaning, aerospace, pharmaceutical and metal industry [5].

Carbontetrachloride (CT) was the first chlorinated solvent produced and brought into use around 1900. In 1940, PCE had overtaken CT in terms of its application in industry [5]. Its main uses include removing paint, cleaning automotive parts and regenerating catalysts. The high stability of PCE resulted in the availability of high purity up to 99.9%. In the second half of the 20^{th} century PCE was produced with added additives during production, specifically aimed at its application in dry cleaning [5]. The purpose was removing the need for mixing these additives with PCE by the dry cleaner. TCE production started around 1920 with its main application in the chemical, textile, automotive and electronic industry. In commercial products it has been applied in a variety of products including adhesives, paint (removers), lubricants and fire extinguishers among many other products. TCE without stabilizers is typically of 99% purity. However, TCE in this form is susceptible to oxidation by air, light or heat exposure. This introduced the addition of stabilizers to prevent the TCE from oxidizing. [5]

In 1970, the amount of PCE and TCE used and produced was drastically decreased.

This was due to new found information about the toxicity and harmful impact of these compounds and due to newer, stricter environmental regulations [5]. This resulted in new methods of handling, storing and disposing PCE and TCE making them less attractive to use in industry. Nevertheless, the old methods in which TCE and PCE were used, handled and stored had already made a global impact and the consequences are still experienced to this day. In Denmark, TCE and PCE contaminated groundwater is still found in multiple groundwater sites [6]. In Figure 1.1 the Danish groundwater sites which have been measured on PCE and TCE content are illustrated. Green markers indicate that the measured concentration poses no significant threat, orange markers indicate possible threat and red markers indicate high concentrations of PCE and TCE requiring remediation to reduce the concentrations [6].

In the area near Esbjerg there is a contaminated area, the kærgård plantation, containing high concentrations of PCE up to 10.000 $\mathrm{mg\,kg^{-1}}$ [7]. Action is required to reduce the TCE and PCE content in these contaminated sites in order to reduce the threat to environment, human and aquatic life in the surrounding area. This contaminated site is used as a case study in this work where contaminated soil from the kærgård plantation is used as a relevant contamination source in order to test the developed technology in earlier stages. In section section 2.4, the kærgård plantation and its history in contamination and recent remediation attempts will be discussed in more detail.



(a) **(b)**

Figure 1.1: PCE and TCE concentrations in groundwater sites in Denmark and area surrounding Esbjerg. **(a)** PCE **(b)** TCE **(c)**: PCE in Esbjerg area **(d)**: TCE in Esbjerg area .

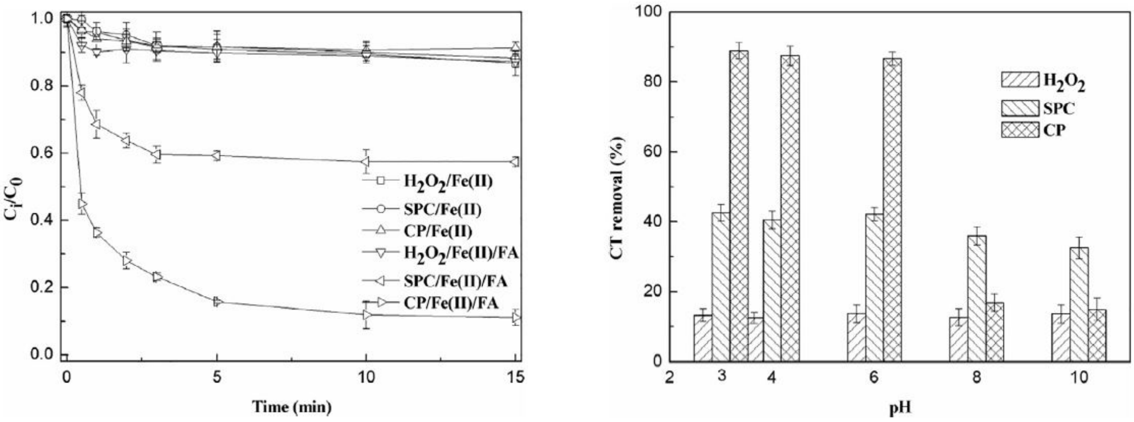
After the global realization about the adverse affect of the wide range of contaminants found in soil and groundwater, technologies were developed and utilized for the remediation of these contaminated sites. The technologies developed can be classified into three types: immobilization, destruction and separation of the contaminants. Immobilization techniques are based on containing the contamination in soil by the use of barriers or landfills that inhibit the contamination from migrating. Separation of the contaminants is utilized if the destruction of certain types of contaminants is not a feasible option, in which case the contamination should be separated from the contaminated soil and groundwater. This can be done by using solvents or surfactants or by washing the soil. The destruction of the contaminants can be achieved through the application of multiple techniques, most commonly used are bio-remediation and chemical oxidation. Both methods can be used on-site (*in-situ*) and off-site (*ex-situ*). This work will focus on the in-situ remediation of organic contaminated soil and (ground)water, therefore the other methods mentioned above will not be discussed further since they are beyond the scope of this thesis. [8]

Many contaminants found in the environment are in fact readily degraded by application of oxidation processes, which are applied to great extent in waste water treatment in industry and municipality water treatment [2]. The process of chemical oxidation is based on the formation of reactive oxygen species (ROS) capable of mineralizing contaminants or at least reducing them to more readily degradable intermediates. Diluted hydrogen peroxide (HP), 1-2%, with Fe(II) or Fe(III) as activator is the most commonly known chemical oxidation process [9]. This is referred to as Fenton's reagent. A system that utilized a more concentrated form of HP, modified Fenton's reagent or catalyzed HP (CHP), was the first oxidant applied on large scale for the remediation of formaldehyde contaminated groundwater [9]. The successful use of HP in the advanced chemical oxidation process (AOP) led to research, development and eventually to application of other AOPs with oxidants like ozone, permanganate and persulfate in-site, referred to as *in-situ chemical oxidation* (ISCO). ISCO applied using permanganate is considered the most developed method compared to other oxidants but is limited in its applicability [10]. ISCO with catalyzed HP (CHP) and activated persulfate have been utilized in practice at a considerable number of sites in the removal of a wide range of contaminants [11]. With HP as oxidant, however, drawbacks in the form of reactive intermediates and mechanism occurring during the oxidation process are observed in addition to a high total oxidant demand [11]. Calcium peroxide (CP) has gained attention only in recent years as a possible oxidant in ISCO applications acting as a slow HP releasing compound [2]. However, most research and literature focuses on the performance of analytical grade calcium peroxide at laboratory scale in degradation of different contaminants in aqueous systems. Moreover, the application of calcium peroxide in ISCO is not well documented and practically non-existent in Europe. One of the goals of this thesis will be to provide more insight in the possibilities of the application of calcium peroxide in ISCO processes targeting various contaminants.

1.1 State of the art research in calcium peroxide oxidation

Despite the lack of knowledge on large scale application of CP in ISCO, a lot of research has been published on the application of the advanced chemical oxidation process using CP catalyzed by Fe(II)/Fe(III) (CCP) in the degradation of a wide range of possible contaminants. In 2008, Cassidy and Northrup applied technical grade CP in the degradation of PCE using CCP. Results show that at low pH technical grade CP (50%) released HP in a more effectively in comparison to the use of liquid HP and CP performed better in the degradation of PCE in a pH range of 6-9 [12]. However, PCE was not fully removed indicating that there is a limitation to the application of calcium peroxide at circum neutral pH. Benzene was successfully degraded using a CP/Fe(II) CCP approach by Xue et al. The molar ratio for optimal degradation (CP/Fe(II)/Benzene) was found to be 4/4/1 [13].

Recent research shows the benefit of using chelating agents in combination with the Fe(II) (or in some work Fe(III)). Zhang et al. investigated the degradation of TCE with CP as oxidant and compared the degradation efficiency and speed in systems with and without chelating agents. (S,S)-ethylenediamine-N,N′-disuccinic acid (EDDS) was used as chelating agent. Results showed that degradation in the CP/Fe(II) system was fast in the very beginning of the process but the degradation did not proceed any further to any significant extent after the first 10 minutes. However, in the CP/Fe(II)-EDDS system, the degradation was less significant in the first 10 minutes but 98.4% degradation of TCE was achieved in 180 minutes compared to just little above 70% degradation in the CP/Fe(II) system. Increasing the dosage of Fe(II)-EDDS seemed to have adverse effects on degradation efficiency. The most efficient ratio of Fe(II)/EDDS was found to be 1/1. In addition, the system was more sensitive to varying complex concentrations compared to varying CP concentrations [14]. Pan et al. compared the performance of oxidants in presence of ethylenediaminetetraacetic acid (EDTA).A comparison was made between CP/Fe(III)-EDTA and HP/Fe(III)-EDTA systems in the degradation of phenol. Not only did CP/Fe(III)-EDTA performed better, it degraded phenol in a shorter time-span compared to the HP system. An increase in the molar ratio of EDTA/Fe(III), (1:7 to 1:2), resulted in more efficient degradation of phenol. Moreover, it was shown that CP/Fe(III)-EDTA resulted in a higher production of superoxide radicals ($O\cdot^{2-}$ [15]. X. Zhang et al. investigated the use of reduction agent ascorbic acid in CP/Fe(III) system to enhance Fe(II)/Fe(III) cycling and avoid precipitation of Fe(III) at near neutral pH. The results showed successful degradation of TCE at lower pH environments. However, an increase in the pH resulted in a decrease in degradation efficiency. The research posed an alternative route to the possible application of CP as oxidant [16]. In the same way, Tang et al. 2018, investigated degradation of CT using a CP/Fe(II) system in presence of ethanol. Addition of ethanol to the system improved the stability of superoxide radicals and formed a new reactive species, hydroxy ethyl radicals which could participate in the degradation of CT. These two radical species were proved to be the main ROS in the system. Full degradation was achieved in pH values ranging from 3-5, pH conditions outside of this range would inhibit the degradation [17]. Wenchiao Jang et al. investigated the permormance of three different oxidant/Fe(II)-Formic Acid systems: CP/Fe(II)-FA, HP/Fe(II)-FA and sodium percarbonate (SPC)/Fe(II)-FA in the degradation of CT. In acidic environments, CP performed better than the other two oxidants as is observed from Figure 1.2b. With the initial pH of 6, CP performed better than SPC, whereas at a pH of 8, SPC performed better, as illustrated in Figure 1.2b [18].



(a) **(b)**

Figure 1.2: Comparison of CHP, CCP and catalyzed SPC in the degradation of aqueous CT, [HP]=[SPC]=[CP]=[Fe(II)]=[FA]= 1.56 mM, [CT]=0.13 mM [18]. **(a)** CT degradation performance with and without formic acid, and **(b)** Effect of initial pH. Reprinted with permission. [18]

However, the pH changed drastically over the course of the experiments. Experiments where the pH is kept constant by means of using a buffer solution is missing. Zhou et al. compared the use of four chelating agents in the degradation of bisphenol A with Fe(III) as catalyst with CP as oxidant. Oxalic acid (OA), citric acid (CiAc), EDTA and tartaric acid were used as CAs. Degradation of bisphenol A was increased from 21.3% without CAs to 98.3% (CA) 98.9% (OA) 95.5% (EDTA) and 95.0% (tartaric acid). Results indicates that OA and CiAc are the most effective CAs under the same dosage [19].

The CCP system was successfully used in the degradation of mixed chlorinated solvents (PCE, TCE and CT) using a mixture of FA and CiAc in contaminated groundwater [20]. An oxidant to contaminant ratio of 12/1 resulted in 79.4% removal of PCE and 96.1% removal of TCE. Scavenging experiments showed that HO· is the dominant ROS in the degradation of PCE and TCE. Additionally, through determination of dissolved chloride it was concluded that 70% of the contaminants were completely mineralized An alternative to the use of CAs was investigated by Xue et al. In a study done on the generation of ROS in a CP/Fe(II) system, a comparison was made between adding CP and Fe(II) source at once and adding the Fe(II) in multiple successive doses. Results showed an improvement in the total generation of ROS and H_2O_2 when successive addition was used. This technique could pose a new method for application of CP as oxidant catalysed by Fe(II) [21]. Research on using multiple successive or continuous additions of oxidant and chelated catalysts is missing.

The literature and their results summarized above show the potential of CCP in terms of its oxidation capabilities compared to other AOPs and in its effectiveness in degrading a wide range of contaminants, including short chain chlorinated solvents as CT, PCE and TCE. Although the results in the laboratory removing PCE and TCE from aqueous systems are promising, information about degradation of such compounds in modelled soil systems and actual contaminated soil is limited resulting in knowledge gaps that are important for application in-field. Acquiring information about distribution and behaviour in subsurface soil and groundwater systems is essential in the technology development of CCP.

In previous work by Sørensen MCPA and MCPP were successfully removed (using CCP using analytical grade CP (65% powder) up to 94% from model solutions at ambient temperatures within the first 5 seconds of the reaction, whereas at 10 °C the removal efficiency was 54% in the first 5 seconds of the reaction. In all model solutions both at ambient temperature and 10 °C, the HPLC-UV detection limit of 0.1 mg L^{-1} was reached within 60 seconds. In actual groundwater the detection limit was reached after 45 minutes of reaction, indicating that the composition of groundwater influences the oxidation mechanism. [22]
Column studies showed little to no influence in the flow rate. Increase in CP dosage resulted in more $Ca(OH)_2$ formation and respectively an increase in the pH. During the column studies using actual groundwater, the detection limit was never reached. Instead, the lowest MCPA concentration reached was 1.5 mg L^{-1}. In addition, the concentration of MCPA appeared to increase in the course of the experiments, indicating insufficient amount of oxidant present in the column. Precipitated Fe(III) also caused issues in the experiments, forcing the equipment to be cleaned in the middle of the experiment due to blockage of the flow. [22]

1.2 Aim of this Thesis

This thesis will build upon the work performed in the Master's Thesis of Line Foss Sørensen [22]. The goal of this work will be to remove organic contaminants from groundwater and soil using CCP with 65% CP powder under circumstances similar to in-field circumstances. The main research question to be investigated is as follows:

How do the operating parameters influence the CaO_2 based chemical oxidation system applied in the remediation of contaminated soil and groundwater?

The main research question will be answered by performing a series of experiments where mechanistic aspects of CCP will be investigated. These aspects include oxidant and ROS generation, degradation of benzoic acid (BA) as model contaminant and the remediation of *dense non-aqueous phase liquids* DNAPL contaminated systems. First, batch experiments will be performed in order to investigate the behaviour of analytical grade CP. In the initial batch experiment, the generation of ROS of CP will be investigated by performing comparative experiments of BA hydroxylation using chelating agents at neutral pH. Initial studies will be performed to investigate viability of the determination of hydroxyl radical production using BA as probe compound. Since the focus will be on removing organic contaminants from groundwater and soil at conditions similar to potential in-field scenarios, research shows the need for techniques to overcome the limitations occurring in CCP under these conditions. The influence of chelating agents on the degradation of an organic contaminant in aqueous systems at neutral pH will be investigated. Initially, the effect of CAs on the release rate of hydroxyl radicals and their concentration yield will be investigated in the model solution. The decolorization of an organic dye as model contaminant will be investigated as well as the use of BA as model contaminant. the results will give an indication of the best performing CA in terms of ROS formation and overall degradation efficiency. The optimal ratio between CP/Fe(II)-CA/Contaminant will be investigated by changing the oxidant and Fe(II)-CA amounts while keeping model contaminant concentration constant. Using the optimal parameters obtained, the degradation of PCE will be investigated in drinking water and in groundwater, in order to investigate the influence of the water composition in the oxidation process. The objectives can be summarized into the following research questions which can each be answered individually in order to answer the main research question:

- **How do chelating agents affect the hydroxyl radical production of analytical grade CP activated by Fe(II)?**
- **Which chelating agent results in the most optimal degradation of the model contaminant?**

- **What is the most optimal CP/Fe(II)-CA/contaminant ratio for the degradation of the model contaminant?**
- **How does the oxidant dosage affect the remediation of a contaminated soil slurry?**
- **What is the difference in oxidant efficiency between CCP and CHP?**
- **How does a continuously operated soil packed column affect the HP release of CP and the remediation of contaminated soil using CCP?**
- **How does the presence of DNAPLs affect the oxidant efficiency of CCP and CHP?**

Column studies will be performed in order to investigate the CP dissolution and continuous degradation of contaminants in a soil packed bed. Operating parameters will be investigated including flow rate, CP dosage and temperature.

2. Calcium peroxide based in-situ chemical oxidation

The methods applied in ISCO are based on the oxidation strength of certain chemicals referred to as oxidants. The reduction potential indicates the strength of the oxidant by giving a measure for the capacity of a chemical compound to take up electrons (e.g. be reduced). Multiple oxidants have been investigated and are even applied in in-field applications. Despite the reduction potential of these oxidants being sufficiently large to chemically oxidize most organic contaminants found in the environment, there is a difference in performance and behaviour of these oxidants. The following section will give an overview of the theory and chemistry involved when CP, and consequently HP, is applied in ISCO. [2, 11]

2.1 Calcium peroxide

Calcium peroxide has only came into attention over the past 10-15 years. It is an oxidant that releases HP when it reacts with water (Equation 2.1). As a result, not all of the HP is available at one time and therefore significantly reducing the influence of unproductive reactions that consume ROS: scavenging reactions. This would increase the efficiency of ISCO by using less oxidant compared to liquid HP. As mentioned in, HP encounters large amounts of disproportionation, where HP releases O_2(g) without producing any ROS. This disproportionation occurs at a higher rate as the pH of the system increases, making liquid HP not suitable at neutral pH or above, requiring additional chemicals to be added to the subsurface to control the pH [9, 11]. Besides the reaction products not contributing to the degradation of contaminants, the rapid oxygen formation might clog up pores in the subsurface hindering the further distribution and the contact area of HP with contaminants [9].

$$CaO_2(s) + 2H_2O \rightarrow Ca(OH)_2(s) + H_2O_2(aq) \tag{2.1}$$

The strategy surrounding the use of CP in ISCO is the addition of the CP to the subsurface in the form of a slurry. This slurry is injected into the subsurface where it will come in contact with groundwater, dissolve and release HP. Addition of a catalyst, or natural occurring metals in the subsurface capable of catalysing HP, will react with HP to initiate the degradation process by formation of ROS. After CP has dissolved and released HP, the process will proceed in ways similar to CHP, as will be discussed in the following section.

2.2 Hydrogen peroxide and Fenton's chemistry

HP on its own was the first oxidant that was found to possess properties that allow the compound to be used to oxidize organic compounds was hydrogen peroxide (HP). In 1894, Fenton discovered a powerful oxidation process by using what would later be known as 'Fenton's Reagent': dilute HP catalyzed by dissolved Fe(II) salts in acidic environment [9, 11]. The reaction for the initiation of the oxidation process is given in Equation 2.2. Uncatalayzed HP might dissociate into water and oxygen Equation 2.3 or oxidize organic compounds directly. However, the rate of direct oxidation is proven to be negligible compared to the oxidation rates of ROS [2].

$$\boldsymbol{Fe^{2+}(aq) + H_2O_2(aq) \rightarrow Fe^{3+} + OH^- + OH^\bullet} \tag{2.2}$$

$$\boldsymbol{H_2O_2(aq) \rightleftharpoons H_2O + O_2(g)} \tag{2.3}$$

$$\boldsymbol{H_2O_2 \rightleftharpoons H^+ + HO_2^\bullet} \tag{2.4}$$

Fenton's reagent is applied in several applications including industrial waste water treatment in the middle of the previous century and in ISCO for the remediation of groundwater and soil starting approximately 3 decades ago. When Fenton's chemistry is applied in ISCO, the process increases in complexity due to the numerous amounts of catalysts, radicals and naturally occurring compounds present in the subsurface. The process results in a vast amount of reaction intermediates varying in reactivity. The majority of the reactions are initiation, oxidation, radical scavenging, propagation and termination reactions. [9, 11]

Catalysis of HP by Fe(II) given in Equation 2.2 is the main initiation step for the ROS formation in the CHP and CCP systems and consequently being the main HO· source [9, 11]. For the CCP systems, this reaction can only occur after HP has formed through Equation 2.1.

Often considered the main workhorse in the majority of AOP, HO· has been proven to participate in a variety of reactions. Its main reactions with contaminants are given in Equation 2.5, Equation 2.6 and Equation 2.7. These reactions denote the abstraction of a hydrogen atom, the addition to a double bond and the transfer of an electron respectively. In these reactions, the organic species is activated by HO· turning them in a radical species. [9, 11]

$$\boldsymbol{RH + HO^\bullet \rightarrow H_2O + R^\bullet} \tag{2.5}$$

$$HO^{\bullet} + R_1 = R_2 \rightarrow R_1(OH) - R_2^{\bullet} \tag{2.6}$$

$$RH + HO^{\bullet} \rightarrow R - H^{\bullet +} \tag{2.7}$$

Besides reacting with contaminants directly, this radical can participate in a variety of reactions. HO· can react with HP to form the perhydroxyl radical (Equation 2.10), oxidize Fe(II) (Equation 2.8 or recombine into HP (Equation 2.9. These reactions are most commonly referred to as HO· sink reactions or scavenging reactions because they are not contributing but rather hindering the oxidation of the COC. [9,11]

$$HO^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \tag{2.8}$$

$$2HO^{\bullet} \rightarrow H_2O_2 \tag{2.9}$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{2.10}$$

Organic compounds possessing a free radical can also participate in various reactions, both beneficial and unbeneficial in the degradation of the COC:

$$R^{\bullet} + H^{+} + O_2 \rightarrow HO_2^{\bullet} + R^{+} \tag{2.11}$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \tag{2.12}$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + HO^{\bullet} \tag{2.13}$$

$$HO^{\bullet} + R^{\bullet} \rightarrow ROH \tag{2.14}$$

$$2R^{\bullet} \rightarrow R - R \tag{2.15}$$

In Equation 2.11 and Equation 2.12, the organic radical species reacts with molecular oxygen in the presence of a proton and the absence of a proton respectively. In the first case (i.e. under acidic conditions), the reaction results in the formation of a perhydroxyl radical and terminating the organic radical. In contrast, under more alkaline conditions the organic radical is not terminated but addition of oxygen occurs forming another radical species. Reaction with HP directly (Equation 2.13, resulting in the formation of an alcohol and an hydroxyl radical. The organic radical species can react with HO· to form an alcohol, terminating both radical species Equation 2.14. Chain combination occurs when two active species combine to form a covalent bond effectively terminating both radical species, Equation 2.15 [11].

$$\boldsymbol{R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+}} \tag{2.16}$$

$$\boldsymbol{R^{\bullet} + Fe^{2+} \rightarrow R^{+} + Fe^{3+}} \tag{2.17}$$

Equation 2.17 and Equation 2.16 show the reaction of the organic radical species with the catalyst, where the first reaction scavenges the Fe(II) species before it catalyzes HP and the second reaction promotes Fe(II)/Fe(III) cycling and thus promotes the catalyzation of HP. However, in both reactions the organic radical is terminated [9,11].

The perhydroxyl radical formed in Equation 2.18 is only the predominant species under acidic conditions (pKa = 4.8). Under neutral and alkaline conditions the conjugate base of this species will be predominant: the superoxide anion, Equation 2.18. Perhydoxyl radicals can further react with organic species, but can also be scavenged by the catalyst (Equation 2.19 and Equation 2.20).

$$\boldsymbol{HO_2^{\bullet} \rightarrow +O_2^{\bullet -} + H^{+}} \tag{2.18}$$

$$\boldsymbol{HO_2^{\bullet} + Fe^{2+} \rightarrow OH_2^{-} + Fe^{3+}} \tag{2.19}$$

$$\boldsymbol{HO_2^{\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^{+}} \tag{2.20}$$

The reactive compounds that are confirmed or suspected to likely play a role in the CHP systems are given in Table 2.2.

Table 2.1: ROS known or suspected to play a role in CHP and CCP based chemical oxidation systems.

Compound (formula)	Standard reduction potential (eV)	Comment
Hydrogen Peroxide (H_2O_2)	1.776	Oxidant, main initiation step is given in Equation 2.2 producing hydroxyl radicals. Can also react with a hydroxyl radical to form a perhydroxy radical and water (Equation 2.10). Equation 2.3 illustrates the dissociation of hydrogen peroxide into a proton and a perhydroxyl radical (pKa = 11.26 for this reaction).
Hydrxyl radical ($HO^{\bullet}$)	2.59	The hydroxyl radical is considered the most important reactive species in Fenton chemistry and modified Fenton's Chemistry. Hydroxyl radicals react primarily through the following pathways with organic compounds: abstraction of a proton (Equation 2.5), electron transfer (Equation 2.7) and addition to unsaturated bond (Equation 2.6). Hydroxy radicals are also produced from the direct oxidation of organic compounds (Equation 2.13.
Superoxide anion ($O_2^{\bullet -}$)	-0.33	This radical only fell under attention of research within the last few decades. It is expected to play an important role in the degradation of oxidized organic compounds. While it is not a highly reductant species, it is a good nucleophile. It has been shown that the concentration of superoxide anions and its solubility increases with increasing concentration of HP.
Perhydroxyl radical ($HO_2^{\bullet}$)	1.495	The protonated superoxide anion is the perhydroxyl radical. This radical is only predominantly present at acidic conditions (pKa = 4.8) meaning the superoxide anion is the predominant species at neutral and alkiline conditions.

Hydroperoxide anion (HO_2^-)	0.878	Being the conjugate base of hydrogen peroxide (pKa = 11.6) it is can act as a nucleophile in the case of some contaminants that posses electrophilic regions at alkaline conditions. The recombination with a proton to form hydrogen peroxide is limited to diffusion. However, in certain cases the nucleophilic attack can occur at diffusion rates even allowing the species to react with contaminants at neutral and acidic conditions.
Atmospheric Oxygen (O_2)	1.23	Atmospheric oxygen is released trough the decomposition of HP. Due to slow reaction rates with organic compounds the direct contribution of this reactive species is considered insignificant. However, propagation reactions might receive contribution by atmospheric oxygen as given in Equation 2.11.

Reactions Equation 2.16 and Equation 2.20 show examples of reactions that promote Fe(III)/Fe(II) cycling. Initiation of the Fenton's chemistry initiates a chain reaction results in reaction products that can act as reactants for other reactions allowing for Fe(II)/Fe(III) cycling to occur. Additionally, a significant amount of the reaction products are radical species allowing more radical reactions (or propagation reactions) to occur. Additionally, Fe(III) is also capable of catalyzing HP through the formation of a Fe(III)-peroxocomplex thereby forming perhydroxyl radicals (or superoxide anions, depending on the conditions) as shown in Equation 2.21 [23]. Fe(III) has been proven to be a more effective catalyst in multiple degradation systems [24].

$$\boldsymbol{H_2O_2 + Fe^{3+} \rightarrow Fe - OOH^{2+} + H^+ \rightarrow HO_2^\bullet + H^+} \tag{2.21}$$

Other metals that are able to undergo a single valent transition are also capable of catalysing the Fenton Chemistry including:

- Copper (Cu(I)) is shown to be capable to catalyse the Fenton Chemistry reactions, but the toxicity and cost of this catalyst are two barriers for the use of copper as catalyst in ISCO. The same holds true for molybdenum and ruthenium.
- Molybdenum
- Ruthenium
- Manganese (Mn(II)) is able to catalyze the reaction but is only effective at high concentrations suggesting that Fe(II) is a more suitable catalyst for this purpose.

Iron is the preferred catalyst nonetheless because of its performance, low toxicity and cost. The catalyst is in some cases paired with a chelating agent to improve the catalysis of the process by improving the availability of the metal. The use of chelating agents and the complexation of Fe(II)/Fe(III) will be discussed in a later section.

Reaction Kinetics

The vast amount of reactions occurring during the chemical oxidation process of an organic contaminant will in most cases only cease to occur until one of the reactants is depleted. In addition, this will also result in a wide range of kinetic data to consider in the design of the AOP [9, 25]. Generally, the most important factors are the depletion of the limiting reactant, in most cases the oxidant, and the depletion rate of the organic contaminant. In literature, a wide range of kinetic data is available for the depletion of HP and the degradation rate for a variety of organic contaminants. The reactions are dependant on the reaction rate constant and on the concentration of reactants meaning the reactions are of the second order given in Equation 2.22. Where k_2 is the second order rate constant.

$$\frac{d[COC]}{dt} = -k_2[HO\cdot][COC] \tag{2.22}$$

The second order reaction rate constant for some chlorinated solvents with the hydroxyl radical are given in Table 2.2.

Table 2.2: Reaction rate constant (2^{nd} order) for the reaction between HO· a variety of contaminants. [9,11]

Contaminant	**Reaction constant k_2 ($\mathrm{L\,mol^{-1}\,s^{-1}}$)**
Carbon tetrachloride	$2 * 10^4$
Chloroform	$5.5*10^6$
Methylene chloride	$5.8 * 10^7$
2-Chlorophenol	$1.2*10^{10}$
Chloro-benzene	$5.5*10^9$
Perchloroethene	$2.6*10^9$
Trichloroethene	$4.2*10^9$
Vinyl chloride	$1.2*10^{10}$
Benzoic acid	$4.2*10^9$

As a general rule of thumb, ISCO can be used when the reaction rate of HO· with the COC: $k > 10^9\ \mathrm{L\,mol^{-1}\,s^{-1}}$. Indicating that the rates are close to diffusion controlled ($k \approx 10^{10}\ \mathrm{L\,mol^{-1}\,s^{-1}}$). Reaction rates lower than this value usually indicate that the removal will not be effective enough to justify the use of ISCO [26]. The values listed above indicate that hydroxyl radicals are incapable of oxidizing CT, chloroform or methylene chloride. However, literature reported the effective remediation of these compounds using CHP and CCP. In the case of CHP, the superoxide anion proved to have a significant role in the degradation of CT and chloroform [27]. For the case of CCP, it was found that adding formic acid promotes the formation of $CO_2\cdot$, which in turn promoted the reductive dechlorination of CT [20].

2.3 Subsurface and contaminant properties

In this section the challenges posed to the effective use of ISCO created by common characteristics of both the subsurface geochemistry and the nature of contamination are presented and discussed.

Investigation of the contaminated site to be remediated is a vital step in the design process of a remediation strategy including ISCO. Important parameters include the type of contaminant, its distribution and concentration and subsurface geochemistry. These parameters are used as the basis for an estimation of the oxidant type and dosage to be used in the case of ISCO. [26]

2.3.1 Contaminant properties

One of the biggest challenges faced in the remediation of contaminated soil and groundwater is the formation of immiscible liquid phases known as NAPL or DNAPL [3, 26, 28]. Generally, the contaminants dissolved in the aqueous phase pose no problems with the use of ISCO and are readily oxidized by the formed ROS during the process provided the rate of reaction is fast enough. However, the oxidants used in the process are solely soluble in water therefore limiting the process to the aqueous phase. As a result, the ROS are not able to degrade the contaminants that are concentrated in non-aqueous phases, such as DNAPL [2,3].

Chlorinated solvents are known to form DNAPLs when they enter the subsurface in large quantities. Figure 2.1 illustrates the formation of DNAPLs and the pollution of soil and groundwater as a result of a leak in a storage tank containing chlorinated solvents. Other contaminants that form NAPLs include fuels and polychlorinated bisphenyls [28].

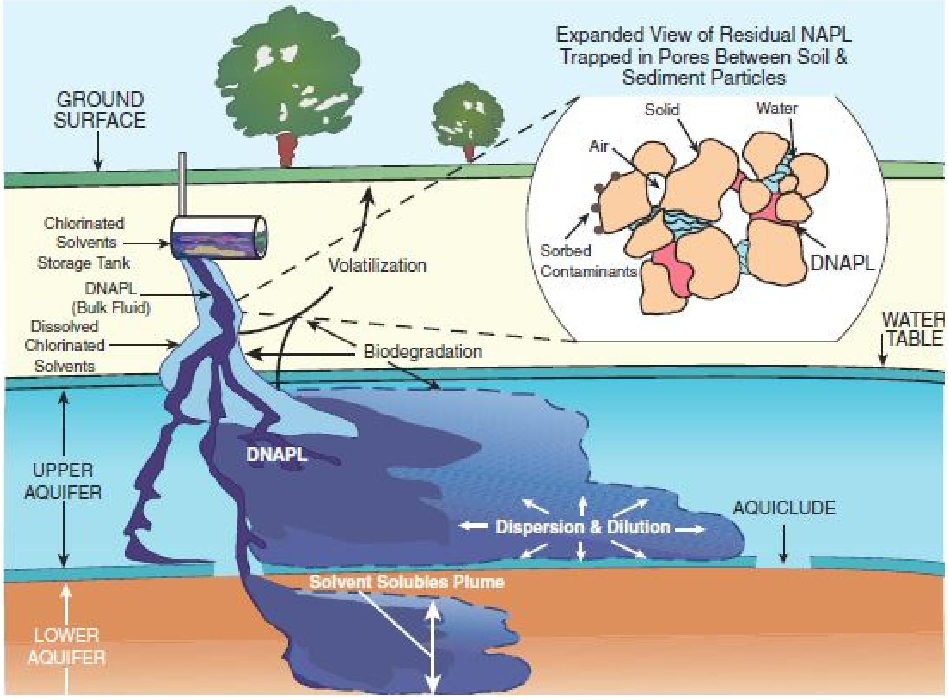


Figure 2.1: Schematic illustration describing the contamination of soil and groundwater by chlorinated solvents resulting in the formation of DNAPLs. [28] (reprinted with permission)

Since the density of the chlorinated solvent is larger than that of water, it will migrate downwards into the subsurface. This stream is above illustrated as the DNAPL bulk fluid. At the surface of the bulk fluid with the groundwater, chlorinated solvents dissolve into the groundwater. In the saturated aquifer the DNAPL disperses and dilutes further. The groundwater flow will cause the contamination to spread, creating a 'plume' of contaminated groundwater migrating through the subsurface. The DNAPL spreads through the pores of the aquifer downward until a non-porous layer of rock is encountered where the DNAPL accumulates. [2, 3, 28]

As is seen from the expanded view of the pore distribution, DNAPL, aqueous and air are trapped in the pores of the soil in the unsaturated layer. At the interface of the these three phases equilibrium exists: the volatile nature of chlorinated solvents result in mass transfer between the DNAPL-air and water-air interfaces. The chlorinated solvent vapour can potentially migrate to the ground surface and potentially end up in buildings located above the contaminated zone [2].

2.3.2 ISCO for remediation of DNAPLs

The use of ISCO for the remediation poses several problems. The main problem needed to overcome is the rate limiting step in degradation of DNAPLs, which is DNAPL dissolution: the mass transfer of contaminant between the NAPL and the aqueous phase [25,26,29]. Since the dissolution occurs at a slower rate compared to the oxidation of organic species in AOPs the total oxidant demand increases significantly when DNAPL are present [26].

The mass transfer between the NAPL and the aqueous phase can be modelled based on Fick's law of diffusion (Equation 2.23) [26]. Where $\boldsymbol{\Phi}'_{\text{mass}}$ is the mass flux in $\text{gm}^{-2}\text{s}^{-1}$, $\boldsymbol{D_m}$ is the diffusion constant (m^2s^{-1}) and $\frac{dC}{dx}$ is the change in concentration in the x direction (x-direction is horizontal and parallel to the paper).

$$\boldsymbol{\Phi}'_{\text{mass}} = -\boldsymbol{D_m}\frac{\boldsymbol{dC}}{\boldsymbol{dx}} \tag{2.23}$$

Assuming a stagnant thin film located at the NAPL-water interface. The change in aqueous phase bulk concentration over time can then be expressed: Equation 2.24 [25, 26, 29]. Where k_{La} denotes the dissolution rate of the NAPL (s^{-1}), C_{sat} is the solubility limit of the solute.

$$\frac{\boldsymbol{dC}_{\text{bulk}}}{\boldsymbol{dt}} = -\boldsymbol{k}_{\text{La}} * (\boldsymbol{C}_{\text{bulk}} - \boldsymbol{C}_{\text{sat}}) \tag{2.24}$$

Figure 2.2 illustrates the estimated solute concentration profile and oxidant concentration profile in the thin film. At the interface of the DNAPL-aqueous phases, the solute concentration is equal to the concentration of a saturated aqueous solution [25, 29]. This concentration decreases until it reaches its bulk concentration in the aqueous phase. Applying ISCO, the oxidant will alter the DNAPL dissolution rate increasing mass transfer form NAPL to aqueous phase and enhance the degradation of DNAPL contaminants [30, 31]. The enhanced dissolution was linked to reductive species formed in CHP. The dissolution of PCE still increased in experiments where oxidant species (HO·) were scavenged. Even though the dominant species in the degradation of PCE is the HO· radical, the superoxide radical plays an important role in the degradation of NAPL contaminated soil and groundwater. Enhanced dissolution of the NAPL is achieved through reductive pathways. After which the dissolved contaminants are degraded through, depending on the contaminant species, oxidation (for example TCE and PCE [20, 31, 32] and reductive pathways (CT, chloroform [20, 27]). Crimi and Siegrist found that for the destruction of PCE and TCE DNAPLs, permanganate was the most effective in terms of total contaminant destruction whereas CHP was more effective in terms of oxidant efficiency (mole oxidant needed per mole contaminant degraded) [33].

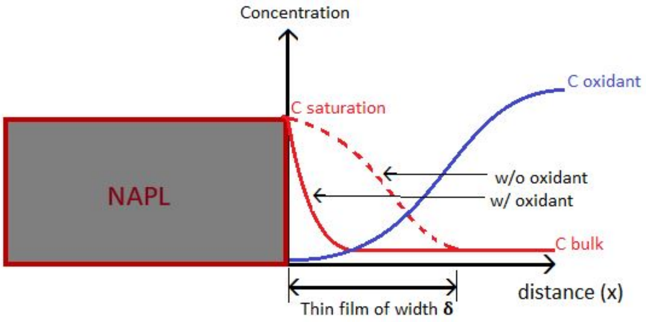


Figure 2.2: Schematic illustration of thin film NAPL dissolution into the aqueous phase. [30]

Published literature has not focused on the destruction of DNAPL contaminated soils using CCP but rather on the aqueous remediation of chlorinated solvents. However, the ability of CHP to successfully remediate DNAPLs and the promising results obtained in the aqueous degradation of chlorinated solvents using CCP gives a theoretical basis for the possibility to use CCP in the treatment of DNAPL contaminated soil. This last stage of the experiments in this work will focus on the destruction of a PCE DNAPL in soil from the Kærgård plantation.

2.3.3 Scavenging

In the previous chapter, the influence of non-productive reactions has been discussed. Scavenging reactions also occurs through naturally occurring ions in soil and groundwater. Their effects on the performance of CCP system has been extensively researched. The most significant ions contributing to the scavenging ROS are chloride and (hydrogen) carbonate ions [34]. These ions can scavenge HO· radicals when present in significant amount through Equation 2.26, Equation 2.27 and Equation 2.28 forming new radical species [34].

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad pKa = 10.33 \tag{2.25}$$

$$HO^\bullet + HCO_3^- \rightarrow HO^- + HCO_3^{\bullet -} \tag{2.26}$$

$$HO^\bullet + CO_3^{2-} \rightarrow HO^- + CO_3^{\bullet -} \tag{2.27}$$

$$HO^\bullet + Cl^- \rightarrow ClHO^{\bullet -} \tag{2.28}$$

These ClHO· can react with a proton through to form a chloride radical and water, Equation 2.29. This radical can in turn combine with a chlorine ion, Equation 2.30 [34, 35].

$$ClHO^{\bullet -} + H^+ \rightarrow Cl \cdot + H_2O \tag{2.29}$$

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet -} \tag{2.30}$$

The formed radical can then participate in Equation 2.31 and Equation 2.32 [34].

$$2Cl_2^{\bullet -} \rightarrow 2Cl^- + Cl_2 \tag{2.31}$$

$$Cl_2^{\bullet -} + H_2O \rightarrow ClHO^{\bullet -} + H^+ + Cl^- \tag{2.32}$$

It has also been reported that chloride species have the ability to scavenge catalyst through Equation 2.33, Equation 2.34 and Equation 2.35 [34]. Scavenging of Fe(II) species by chloride radical species might be counter-productive in the CCP system.

$$Cl^\bullet + Fe^{2+} \rightarrow Cl^- + Fe^{3+} \tag{2.33}$$

$$ClHO^{\bullet -} + Fe^{2+} \rightarrow Cl^- + HO^- + Fe^{3+} \tag{2.34}$$

$$Cl_2^{\bullet -} + Fe^{2+} \rightarrow 2Cl^- + Fe^{3+} \tag{2.35}$$

2.3.4 Natural organic matter

Natural organic matter (NOM) present in the subsurface is a factor that varies from site to site that can potentially influence the remediation process using ISCO. NOM present in both aqueous and solid phase can [9]:

- React with the ROS
- Bind with Fe(II)/Fe(III)
- Donate and/or accept electrons
- Act as adsorbent for the COC

NOM is the term used for a mixture of naturally occurring organic compounds in the subsurface including humic acids, fulvic acids, phenols and quinones, resulting in a mixture spanning a wide range of molecular weights. The presence of these compounds implicate the presence of a large number of functional groups including carboxyl groups, hydroxyl groups and aromatic rings. Hydrophobic groups have the ability to adsorb onto soil which in turn can act as adsorbent for the COC, whereas hydrophilic group such as carboxylic acid have the ability to form complexes with metal ions, including the catalyst used in ISCO [9].

The complexity and the amount of processes involving NOM in ISCO can have either a positive or a negative effect on the degradation of the COC. Quinones have for example been shown to act as an activator in APS systems and assist in Fe(III)/Fe(II) cycling in CHP systems by reducing Fe(III) to Fe(II) [36,37]. Carboxylic and phenolate groups present in humic acids enable them to chelate Fe(II) and Fe(III), increasing the performance of CHP at neutral pH [38]. Consequently, a negative effect of the NOM present in a contaminated site on the oxidation of the COC will increase the total oxidant demand for that contaminated zone. Therefore, investigation of the NOM present in the subsurface and its impact on the application of ISCO is an important step in the design of a remediation process.

2.3.5 Kinetic data for common scavengers

Previous sections discuss the potential influence of scavengers on the application of ISCO. An important factor is the reaction rate of a scavenging species with $HO\cdot$. From Table 2.2 it is evident that there is a variety in the reaction rates of different COC with $HO\cdot$, the same is true for scavenging compounds. Table 2.3 lists the reaction rates of common scavenging compounds with the $HO\cdot$ species.

Table 2.3: Reaction rate constant (2^{nd} order) for the reaction between HO· a variety of scavenging compounds. [9,11,39]

Compound	Reaction constant (2^{nd} order, [$L\,mol^{-1}\,s^{-1}$])
HP	$2.7 * 10^7$
HO^-	$1.2*10^{10}$
CO_3^{2-}	$3.9*10^8$
Cl^-	$4.3*10^9$
HCO_3^-	$8.5*10^6$
OA	$1.4*10^6$
CiAc	$3.2*10^8$

2.4 Kærgård plantation

During later stages of the experiments performed in this work the Kærgård plantation is used as a case study. This site is of great relevance to the technology development of CCP based ISCO because of the zone is contaminated with chlorinated solvents among other organic contaminants. However, the PCE contamination is viewed as the biggest obstacle to overcome on this contaminated site [11].

The Kærgård plantation is located on the west coast of Denmark and was used as a pharmaceutical waste site between 1956 and 1973 [26]. Around 280.000 ton of waste products from production of medicinal materials was discarded into 6 pits around 400 - 800m away from the shoreline, classifying the Kærgård plantation as a mega-site [26]. Included in this waste were various (in)organic (acid) salts, aromated organics, hydrocarbon fuels, chlorinated solvents and heavy metals(i.e mercury and cyanides). In Figure 2.3 illustrates the situation at the waste site in pit #1. The residual DNAPL contamination after excavation is present more than 10 meters below the saturated zones of the subsurface. Dissolution and diffusion of DNAPL PCE, among other contaminants, cause harm to the environment. As can be seen in Figure 2.3, groundwater containing high concentrations of chlorinated solvents flows towards the shore and to the surface contaminating the beach and shore located near the Kærgård plantation. [11,26]

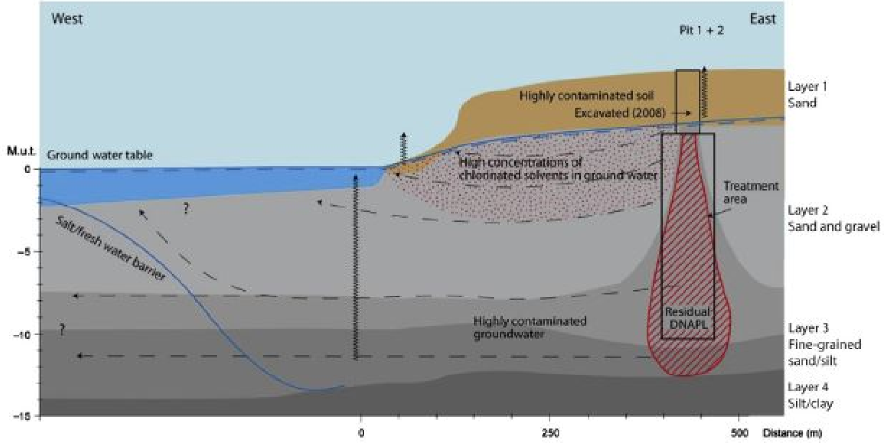


Figure 2.3: Overview of the PCE contaminated waste pits located at the Kærgård plantation [11].

In the period between 2007 and 2011 the contaminated site various treatment methods have been tested and performed in-field. From two of the waste pits, the most highly contaminated soil has been excavated and replaced with clean sand. The deeper layers of the subsurface have been treated with ISCO and biological remediation in the form of enhanced reductive dechlorination (ERD). ERD is a technique where bacterial cultures are introduced to the contaminated area that are able to dechlorinate chlorinated solvents to non-toxic products. ISCO was performed with a combination of CHP and (activated) persulfate (APS). Combination of these two methods were proven to increase the remediation of PCE DNAPL contaminated soil most effectively. Iron was added in the form of CiAc chelated iron.

Full scale treatment was performed in layer 2 using CHP followed by ERD. In layer 2.1 the concentration of PCE was reduced from 160 to 1 $\mathrm{mg\,kg^{-1}}$ while in layer 2.2 290 kg out of 600 kg PCE was remdiated. The soil and groundwater at this site do not contain any significant buffer capacity, which caused the pH to drop significantly, reaching a pH of 1 - 2. Before application of ERD, the pH was increased by adding buffer to the ground surface until neutral pH was achieved. Bacterial cultures and electron donors were introduced to the subsurface after which the bacteria population was monitored. This population was measured to have increased significantly within 2 weeks, in addition to an increased concentration of PCE degradation products (i.e. ethene and vinyl-chloride). Combining ISCO and bioremediation was proven to be a effective method in remediating the contaminated site at the Kærgård plantation including the PCE DNAPL. [11]

2.5 Chelating agents

It is well known that acidic conditions (pH = 3) are optimal for the application of CHP and CCP [14, 16, 32, 40]. However, often times subsurface contaminated soil and groundwater possess high buffer capacities at neutral pH. This neutral pH impacts the catalysis of HP in a negative way by precipitation of Fe(III) into iron hydroxide (i.e. $Fe(OH)_3$) as shown in Equation 2.36.

$$\boldsymbol{Fe^{3+}} + \boldsymbol{nH_2O} \rightarrow \text{precipitate} \tag{2.36}$$

$Fe(OH)_3$, ferric hydroxide, is insoluble in water at a pH of 7, therefore the formation of this precipitates negatively impacts the catalysis of HP into ROS by taking iron out of solution. $Fe(OH)_2$, ferrous hydroxide, has a higher solubility of $0.072\,g\,L^{-1}$ and therefore able to catalyze HP under neutral pH. However, the formed Fe(III) will immediately precipitate, affecting the iron cycle and the direct catalysis of HP by Fe(III) [9, 11, 41].

To bypass this problem occurring at neutral pH several techniques have been employed. These methods include lowering the pH by introducing acid (i.e. sulfuric acid) to the subsurface, iron minerals and the addition of CAs. Addition of CAs has been extensively researched as described in chapter 1. Most often organic CAs are used but inorganic CAs have also been proven effective in the degradation of polyaromated hydrocarbons contaminated soil using CHP [42].

Unchelated Fe(II) and Fe(III) ions in the aqueous phase forms a complex with six water molecules acting as ligands, the hexaaquairon(II) ion $[Fe(H_2O)_6]^{2+}$ and the hexaaquairon(III) ion $[Fe(H_2O)_6]^{3+}$. The coordination number of Fe(II) and Fe(III) is 6, meaning that 6 electron donating ligand sites are utilized in the formation of the iron complex. Organic molecules containing carboxylic acid or nitrogen functional groups can be used to complex iron(II) and iron(III) molecules, increasing their solubility in aqueous systems preventing precipitation from occurring (Equation 2.36). As a result, their availability for the catalysis of HP is increased. However, the organic compounds used to chelate the iron can itself also react with the ROS formed during the oxidation process, thus increasing the total oxidant demand of the system. Despite this, at neutral pH and above the degradation efficiency is increased significantly when CAs are added to the system.

The redox properties and the stability of the catalyst are changed depending on which CA is used. The stability constant, β, is an important property used to describe the strength of a metal complex: the higher this constant, the larger the tendency of the complex to form. The stability constant of an iron complex increases by:

- Increasing pKa of the ligand (e.g. increasing tendency of the ligand groups to donate electrons to the central iron atom

- Substituents on the ligand molecule that might alter the pKa value or cause steric hindrance
- Nature of the electron donating group: Fe(II) binds stronger (thus forming a complex with higher stability constant) to N-donor ligands compared to O-donor ligands, for Fe(III) O-donor ligands tend to form more stable complexes.
- Increasing charge of the central ion
- Number of electron donating groups on the ligand molecule

The ability of Fe(II)-complexes to react with HP depends on the stability constants of the respective Fe(III)-complex and of the redox potential of the Fe(II)/Fe(III)-complex. If the stability constant of the Fe(III)-complex (β_{III}) is larger than the stability complex of the Fe(II)-complex (β_{II}) it is favoured to reduce the Fe(II)-complex to its respective Fe(III)-complex (i.e. by HP in CHP and CCP systems). The redox potential of the complex should be lower than the redox potential of HP, given in Equation 2.37 (for pH $\approx$ 7), to be able to transfer an electron to HP (Equation 2.2) while simultaneously the redox potential should be sufficiently high to allow the reduction of the Fe(III)-complex to Fe(II)-complex [39, 43].

$$\boldsymbol{H_2O_2 \rightarrow HO^- + HO\cdot \qquad E^{\ominus} = +0.46V} \tag{2.37}$$

Table 2.4 presents pKa values, stability constants and redox potentials of the most common and best performing CAs in CCP systems. It can be seen that the redox potentials are lower compared to the Fe(II)/Fe(III) redox potential, Equation 2.38 [44].

$$\boldsymbol{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \qquad E^{\ominus} = +0.77V} \tag{2.38}$$

As a general trend, CAs containing basic -$\mathbf{NH_2}$ electron donor groups form the most stable complexes. EDTA has been used extensively in CCP and CHP systems and shows a more significant increase in oxidation capacity compared to other CAs. However, problems arise with EDTA when using it in actual contaminated sites because of its low biodegradability [45]. As a result, EDTA itself has the potential to become a persistent pollutant. EDDS is an alternative CA to EDTA also containing two N-donor groups. However, this molecule contains two chiral centers of which only the [S,S]-EDDS configuration is readily biodegradable. Its performance in AOPs at neutral pH was found to be similar to EDTA in addition to possessing similar stability constants and redox potential for its complex with Fe(II) and Fe(III), indicating that using [S,S]-EDDS as a CA could be a viable option due to its performance and biodegradability. Another extensively researched CA is NTA, containing 1 N-donor group and 3 O-donor groups allows for formation of stable Fe-NTA complexes and subsequently enhances contaminant degradation of AOPs at neutral pH. One advantage of NTA over EDTA and EDDS is its biodegradability [46].

CiAc and OA are two organic acids commonly used as CAs in AOPs. Although their respective complexes with iron are not as stable compared to the CAs mentioned previously, they are still able to improve the remediation of contaminants in systems with a neutral pH [19,47]. The advantage of CiAc and OA is their abundance in nature. CiAc and OA are produced by plants, fungi and bacteria and can therefore be present in the subsurface environment and are readily biodegradable. OA has been shown to chelate Fe(II) and Fe(III) in a molar ratio of 3:1, whereas CiAc forms Fe-complexes in 1:1 molar ratio [39]. The stability of the complexes formed by OA and CiAc with iron are comparable, however the redox potential of the Fe(II)-OA/Fe(III)-OA is lower than that of the Fe(II)-CiAc/Fe(III)-CiAc complex. Nonetheless, CiAc and OA have both been successfully applied in AOPs as chelating agents, enhancing the degradation of contaminants. [1]

Table 2.4: Properties of common ligands used in AOPs. [39]

Compound	**pKa values**	**log(β_{II})**	**log(β_{III})**	**Redox potential[1] (V)**
EDTA	$pKa_1 = 2.10$, $pKa_2 = 2.80$ $pKa_3 = 6.20$, $pKa_4 = 10.30$	14.30	25.10	0.10
EDDS	$pKa_1 = 2.40$, $pKa_2 = 3.90$ $pKa_3 = 6.80$, $pKa_4 = 9.80$	-	20.60	0.19
NTA	$pKa_1 = 1.89$, $pKa_2 = 2.49$ $pKa_3 = 9.73$	8.05	15.90	0.39
CIT	$pKa_1 = 3.00$, $pKa_2 = 4.60$ $pKa_3 = 5.80$	3.20	11.5	0.37
OA	$pKa_1 = 1.23$, $pKa_2 = 4.19$	4.70	9.40	0.002

[1] The Fe(II)-complex/Fe(III)-complex redox potential is given for the corresponding CA.

The focus in this work is on the performance of the organic acids CiAc and OA as CAs in the CCP process in the degradation of contaminants in aqueous and soil systems. CiAc and OA are chosen as CA because of their performance in previous literature, low environmental impact when introduced to the subsurface and their biodegradability.

3. Experimental considerations

In this chapter, the considerations and relevant literature are presented. Additionally, an overview of the performed experiments is given.

The experiments are separated into four stages. An overview of these stages is given in Table 3.1 along with a short objective and description of the experiments listed. In the coming sections of this chapter a more detailed description will be presented.

Table 3.1: Experimental overview.

	Description	**Goal**
Stage I Water system	A: Hydroxylation of BA	HO· quantification
	Degradation of BA	Determination of optimal parameters for BA degradation using CCP at neutral pH,in drinking water
Stage II	A: Degradation of the model contaminant in soil slurry	Comparative studies of CHP and CCP in soil slurry with BA as contaminant
Soil slurry	B: Degradation of PCE in soil slurry	DNAPL PCE degradation in contaminated soil
Stage III	A: Oxidant delivery and CP dissolution	A continuously operated column is used to determine HP Profile
Continuous operated column studies	B: Degradation of BA	Continuous BA acid degradation
	C: Degradation of PCE	Continuous PCE degradation

3.1 I-A: Hydroxyl radical yield determination

A set of experiments is designed to develop a method to determine the hydroxyl radical generation. BA is hydroxylated by hydroxyl radical formed during the catalysis of HP by Fe(II) to form ortho-,para- and meta-hydroxybenzoic acid (HBA) as shown in Equation 3.1.

$$HO\cdot + BA \rightarrow \textbf{\textit{p-HBA + o-HBA + m-HBA + other products}} \qquad (3.1)$$

It has been shown that using HPLC-UV, p-HBA can be quantified individually [21,48]. Through this method a conversion factor can be employed in order to estimate the amount of hydroxyl radicals that reacted with BA. The experiments will explore the generation of hydroxyl radicals at acidic pH and at neutral pH using two chelating agents selected through published literature review and by the criteria discussed in section 2.5. This method allows for the determination how CAs affect the availability of Fe(II) by directly looking at the formation of HO· as opposed to looking at general rate of degradation.

3.2 I-B: Influence of oxidant/catalyst ratio on benzoic acid degradation in drinking water

In this set of experiment BA is used as a model compound to investigate the oxidation capacity of CP catalyzed by OA and CiAc chelated Fe(II) in a phosphate buffer solution made of drinking water (pH 7). Instead of an organic dye which is bleached and quantified using a spectrophotometric method, a different approach is tested in these experiments. The organic dye used in previous research (p-nitrosodimethylaniline, (RNO)) resulted in some difficulties quantifying the amount of dye bleached because one of the reaction product resulted in a UV-vis absorption signal in the same region as the dye skewing the outcomes [22]. In initial investigative experiments azorubine was tested as a possible model contamination able to be quantified using the spectral method. Even thought the azorubine was visually bleached, the spectrophotometric method was not a viable approach due to two main flaws. Firstly, the azorubine is filtered out of the solution when filtered through a 0.45 µm sterile nylon filter. Secondly, the reaction mixture is cloudy resulting in interference with the UV-vis spectra making filtration before measurements unavoidable. As an alternative, BA is used as a model contaminant representing organic contaminants that have relatively high solubility in water compared to NAPL forming contaminants allowing for determination of oxidation capacity of the systems tested.

The oxidation capacity is investigated for different oxidant/catalyst ratios and for the two chelating agents. The chelating agent with the highest oxidation capacity is used to test the influence of the oxidant/catalyst ratio. The efficiency is defined as the amount of BA removed from the buffer solution over the specified time interval.

3.3 II-A: Degradation of model contaminant in a soil slurry: batch experiments

The next stage in experiments is the investigation of oxidation capacity of CP in soil systems. Points of interest include the degradation of BA using the same concentrations as in the water experiments and the period of time over which the degradation occurs. A comparison experiment with CHP is performed to compare the degradation and the degradation time for both AOPs. It has been shown before in aqueous systems that CHP is more efficient in the degradation of dissolved organic contaminants [20]. This is done by using a model soil matrix made of filter sand and a buffer solution made of drinking water. The buffer solution is used to replicate the buffer capacity of natural occurring soil in the subsurface.

3.4 II-B: Degradation of PCE contaminated soil: batch experiments

In section 2.3, the issue of contaminant properties and the application of ISCO have been discussed. In these experiments a contaminant will be introduced that has different properties compared to the BA used in earlier experiment. PCE is used as contaminant due to its low solubility in the aqueous phase. Due to the low solubility of PCE, DNAPL are formed when it is introduced to soil systems [2, 3]. The presence of PCE DNAPLs have been proven to be a challenging factor when applying ISCO for soil and groundwater using CHP, with limiting factors being NAPL dissolution into the aqueous phase and the lifetime of HP in the subsurface. The goal of this experiment is to investigate the performance difference between CCP and CHP in remediation of DNAPL contaminated soil systems. Despite published literature covering the performance difference in aqueous remediation of chlorinated solvents such as PCE, TCE and CT using CCP, research on the remediation of these contaminants using this same method in soil systems at contaminant concentrations exceeding solubility limits appears to be missing in the investigation and development of CCP. In addition to measuring the PCE content in the systems, determining the Cl^- concentrations in the aqueous phase is proven to be a successful method in determining the degree of mineralization of chlorinated solvents and will be used in this experiment [20].

3.5 III-A: Oxidant delivery and CP dissolution

An important factor affecting the remediation effectiveness in ISCO is the oxidant delivery and behaviour in the subsurface. HP is known to have a short lifetime in the subsurface ranging from minutes to hours and therefore limiting the penetration depth of the oxidant to 3 to 4 meters from the injection point [49]. Using CP as slow HP releasing compound would decrease the decomposition rate of HP while increase the penetration depth, oxidant efficiency and oxidant lifetime [50]. The goal of this experiment is to investigate the behaviour of CP and the release of HP in continuously operated soil systems. This is done by investigating factors such as bed height, pH, temperature and delivery method.

3.6 III-B: BA degradation in continuously operated column

Besides the investigation of contaminant degradation in batch tests, the degradation of contaminants in continuous operated systems is of importance. In previous research, a CP packed bed used and an acidic mixture of MCPA, MCPP and catalyst was pumped through the column while measuring the MCPA and MCPP concentrations at the outlet of the column. MCPA and MCPP, despite complications with the experimental set-up, was successfully degraded [22]. In these experiments, the soil is not packed with CP, but rather contaminated with BA beforehand. The oxidant is added in a single addition while the catalyst-CA mixture is added continuously. The degradation is tested at neutral pH, where the availability of Fe(II) is enhanced with the use of CAs. The goal of this experiments is to design a set-up capable of continuous degradation of contaminated soil, parameters tested are flowrate, oxidant and catalyst dosage and temperature. In order to avoid the problems as was encountered in previous work using this set-up, the amount of oxidant and catalyst is reduced to avoid clogging of the column exit.

3.7 III-C: PCE degradation in continuously operated column

Chlorinated solvent contaminated soil and groundwater remediation is an important research area for the application of ISCO as discussed in section 2.3 and section 3.4. The aim of this experiment is to remediate DNAPL contaminated soil in a continuously operated column. As in the previous experiments, the soil will be contaminated beforehand and oxidant will be added to the systems using one addition. Research has shown that continuous addition of a HP and stabilizer increases the amount of TCE treated in a column packed with contaminated soil [51]. In this experiment, CP is used as slow HP releasing compound and a catalyst/CA mixture is pumped through the column in order to generate ROS that are able to enhance PCE dissolution and destruction.

For all the column experiments performed in stage III, the aimed set-up is schematically illustrated in Figure 3.1 which is based on previous research [22]. All the experiments performed will be operated top to bottom in the column.

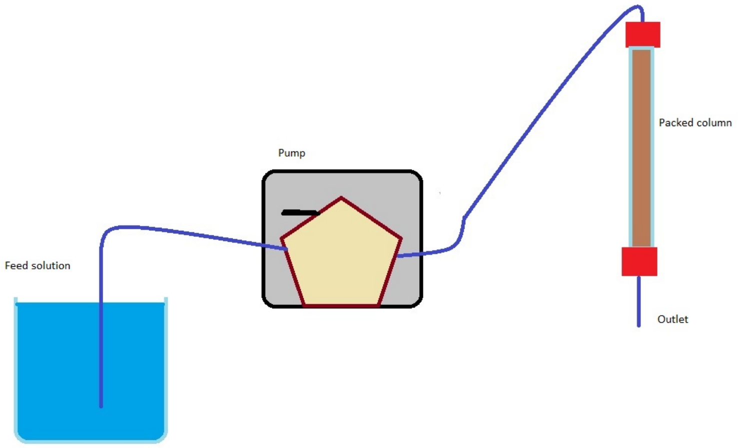


Figure 3.1: Schematic illustration of the column set-up consisting of feed solution (left), pump (middle) and column (right).

3.8 Hydrogen peroxide analysis

In order to be able to determine the amount HP in a system at any given moment a method is developed for fast and efficient determination of HP. This method is based the spectrophotometric method as developed by Bennedsen [52]. The approach is based on the reaction given in Equation 3.2.

$$\boldsymbol{H_2O_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)} \tag{3.2}$$

Where I_2 will give the solution a yellow colour that can be quantified through the Beer-Lambert law given in Equation 3.3 [53].

$$\text{Absorbance} = \epsilon * [\boldsymbol{I_2}] * \boldsymbol{L} \qquad \text{with} \qquad \text{Absorbance} = \log \frac{\boldsymbol{I_0}}{\boldsymbol{I}} \tag{3.3}$$

The absorbance is linearly correlated to the concentration of I_2, the molar absorption constant ϵ and the sample thickness L. In turn, the absorbance is proportional to the logarithm of ratio between the incident intensity over the measured intensity [53]. Therefore, UV-vis spectroscopy can be utilized to quantify I_2(aq) concentration and consequently the H_2O_2 concentration [52].

3.9 Chloride analysis

The degradation pathway of PCE involves the dechlorination of PCE and the dechlorination of the respective reaction products. Figure 3.2 present a schematic illustration of the degradation pathway of PCE. In this pathway, each step will result in one chloride ion released from the respective molecule until ethene is formed. Ethene can in turn be mineralized into carbon dioxide and water. However, full mineralization of ethene is not considered a necessary step since ethene is a non-toxic molecule and posses no harm to the environment.

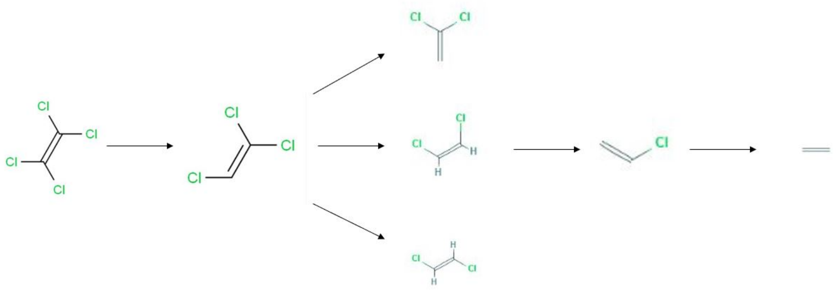


Figure 3.2: PCE degradation pathway. Starting left to right the compound names are: PCE, TCE, 1,1-dichloroethene (top), cis-1,2-dichloroethene (middle), trans-1,2-dichloroethene (bottom), vinyl chloride and ethene.

Full oxidation of PCE by HO·, proven to be the main ROS responsible for PCE oxidation, can be described with Equation 3.4 [41, 54].

$$CCl_2 = CCl_2 + 4HO\cdot \rightarrow 2CO_2 + 4H^+ + 4Cl^- \tag{3.4}$$

Since the reaction between ROS and PCE only occurs in the aqueous phase, measuring the chloride content can a useful method in determining the amount of PCE that has been completely dechlorinated or mineralized. The reaction stoichiometry of the complete dechlorination of PCE is 4 mole chloride will form from the dechlorination of 1 mole of PCE. Chloride concentration measurements are possible with ion chromatography methods [18, 41, 54].

4. Materials and methods

This chapter will outline the experimental procedures, equipment and materials.

4.1 Materials

In the introduction a brief history of chlorinated solvents, focusing on PCE and TCE, has been presented. In this chapter the properties of the materials used will be given in more details. In addition, all materials used in the experiments are presented as well.

4.1.1 Contaminants

As mentioned earlier, the experiments will be performed with two types of contaminants. One of which is a harmless and easy to use model contaminant, while the other is the contaminant of interest that posses certain risks and challenges to its remediation.

Benzoic Acid

The purpose of using BA was initially to monitor the hydroxylation of BA to HBA acid. This would allow for accurate quantification of hydroxyl radical formation over the course of the oxidation process when used in excess [21,47,48]. BA was purchased from VWR Chemicals.

This compound proved to be a suitable model contaminants because of its properties and ease of quantification. BA is not directly toxic (LD50 (rat) for oral ingestion is $>2000\,\mathrm{mg\,kg^{-1}}$) and its solubility in water allows for the use of BA in the batch tests in the desired quantities. Additionally, BA has low volatility minimizing the loss of BA due to vaporization during the experiments [55]. The structure of BA has no direct similarities to PCE or TCE, but the degradation still allows for determining the oxidation capacity of CP. Under neutral conditions, however, it is not BA that is predominantly present in the solution but its conjugate base: benzoate. In **??** the chemical and physical properties of BA are given.

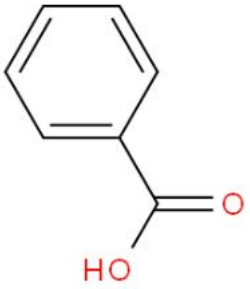


Figure 4.1: Molecular structure of benzoic acid [56].

Chlorinated Solvents

PCE (>99% purchased from J.T Baker) is used as contaminant forming DNAPL phases in soil and groundwater systems. Its low solubility and high volatility causes PCE to form a separate phase that can readily vapourize if the contaminant is located in unsaturated zones in the subsurface. PCE is toxic to aquatic life and a suspected carcinogen [55]. The structure of PCE and TCE are given in Figure 4.2a and Figure 4.2b respectively.

(a)

(b)

Figure 4.2: Molecular structure of **(a)**: PCE [57] and **(b)**: TCE [58]

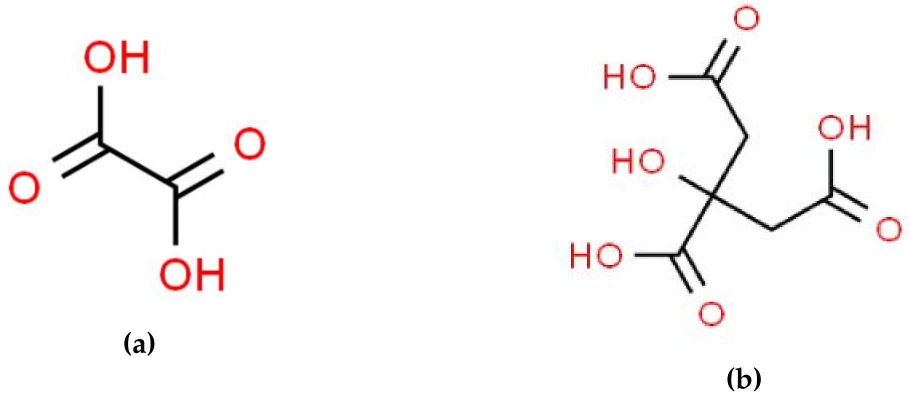
Their properties are given in Table 4.1. PCE and TCE solubility in water is low, as would be expected. The density of PCE and TCE is larger than that of water, which means these contaminants will form DNAPL phases.

Table 4.1: Chemical and physical properties of COC. [55]

Property	BA	PCE	TCE
Molar mass	$122.13\,\mathrm{g\,mol^{-1}}$	$165.82\,\mathrm{g\,mol^{-1}}$	$131.38\,\mathrm{g\,mol^{-1}}$
Density (20 °C)	$1.321\,\mathrm{g\,cm^{-3}}$	$1.623\,\mathrm{g\,cm^{-3}}$	$1.46\,\mathrm{g\,cm^{-3}}$
Solubility (water)	$2.9\,\mathrm{g\,L^{-1}}$	$206\,\mathrm{mg\,L^{-1}}$ [59]	$1.12\,\mathrm{g\,L^{-1}}$
pKa value	4.20	-	
Vapour Pressure	$<1.3*10^{-4}$ bar	$2.46*10^{-2}$ bar	0.103 bar

Catalyst and chelating agents

The chelating agents used in the experiments are CiAc and OA. CiAc has been applied in ISCO on large scale, whereas OA is mainly limited to application in laboratory scale experiments. Nevertheless, both of these CAs increase the effectiveness of the CHP and CCP process at neutral pH.



(a)

(b)

Figure 4.3: Molecular structure of **(a)**: Oxalic acid [60] and **(b)**: Citric acid [61]

The properties of the CAs and the catalyst used are given below in Table 4.2. OA was added in the form of oxalic acid-dihydrate (purchased from Merck), CiAc as anhydrous citric acid (purchased form Merck) and iron was added as iron(II)sulfate-heptahydrate (purchased from Fluka) . The compounds are soluble in unbuffered water. As mentioned in section 2.5, the solubility of Fe(III) is negligible at neutral pH. The vapour pressures indicate no loss of CAs due to vaporization.

Table 4.2: Chemical and physical properties of CAs. [55]

Property	**Oxalic Acid**	**Citric ACid**	**$Fe(II)SO_4 \cdot 7 \cdot H_2O$**
Molar mass	122.13 $g\,mol^{-1}$	165.82 $g\,mol^{-1}$	278.05 $g\,mol^{-1}$
Density (20 °C)	1.321 $g\,cm^{-3}$	1.623 $g\,cm^{-3}$	1.89 $g\,cm^{-3}$
Solubility (water)	220 $g\,L^{-1}$	999 $g\,L^{-1}$	256 $g\,L^{-1}$
Vapour Pressure	«0.001 bar	«0.001 bar	-

Oxidants

The oxidants used in the experiments are 65% CaO_2 (purchased form Alfa Aesar) and 33% H_2O_2 (purchased from VWR Chemicals) purchased from VWR Chemicals. Depending on the concentrations required for each experiment, the oxidant was diluted accordingly. In the case of CP the oxidant was added in the form of a slurry, or directly as powder depending on the experiment.

(b)

(a)

Figure 4.4: Molecular structure of **(a)**: Calcium peroxide [26] and **(b)**: Hydrogen peroxide [26]

The properties of CP and HP are given in Table 4.3.

Table 4.3: Chemical and physical properties of CAs. [55]

Property	**Calcium peroxide**	**Hydrogen peroxide**
Molar mass	72.08 $g\,mol^{-1}$	34.02 $g\,mol^{-1}$
Density (20 °C)	N.A.	1.39 $g\,cm^{-3}$
Solubility (water)	N.A.	488 $g\,L^{-1}$
Vapour Pressure	N.A.	$2.63*10^{-3}$ bar

4.1.2 Soils

In the experiments two types of soil were used. For stages II-A and III a model soil was used consisting of filter sand that varied in diameter from 0.7 mm to 1.1 mm. In stage II-B, soil was used that originated form pit 3 at the Kærgård plantation. This soil consisted of a mixture fine sand, smaller than the sand particles in the model soil, to relatively large rocks with diameters up to 3 cm. Therefore the Kærgård soil is more heterogeneous of nature compared the model soil. This soil originated from layer 2.1, 6 meter below ground. This soil originated form the layer treated by ISCO and ERD which has greatly reduced the extent of PCE contamination. However, there is still organic matter present in one of the soils used (B3312), which might have an influence on the total oxidant demand section 8.4. However, the amount of PCE is negligible for all of the soils (<0.1 $mg\,kg^{-1}$).

4.1.3 Buffer solutions

The buffer solutions used in this experiments are made by adding $NaH_2PO_4{\cdot}2{\cdot}H_2O$ and $Na_2HPO_4{\cdot}2{\cdot}H_2O$ to drinking water unless stated otherwise. After which the pH is adjusted to the desired value by adding 1 M NaOH (purchased from VWR Chemicals) or H_2SO_4 (purchased from Fischer Scientific) to the buffer.

Table 4.4: Strength and pH of the three types of phosphate buffer solutions using in the experimental work.

Strength	**pH**	**$NaH_2PO_4 \cdot 2H_2O$** ($g\,L^{-1}$)	**$Na_2HPO_4 \cdot 2H_2O$** ($g\,L^{-1}$)
0.25 M	7	47.20	45.30
0.05 M	7	3.276	5.162
2.0 M	7	8.8995	152.12

Further equipment

- Measurements of pH were carried out with a Metronohm 826 pH mobile pH meter
- Soil samples were placed on a shaker plate of type: IKA HS501 Digital
- COLUMNNNN and PUMP

4.2 Analytical methods

4.2.1 Hydrogen peroxide analysis

Potassium Iodide was dissolved in demineralized water (4 g) per 50 mL together with 0.2 g of potassium hydrogen carbonate in order to control pH fluctuations. For the calibration curve, a 5 mM stock solution of HP was used to create a range of samples with concentrations of 0.01 mM to 0.1 mM. This was achieved by adding 0.1 to 1 mL to 40 mL of the iodide solution. Demineralized water was added in order to obtain a total volume of 50 mL, the reactions are shaken by hand and left to react for a minimum of 30 minutes. UV-vis calibration was carried out at a wavelength of 353 nm on a Agilent Technology Cary 60 UV-vis spectrometer. Stock solution with KI and $KHCO_3$ are used as blank measurements. The absorbance of each sample was measured 3 times, averaged and plotted in a graph against their respective concentration. The data was fitted using the basic linear fitting tool in MATLAB. The calibration curve is presented in section 8.1.

4.2.2 Benzoic acid analysis

The BA and p-HBA concentration were determined by HPLC-UV. These HPLC-UV measurements were carried out HPLC (Agilent Poroschell 120, EC.C18 column) from Agilent Technologies in combination with a UV detector. The first mobile phase consisted of 60% 0.050 M ammoniumacetate (pH 4.0) while the second mobile phase consisted of 40% methanol. The flow rate was set to 1 $mL\,min^{-1}$ with a pressure of around 300 bar and injection volume of 5.0 µL. Calibrations were made in the range of 0 to 200 mg L^{-1} for both BA and p-HBA, the detection limit was 0.1 mg L^{-1}. The detection wavelength was set to 234 nm for both species, the retention time was 1.694 and 3.574 minutes for p-HBA and BA respectively.

4.2.3 Chloride analysis

Ion chromatography was used to determine the Cl^- concentration in the aqueous phase of the soil systems during the PCE degradation experiments. The system in which these measurements were carried out consists of a HPLC pump (818 IC) to pump the eluent. The column cabinet consists of an 820 IC Separation Center. For detection, an 819 IC detector is used. The interface is an 771 IC compact interface. The column used is an anion exchanger (metrosep A sup 5 100/0.4 mm) ct.nr 6.1006.510. The eluents used were 1 mM $NaHCO_3$ and 3.2 mM Na_2CO_3. The concentration range in which Cl^- could be detected was 5 mg L^{-1}(lower limit) and 100 mg L^{-1}. Samples were diluted 10 times in order to stay in this calibration range.

4.3 Experimental methods

4.3.1 I-A: Hydroxyl radical yield determination

BA was added to a buffer solution. Buffer solutions used were near acidic (pH 4) and neutral (pH 7) phosphate buffers made in drinking water. Excess of BA was utilized to decrease the occurrence of hydroxyl radical scavenging reactions and to increase the pre-dominant nature of the BA hydroxylation reaction. The reactions were carried out in 500 mL quartz glass beakers under continuous mixing using a magnetic stirrer set to 250 rpm. The amount of buffer solution used for each of the experiments was 200 mL. To this buffer solution 3 mmol of BA was added to achieve a 15 mmol solution. The solution was stirred and heated on a hot plate for a maximum of 1 minute to speed up dissolving process of the BA. After the solution has cooled back down to room temperature, 1.4 mmol of $Fe(II)SO_4{\cdot}7H_2O$ is added. Once the solution was mixed 0.1 g (1.4 mmol) of CP is added to initiate the reaction. At time intervals specified before hand a sample was taken and filtered with a 0.45 µm into a glass vial or beaker placed in ice water. After the experiment was over the samples were placed in HPLC-UV vials and analyzed on the amount of p-HBA.

4.3.2 I-B: Influence of oxidant/catalyst ratio on BA degradation in drinking water

In this experiment the influence of the molar ratio between oxidant and catalyst was investigated on the degradation of BA in drinking water at neutral pH. The experiments consisted of a number of batch experiments performed using 200 mL buffer solution in 500 mL quartz glass beaker. In the solution BA is dissolved to create a concentration of 14 mg L^{-1} corresponding to 0.115mM. The solution was refrigerated over night at a temperature of 4 °C and left to warm up to a temperature of around 10 °C before adding the oxidant and catalyst. The first molar ratio investigate was the 1/1-1 ratio between CP and catalyst-chelating agent. The initial dosage of CP was 0.5 g L^{-1} (0.1 g in 200 mL) corresponding to a 1.4 mmol (7 mM) dosage. The same dosage was utilized for Fe(II)SO_4·7·H_2O (7 mM, 0.39 g in 200 mL). The ratio between catalyst and CA was kept constant at a 1-1 ratio throughout all experiments. In the first experiments, the total amount of moles of oxidant and catalyst combined is kept constant at 2.8 mmol while the molar ratio was varied. Any ratio given from this point onward is of the format: oxidant/Fe(II)-CA/contaminant.

Table 4.5: Molar ratios investigated. The total amount of moles (oxidant + catalyst) is kept constant. The molar ratio between catalyst and chelating agent was kept constant.

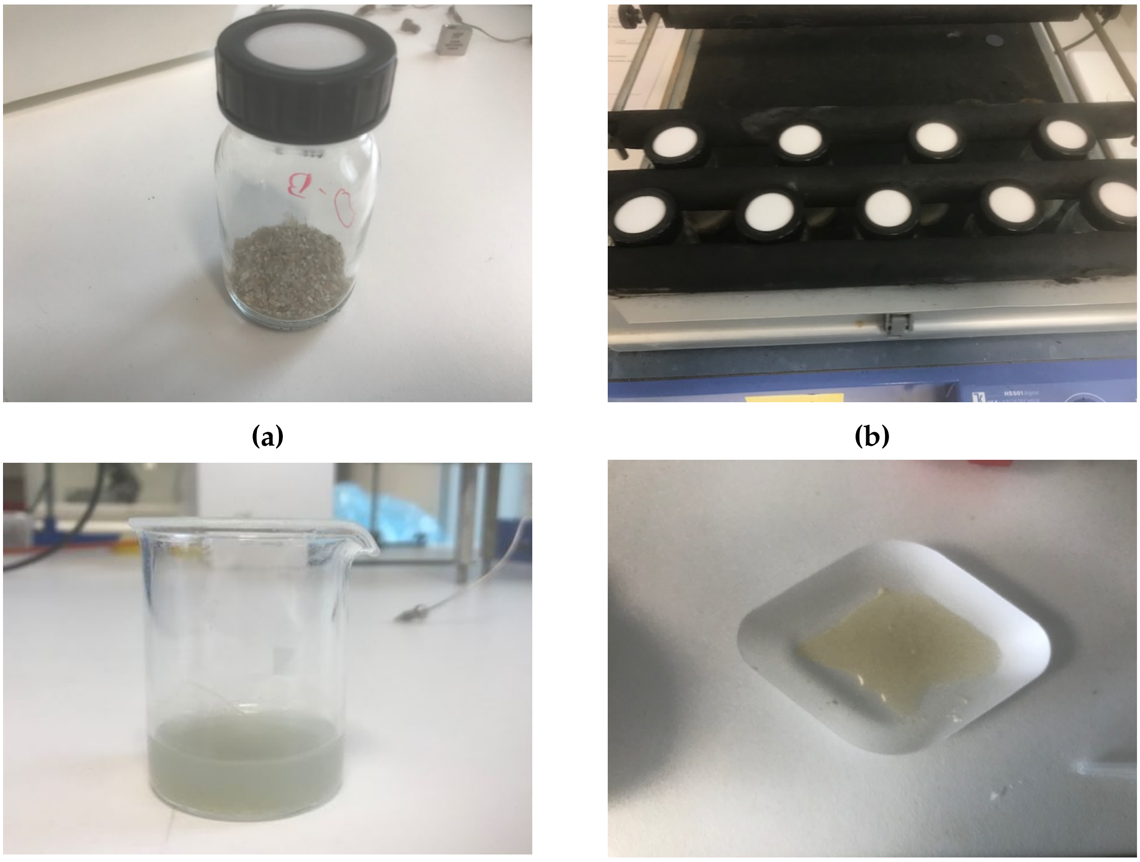
System ratio (CP/Fe(II)-CA/BA)	CP (mmol)	Fe(II) (mmol)	OA (mmol)
66/66-66/1	1.4	1.4	1.4
81/40-40/1	1.87	0.93	0.93
91/30-30/1	2.1	0.7	0.7
97/24-24/1	2.24	0.56	0.56
108/13-13/1	2.49	0.31	0.31
40/80-80/1	0.93	1.87	1.87
30/90-90/1	0.7	2.1	2.1
24/97-97/1	0.56	2.24	2.24
13/108-108/1	0.31	2.49	2.49

The samples were prepared using the identical method as mentioned before where samples are taken at a specific time interval. The experiments last 30 minutes due to the fact that there was no possibility to keep the temperature constant at 10 °C while keeping the contents of the glass beaker continuously mixed. Measurements were again performed using the HPLC-UV method quantifying BA. The measurements are presented in a time versus $\frac{C_i}{C_0}$ where C_i is the concentration of BA measured at time interval i and C_0 is the BA concentration before addition of reagents.

The most efficient ratios tested were used for a new set of batch tests. In this test the amount of reactants was increased in order to see the effect of the ratios at increased oxidant and catalyst dosage. The results will be presented in in identical fashion as described before.

4.3.3 II-A: Degradation of model contaminant in a soil slurry: batch experiments

The BA degradation batch reactions were carried out in 80 mL glass bottles with a plastic screw cap. 20 g of model soil was placed inside the bottle. 5 mL of a 40 mg L^{-1} BA stock solution was added to the sand and placed on a shaker plate for 45 minutes to achieve complete mixing. Afterwards, they were placed inside an oven overnight at 105 °C in order to evaporate the water leaving the soil contaminated with BA. In 7 mL of the drinking water buffer solution the Fe(II) and OA were dissolved and shaken by hand to a homogeneous mixture. CP were made into a slurry-like substance in 3 mL of demineralized water. The catalyst solution was added to the reactor first followed by the CP slurry and the reactor placed on the shaker plate. At a specific time interval, one reactor was sacrificed and taken of the shaker plate and the reaction quenched by cooling down in ice water. With a funnel and filter paper the aqueous phase was separated from the solid phase. pH measurements were taken from the aqueous phase and an HPLC-UV sample was prepared through filtration with a 0.45 µm syringe filter. To the solid phase, 20 mL of demineralized water was added and left to shake in the shaker plate for 45 minutes in order to extract the BA from the solid phase. HPLC-UV samples were made through filtering the demineralized water taken form the solid phase with a 0.45 µm syringe filter. BA concentrations were measured using the same method as before (subsection 4.2.2).



(a) (b) (c) (d)

Figure 4.5: Experimental setup used in the soil slurry experiments showing **(a)**: Glass bottle used as a model batch reactor **(b)**: Shaker plate setup **(c)**: Catalyst + OA mixture **(d)**: CP slurry

The results were plotted using MATLAB in a $\frac{w_i}{w_0}$ vs. time plot, where w is the combined total mass of BA measured in both phases. For the solid phase this was done through Equation 4.1, where C_i is the concentration BA at time i in mg L^{-1} and $\frac{1}{100}$ is the multiplication factor needed to calculate the absolute mass of BA in 10 mL of aqueous phase. For the solid phase, 20 mL of solvent was used, therefore a multiplication faction of $\frac{1}{50}$ is necessary to calculate the mass of BA extracted from the solid phase, Equation 4.2. The total mass was obtained by adding up the mass in the two phases, Equation 4.3. The measurement point at $i = 0$ was obtained by extracting the dried solid phase containing BA without the addition of any reactants.

$$w_i^{aq} = C_i^{aq} * \frac{1}{100} \tag{4.1}$$

$$w_i^{s} = C_i^{s} * \frac{1}{50} \tag{4.2}$$

$$w_i^{tot} = w_i^{aq} + w_i^{s} \tag{4.3}$$

Three experiments were carried out with BA as contaminant:

- 66/66-66/1 CP/Fe(II)-OA/BA to investigate the oxidation capacity of CP in a soil slurry system
- 99/99-99/1 CP/Fe(II)-OA/BA to see the influence of an increased dosage on the degradation of BA
- 66/66-66/1 HP/Fe(II)-OA/BA as comparison test between CP and HP as oxidant

The CP reaction were left to react for a period of 14 days with samples taken at 1 day, 4 days, 8 days and 14 days. As a reference, contaminated soil was used without addition of any reactants.

4.3.4 II-B: Degradation of PCE contaminated soil: batch experiments

Similar to last experiments, these experiments consisted of a series of batch tests using a soil/groundwater system. However, the transition was made from model contaminant to the COC: PCE. In the first series, the same soil was used as in the previous soil slurry tests. This soil was contaminated manually by adding PCE to the soil. This was done by adding 10 µL of PCE (>96%) stock directly into the soil resulting in a PCE contamination of $500\,\mathrm{mg\,kg^{-1}}$ of soil. Using a contamination of $500\,\mathrm{mg\,kg^{-1}}$, the extent of contamination allowed for quantification of oxidant efficiency with one addition over a relatively short time without the need for multiple oxidant additions. In addition, the PCE concentration was high enough to allow the formation of DNAPL in the soil system because it exceeded to solubility limit in water(206 mg/L).

The PCE contaminated soil was then mixed with an aqueous phase consisting of 50 v% groundwater and 50 v% buffer solution to which the predetermined amount of oxidant, catalyst and CA was added. The CA agent used in this experiment was again OA. This method was changed during the second round of experiments due to a strong decrease in pH. Instead, for the second set of experiments the buffer was created directly in the groundwater.

In Table 4.6, the parameters used during the PCE batch tests are given. In all cases, 3 replicates were created for each reactor of which two were measured on their PCE (and products) content whereas one extra replicate was used for pH measurement, residual oxidant determination and ion chromatography measurements (IC) for determination of Cl^- concentrations in the aqueous phase.

Table 4.6: Conditions used in the batch experiments using PCE as contaminant.

Reactor	soil (g)	GW (mL)	Buffer (mL)	[CP]	[HP]	[Fe(II)]	[OA]	days	R
First round of experiments using model soil									
# 1	30	7.5	7.5	-	-	-	-	28	3
# 2	30	7.5	7.5	264	-	264	264	28	3
# 3	30	7.5	7.5	-	264	264	264	28	3
Second round of experiments using Kærgård soil									
# 4	20	10	-	-	-	-	-	14	3
# 5	20	10	-	132	-	132	132	1	3
# 6	20	10	-	132	-	132	132	7	3
# 7	20	10	-	132	-	132	132	12	3
# 8	20	10	-	132	-	132	132	28	3
# 9	20	10	-	-	132	132	132	1	3
# 10	20	10	-	-	132	132	132	6	3
# 11	20	10	-	-	132	132	132	12	3
# 12	20	10	-	-	132	132	132	28	3

The ratio of oxidants/catalyst-CA/PCE used are approximately 40/40-40/1 in the first round of experiments and 20/20-20/1 in the second round of experiments. These concentrations were taken based on previous experiments using PCE contaminated soil from the Kærgård plantation where a significant change in PCE concentration was observed using CHP with similar concentrations [7].
In the second round of experiments, the dosage of oxidant and catalyst were lowered due to problems in experimental procedure (i.e. issues in chelating the iron in the aqueous phase) resulting in incomplete addition of catalyst.

The results obtained were analyzed on their total PCE content (solid and liquid phase combined). Separate phase analysis was not a viable method since the mass transfer rate between DNAPL and aqueous phase is changed due to the addition of oxidant as is described in subsection 2.3.2 (see Figure 2.2). The difference in total mass PCE between control and CCP or CHP reactors was used to determine oxidant efficiency.

Ion chromatography was used to measure the chloride content of the aqueous phase using the method outlined in subsection 4.2.3. The concentration difference between the untreated systems and the treated systems and the total PCE content can be used as an indication for the degree of mineralization of PCE [20].

The total amount of Cl^- per reactor is obtained by converting the concentration in the aqueous phase in $mg\,L^{-1}$ by a factor 0.015, as shown in Equation 4.5. This results in the amount of Cl^- in the total aqueous phase. Based on the the theoretical knowledge presented in subsection 2.3.2 it is assumed that all of the Cl^- formed is present in the aqueous phase. The amount of Cl^- in each reactor based on the amount of PCE degraded in that particular reactor (determined from the difference in PCE content of the CCP or CHP reactors and the control reactor) is then calculated using Equation 4.5.

$$\text{Actual Cl}^- \text{ in reactor (mmol)} = \text{measured Cl}^- \text{ (mM)} * \frac{\mathbf{15}}{\mathbf{1000}} \tag{4.4}$$

$$\text{Cl}^- \text{ in reactor (mmol)} = \text{degraded PCE (mmol)} * 4 \tag{4.5}$$

The percentage of mineralization is then calculated through Equation 4.6.

$$\text{\% PCE mineralized} = \frac{\text{Actual Cl}^- \text{ in reactor (mmol)}}{\text{Cl}^- \text{ in reactor (mmol)}} * \mathbf{100} \tag{4.6}$$

4.3.5 III: Continuous operated column studies

In these experiments, the transition was made from batch soil slurry systems to continuous operated soil slurry systems. This was done through the use of a packed bed column operated from top to bottom. The set-up is given in Figure 4.6.

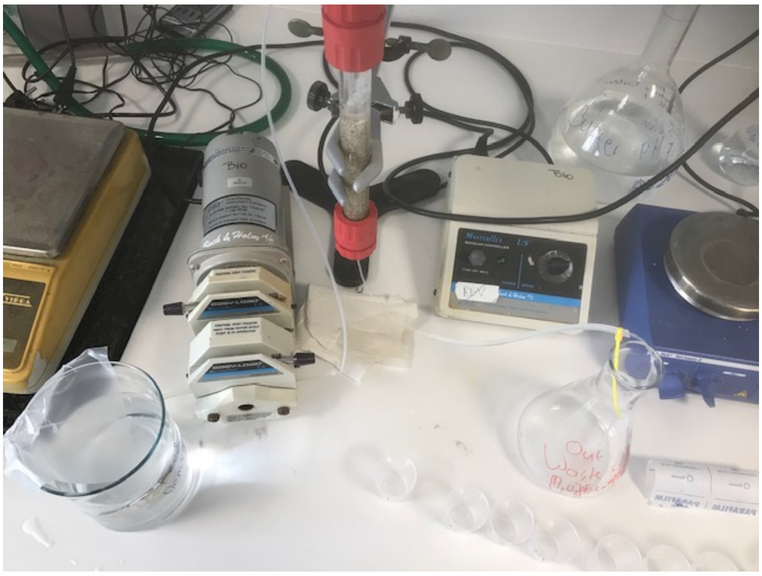


Figure 4.6: Illustration of the column set-up used with pump (left), column

The column used was from BRAND (width: 1.6 cm, length: 20 cm). Hence, the total volume is 40.21 mL . In preliminary experiments the column was packed with a known amount of model soil and flooded at a specified flowrate. The volume difference before and after complete flooding in the feed solution was measured for various amounts of soil used in the column. This process was repeated 3 times for each amount of sand

and an average value was obtained for the pore volume. The obtained value was $0.28\,\mathrm{mL\,g^{-1}}$. Depending on the bed height and amount of soil used in order to reach this bed height, the pore volume was calculated. With the flowrate, this allowed for the calculation of the retention time for a specific system. The calibration data is given in section 8.2.

The pump used to operate the column is TYPE. It was calibrated by measuring the amount of demineralized water pumped through the feed tube in 30 seconds for a certain button setting. This process was repeated 3 times for each button setting used. The results of this calibration are given in section 8.3.

4.3.6 III-A: Oxidant delivery and CP dissolution

The first objective is to obtain an indication of the CP dissolution when continuously operated after a single addition of CP in the top of the column using various flowrates. To avoid clogging of the column exit, as was experienced in previous research with the same equipment [22], which is equipped with a filter the amount of CP powder used was limited to 0.2 g. The model soil (subsection 4.1.2 was used as the packing material, the packed bed was flooded operating from bottom to top to assure complete saturation of the pore space with water. The top layer (around 1.5 cm) was left unsaturated to allow for addition of the CP in the form of a slurry (0.2 g in 2 mL of water). The column is operated at a flowrate ranging from 2 to $8.3\,\mathrm{mL\,min^{-1}}$ for up to 8 hours while taking a sample at the exit of the column at specified time intervals. From the sample 2 mL was taken, depending on the expected HP concentration, filled up to 4 mL with KI solution, after which the solution was mixed and left to react for a minimum of 30 minutes. The samples were measured and quantified for their HP content through the method described in subsection 4.2.1. This procedure was repeated for various amounts of bed heights ranging from 10 cm to 16.5 cm. Comparative studies were performed with liquid HP (33%), where equal molar amounts were added to the column in order to determine the difference in oxidant delivery and dissolution in continuous systems.

4.3.7 III-B: BA degradation in continuously operated column

The second set of experiments involved the addition of a model contaminant to the packed bed to which the oxidant is delivered in identical way. The packed bed was contaminated by adding 36.6 mL of a $0.5\,\mathrm{g\,L^{-1}}$ BA solution to 50 grams of sand, left on a shaker plate for a minimum of 30 minutes and evaporated overnight resulting in 50 g of soil contaminated with 18.32 mg ,equivalent to 0.15 mmol, BA. CCP reagents were added in 20/20-20/1 ratio. CP was added in the form of a slurry by adding 2 mL of water to 216.2 mg (3 mmol) of CP. The catalyst was added through continuous addition of OA chelated Fe(II) (3 mmol of Fe(II) and OA) in 250 mL buffer solution of pH 7. At specific time intervals a sample was taken from the outlet and placed inside a HPLC-UV vial and measured on the BA concentration. Because of the high solubility of BA, the experiment was stopped after 16 pore volumes were pumped through the column. The degree of BA degraded was determined through comparison of a control test, where the buffer was pumped through the column without oxidant or catalyst.

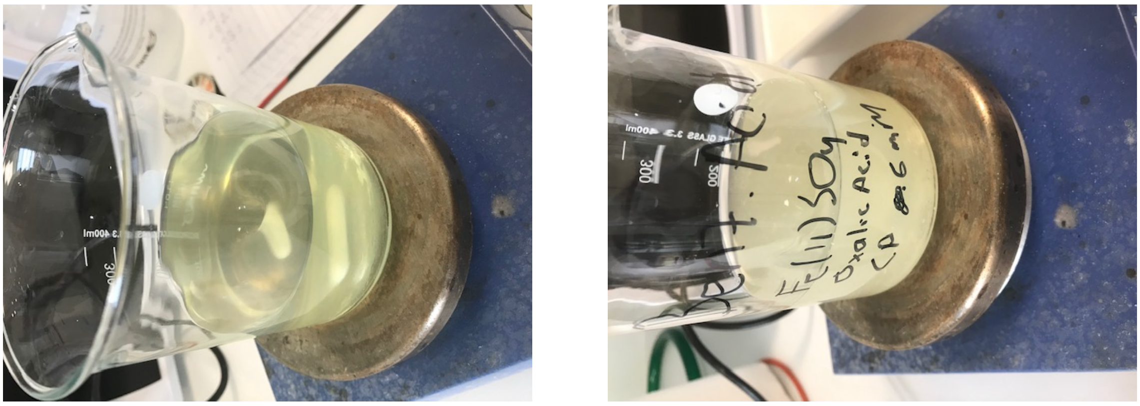
5. Results and Discussion

In this chapter the results from the experiments are presented and discussed.

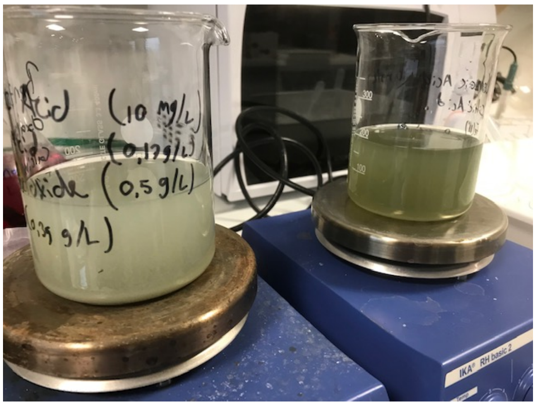
5.1 I-A: Hydroxyl radical determination

The first experiments performed were the batch tests using a buffer at neutral pH made from drinking water. The first two batch tests were performed with a buffer not strong enough (strength was taken from literature) to keep the pH near neutral conditions. This was due to the addition of a large amount of acid in the form of BA resulting in a pH decrease down to a pH of 4. The pH did not change significantly over the course of the experiment itself. Adjustments were made in the buffer by means of increasing its strength resulting in a maximum pH decrease of 0.20 after adding BA and CA, both of acidic nature. As a result, the reaction took place at a pH of 6.80 - 6.85 in the case of all experiments using BA as model contaminant in the buffer drinking water and soil slurry systems. Generally, experiments using OA had a slightly lower pH. This was expected due to the lower pKa values for OA (Table 4.2). The change in pH over the course of the reactions was minimal and typically the pH change is smaller than 0.08, indicating that the buffer capable of keeping the pH constant. Normally, there was an increase in pH as the reaction proceeds due to the formation of $Ca(OH)_2$ [12,21].

Adding the $FeSO_4{\cdot}7{\cdot}H_2O$ to the buffer solution resulted in a cloudy mixture with a greyish blue colour containing some solid precipitation. Addition of one of the two CAs changed the mixture to clear yellow (OA) and clear greenish (CiAc) mixture at a lower pH. At neutral pH, the mixture remained slightly turbid, in Figure 5.1a and Figure 5.1b the solutions mentioned are illustrated. Moreover, the solid precipitation changed colour and dissolved indicating the chelation of Fe(II). After the addition of CP, the solutions became more turbid, forming the OA solution into a white milky mixture and the CiAc mixture into a dark green turbid mixture. The difference in colour can be accounted for by the different CAs used, while the change in colour over time for each system individually can be explained through the precipitation of $Ca(OH)_2$ [22]. The formation of Fe(II) complexes to Fe(III) complexes can also give rise to colour change in the mixture.



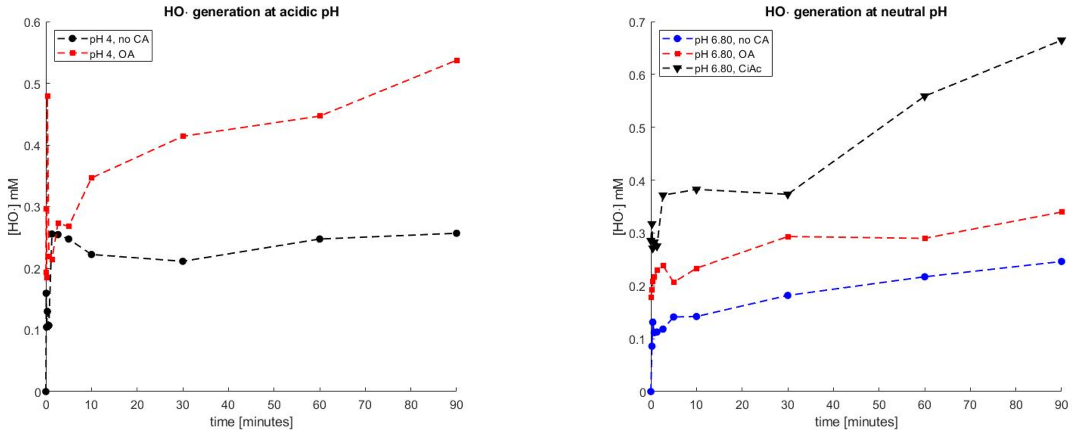
(a) Acidic pH **(b)** Neutral pH



(c) After oxidant addition, neutral pH

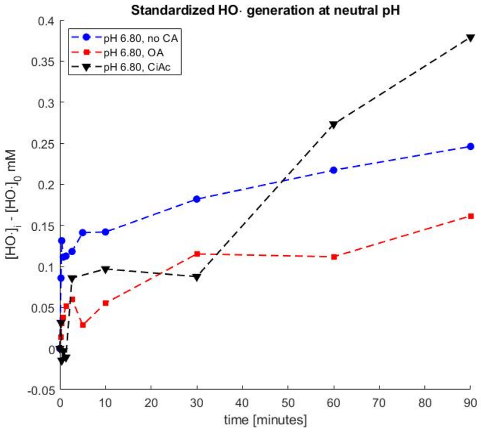
Figure 5.1: Chelated Fe(II) solutions with OA at **(a)** acidic pH, **(b)** neutral pH and **c** after the reaction was stopped for OA (left) and CiAc (right).

In Figure 5.2, the results for the [HO•] determination batch experiments are presented.



(a) Acidic pH

(b) Neutral pH



(c) Standardized

Figure 5.2: Time versus hydroxyl radical concentration plots ($[BA]_0$ = 15 mM, [CP] = [Fe(II)] = [OA] = 7 mM) in **(a)** acidic, **(b)** neutral pH . **(c)**: The data is standardized by making the first concentration equal to zero and subtracting this value from every other measured concentration.

The results indicate that BA was successfully hydroxylated since the amount of p-HBA measured increases significantly after the CP was added. Both plots show curves that satisfy the expectation based on literature [47, 48]. The amount of hydroxyl radicals generated was increasing fast in the beginning of the reaction and levels off as the reaction proceeds. Since the rate at which the amount of hydroxyl radicals were formed in the initial part of the reaction varies, the discussion will focus on the final amount of hydroxyl radicals measured. From Figure 5.2a and Figure 5.2b it becomes clear that the hydroxylation of BA occurred faster when chelating agents were added in both acidic and neutral pH. In the experiments without chelating agent, acidic environments appeared to be more favorable in terms of hydroxyl radical generation.

One thing to note from Figure 5.2 is the initial point at which the measurements start. The concentration at $t = 0$ is 0 in the cases where no chelating agents were used. However, whenever OA or CiAc was added to the Fe(II) and let to mix for up to 30 seconds, the measurement taken before adding the CP turned out to result in a concentration that was of significance (around a third of the final concentration measured). From Figure 5.2b, it can be seen that the concentration HO· at the start of the experiment was higher for the case where CiAc was used. This could be an indication of oxidation of the Fe(II) complex before addition of oxidant by dissolved molecular oxygen for example. This phenomenon was not observed in the published literature [47, 48], introducing the need for a control study where the BA solution is treated by flowing N_2 through it under a vacuum to remove any dissolved oxygen from the solution before starting the experiment.

Looking at the HO· formation in terms of absolute numbers, it can be seen that the absolute HO· from the moment the reaction was initiated until the end of the experiment is different for each experiment. CiAc appears to have the highest value (0.38 mM) followed by no CA (0.23 mM) and OA (0.16 mM). An explanations for this observation can be found in the organic molecules acting as CA can participate in scavenging reactions preventing the BA hydroxylation from occurring. This would indicate that CiAc in this case increased HO· production significantly contrary to OA where the effect was less obvious, which was in line with the results found by Xue et al. [47]. However, this is not in line with kinetic data given in Table 2.3. CiAc has a significantly higher reaction rate than OA. A possible explanation of why CiAc performs better in this experiment could be the stronger complex formed by OA and Fe(II) compared to CiAc and Fe(II), reducing the reaction rate of the complex with HP [9].

In order to obtain conclusive results on the role of OA and CiAc in this experiment it should be repeated. One way to test the influence of the scavenging reactions is to increase the concentration of BA. Creating a larger excess of BA in the solution compared to oxidant and catalyst will make the hydroxylation reaction more dominant compared to scavenging reactions. The assumption made in the design of this experiment, namely the excess created allow for hydroxylation reaction to be dominant enough to eliminate any scavenging reactions, might not have been valid. Published literature used a larger excess at a lower oxidant dosage: 10 mM BA and 1 mM CP [21]. Repetition of this experiment with a larger excess will show of the assumption made earlier is valid. Additionally, performing the experiment in triplicate would results in more consistent results reducing the influence of errors in measurements or experimental procedures in additional to showing the reproducibility of the results.

5.2 I-B: BA degradation in drinking water

This set of experiments uses a lower concentration of BA in a neutral pH drinking water buffer solution. The results are presented in Figure 5.8. All the results are plotted in a time vs. $\frac{C_i}{C_0}$ plot presented in Figure 5.8. During these experiments the starting temperature was 8 °C, the final reaction was around 13 °C unless stated differently.

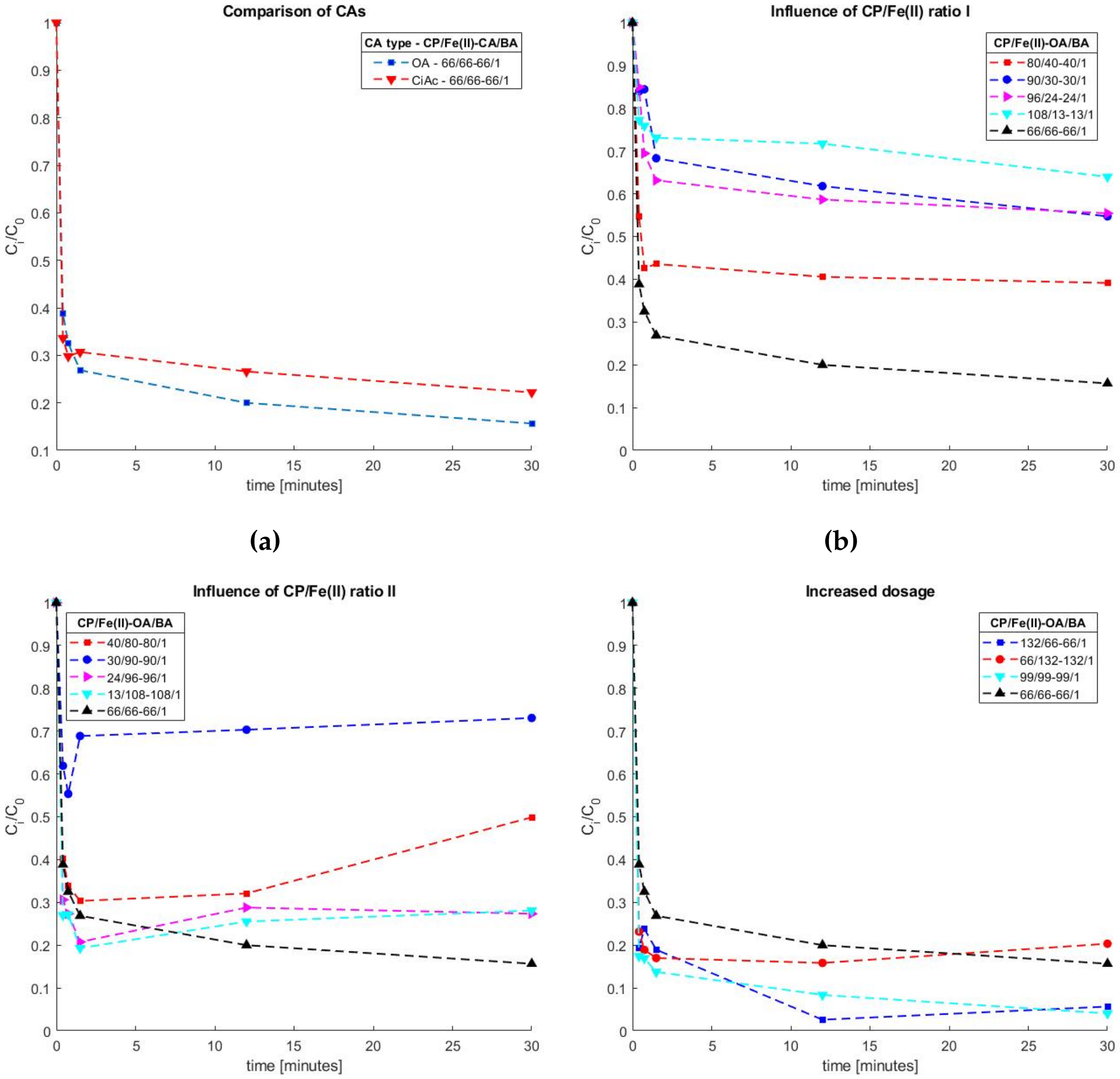
5.2.1 Comparison of chelating agents

The first degradation test performed was a comparison between the two CAs investigated in the project. Equal molar amounts and ratios were used for both CAs. The experiments were conducted in duplicate and the averaged results are presented in Figure 5.3a. The plot shows comparable degradation for both of the chelating agents in the first 100 seconds of the reaction. After that point OA seemed to have a slightly greater impact on BA degradation than CiAc with OA reaching a final degradation of 83% and CIT of 77%. OA was also found to be more effective by Xue et al. [47]. For this reason, OA is the CA used in the following experiments. However, it should be noted that CiAc is also a viable option in terms of its performance in this experiment and should be taken into consideration when more criteria are included (for example cost and biodegradability).

The previous experiment showed a better performance in HO· formation when CiAc was the CA used. This contradicts the results form this experiment. An explanation for this observation could potentially be found in the kinetic data. BA has a rate constant of $4.2*10^9$ L mol^{-1} s^{-1}, whereas the rate constants with HO· for OA and CiAc are $1.4*10^6$ and $3.2*10^8$ L mol^{-1} s^{-1} respectively. Therefore, CiAc will compete with HO· to a larger extent than OA. This might be less of influence in the previous experiment due to the significantly higher BA concentration. The increased concentration reduces the influence of competing scavenging reactions.

5.2.2 Influence of molar ratio

This experiments were performed with OA as the chelating agent. The 66/66-66/1 ratio in both cases was taken from the results of the previous experiment (Figure 5.3a).



(a) **(b)**

(c) **(d)**

Figure 5.3: Batch tests comparing the degradation efficiency of CP using, **(a)**: OA and CiAc **(b)**: increasing oxidant ratio **(c)**: increasing Fe(II) ratio **(d)**: increased reagent dosage. $[BA]_0 = 0.115$ mM.

Increasing CP

First, the molar ratio was increased in direction of CP as documented in Table 4.5. The results are presented in Figure 5.3b. Form the figure it becomes clear that the 66/66-66/1 ratio was the ratio with the highest degradation efficiency with a removal of 83%. Increasing the ratio to 80/40-40/1, 90/30-30/1, 96/24-24/1 and 108/13-13/1 reduced the degradation efficiency to 59%, 43%, 42% and 35%. This indicates that an excess of CP, and therefore HP, compared to the catalyst hinders the degradation of

BA which is in line with observations made in literature [22, 40]. However, in these experiments the 66/66-66/1 ratio seems most optimal whereas in the literature 2/1 or 1/2 ratio between oxidant/catalyst is taken as the most optimal. This is possibly because in these experiments the total dosage in terms of *moles CP + moles catalyst* was kept constant while the molar ratio between them is changed. In contrast, the literature cited is effectively increasing the total molar dosage by increasing the amount of CP or catalyst, depending on which ratio is tested, while keeping the other constant.

The observed decrease in degradation with increasing amount of CP compared to Fe(II) is explained by an increased HP formation rate, which in turn participates in various scavenging reactions. This implies that the HP formation exceeds the rate at which HP is catalyzed into ROS by Fe(II)/Fe(III) molecules.

Increasing Fe(II)

During the next set of experiments the same procedure was followed, but in this case the relative amount of catalyst of Fe(II) was increased with respect to the amount of CP. The amount of OA used was equal to the molar amount of Fe(II) that was used in order to keep the molar ratio between Fe(II) and CA constant.

The results are plotted in Figure 5.3c. From the plot it appears that the 66/66-66/1 ratio had the best removal efficiency in the end of the reaction with 83% followed by 24/96-96/1, 13/108-108/1, 40/80-80/1 and 30/90-90/1 ratios with 72%, 72%, 55% and 30% degradation efficiencies respectively. This observation is not in line with the expectations, there was no trend visible as was the case in previous experiments where the CP amount was increased. Additionally, the plots with increased Fe(II) ratio seem to all show an upward trajectory in the degradation after the 120 second mark. Remarkably, for the 40/80-80/1 ratio there was an increase of 17% between the last two measurement points.

The addition of relatively higher amount of Fe(II) also resulted in higher concentrations of SO_4^{2-}. These ions have shown to either inhibit the rate of oxidation [62], or improve the rate of oxidation slightly [40]. The presence of SO_4^{2-} ions might promote the formation of the sulfate radical, $SO\cdot_4^{2-}$, through its reaction with $HO\cdot$ [32, 40]. This can possibly decrease or increase the rate of oxidation depending on the reactivity of the radicals with the COC although its contribution is negligible in most cases [32].

Because of the significantly higher degradation at the end of the experiment for the 66/66-66/1 ratio, this was taken to be the most optimal ratio in this experiment as well.

Increased dosage

In this experiment three batch tests were performed using a higher oxidant/catalyst dosage. Additionally, three molar ratios were tested: 99/99-99/1, 132/66-66/1 and 66/132-132/1. The results are presented in Figure 5.3d. The 99/99-99/1 seemed to have the highest BA removal with 96% followed by the 132/66-66/1 ratio, 94%. The difference with the higher dosage between the 99/99-99/1 and 132/66-66/1 ratio is less when using a higher dosage compared to a lower dosage. This could be an indication that the dosage used in the previous experiment was not suitable for optimal degradation. The 66/132-132/1 ratio seemed to perform less optimal with a removal of 80%, which is lower than the removal achieved using a lower dosage and a 66/66-66/1 ratio. One possible explanation for this could be the scavenging of hydroxyl radicals by the more abundant Fe(II) and OA molecules in this case [9].

Figure 5.4 shows the results from an experiment performed using the increased dosage with a 1/1 molar ratio between CP and Fe(II). In this experiment the reaction is monitored over a longer period of time. Over a period of 2.5 hours, 97% of the BA was degraded. This reaction appeared to degrade BA slower compared to the 99/99-99/1 system in Figure 5.3d. This observation was attributed to the temperature since this experiment was performed at 22 °C compared to 10 °C in the previous experiment. Increasing the temperature decreases the HP yield from CP dissolution and increases HP decomposition, consequently decreasing ROS generation [12,22].

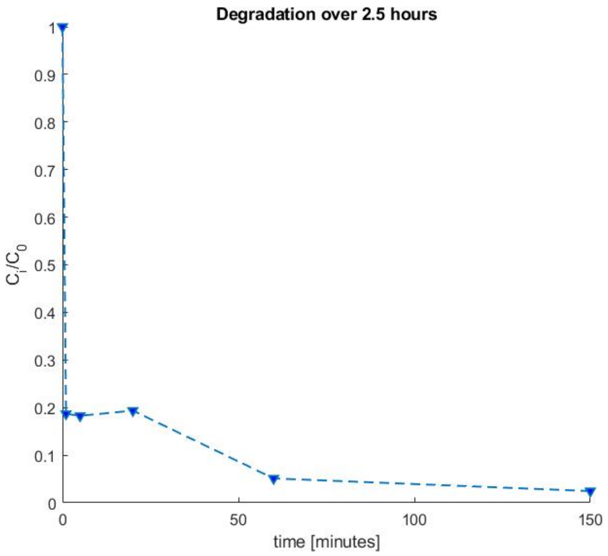


Figure 5.4: Degradation of BA over a period of 2.5 hours. $[BA]_0 = 0.115$ mM, [CP]=[Fe(II)]=[OA]=10.5 mM

5.3 II-A: Soil slurry experiments with model contaminant

This section will present the results from the soil slurry experiments. In this experiment a 1/1 oxidant/catalyst ratio was used. The catalyst consisted of Fe(II) chelated with OA. A comparison was made in degradation of BA using the two dosages investigated in previous experiments: 66/66-66/1 and 99/99-99/1. In addition, a comparison was made to the degradation using CHP using the same dosages and catalyst allowing for a direct comparison of oxidation capacity of HP and CP.

In Figure 5.5, the results from each batch tests are presented. Each point indicates the average removal in total weight of BA from the soil slurry taken from the three reactors sacrificed at each specified time interval. The first ratio used reached 96% removal after 14 days of reaction time, whereas as an increased CP dosage reached 98% removal at this point. When looking at the standard deviations of both measurement points, they seemed to have a small overlap. Performing an ANOVA test between these points resulted in a probability value of $\boldsymbol{p = 0.1531}$. Considering that $\boldsymbol{p > 0.05}$, the difference between these two points was regarded as insignificant. As a result it can be concluded that the increase in dosage might not be more effective for the removal of BA from the soil slurry over a period of 14 days compared to a lower dosage. After 8 days reaction time, the average removal appeared to be significantly different (75% compared to 97% at higher dosage). Performing an ANOVA test on the data obtained for 8 days resulted in $\boldsymbol{p = 0.1279}$, indicating that the difference in removal between the higher and lower dosage can be regarded as insignificant contrary to what the averages indicate. This can be attributed to the large variance in the measured concentrations in the experiment with the lower dosage, where one reactor reached only 50% removal and one reactor removed over 90% of the contaminant, resulting in a large standard deviation. ANOVA comparisons for the data after 4 days and 1 day resulted in p values of $\boldsymbol{p = 0.0422}$ and $\boldsymbol{p = 1.924 * 10^{-5}}$ respectively. Since $\boldsymbol{p < 0.05}$ in these cases it can be concluded that a higher dosage performs significantly better.

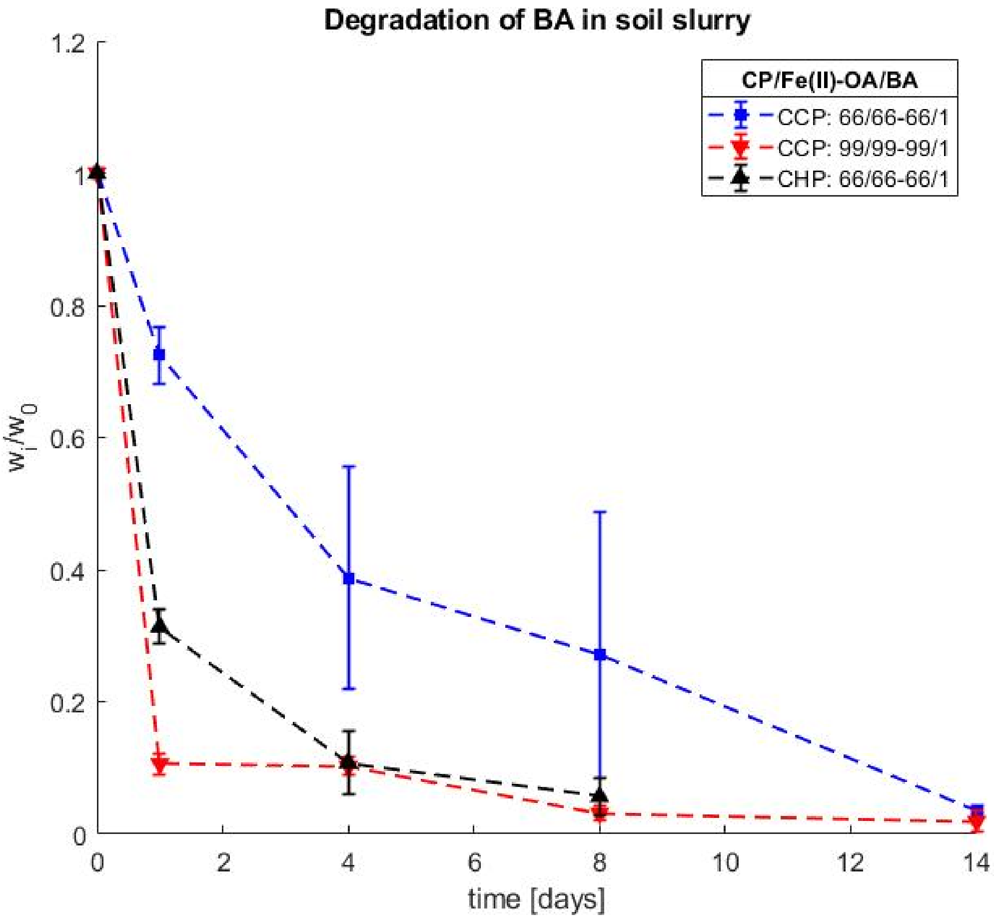


Figure 5.5: Results of the first round of batch experiments using BA as contaminant, $[BA]_0 = 10\,mg\,kg^{-1}$ of soil.

The CHP experiment was stopped after 8 days due to the expectation that the oxidation process had stopped at this point. In Table 5.1 the average HP concentrations in the liquid phase are presented. In the first CCP experiment there was no HP detected in any of the measurements indicating immediate catalysis or reaction of HP as soon at is formed. In the second experiment HP was detected only after 1 day reaction time, indicating the dissolution of CP to HP was larger than in the first experiment and larger than the rate at which the HP was consumed through either catalysis or scavenging reactions. In addition, the rate of BA removal for this experiment decreased significantly after the 4 day measurement. This might be a result of the large amount of HP released from the CP: in the early stages of the reaction it was catalyzed into ROS and BA was degraded. As the BA concentration decreased, however, the HP formed is less likely to react with BA and more likely to participate in scavenging reactions such as HP decomposition and oxidation of OA [47]. Moreover, this is also a possible explanation of why the higher CP dosage does not necessarily result in a higher removal of BA and the use of a lower dosage might be more desirable.

For the CHP experiment the HP measurement gave a direct measure of the amount of oxidant left in the system. After 1 day, 4 and 8 days of reaction time 62.7%, 82.8% and 94.3% of the HP had reacted respectively. This indicated that the HP was not consumed in its entirety after 8 days. It was assumed the low concentration of HP would not significantly increase the BA degradation after the point of 8 days. From the plot it became evident that the removal after 1 day was significantly higher compared to the 66/66-66/1 CCP and not as high as the 99/99-99/1 ratio of CCP. However, after this point the reaction appeared to proceed slower than the 66/66-66/1 CCP indicating a depletion of oxidant as was also shown in Table 5.1. The CHP experiment used the same concentration of oxidant as the highest dosage of CP, 15.3 mM of HP compared to 15.3 mM CP. These two dosages appeared to degrade the BA to a similar degree after the 8 day mark: 95% and 97% for CHP and CCP respectively. However, the HP yield from the CP is 0.47g HP/g CP as established in literature, meaning that the molar conversion of CP to HP is not equal to 100% [12,22]. This indicates that the oxidation process is more efficient in the CCP experiments compared to the CHP. An explanation can be found in the availability of the oxidant in the case where HP is directly added compared to where CP is added. By directly adding HP the contribution of scavenging reactions and HP decomposition is larger compared to the case where HP is slowly released from CP which is shown to have greater degradation in the case of a single addition [18].

Table 5.1: Average HP concentrations in the liquid phase, cells with '-' indicate that no HP was detected and the concentration is hence <0.01 mM

Reaction time (days)	66/66-66/1 CCP	99/99-99/1 CCP	99/99-99/1 CHP
0	-	-	-
1	-	0.1 mM	5.71 mM
4	-	-	2.63 mM
8	-	-	0.87 mM
14	-	-	N.A.

In order to further investigate the efficiency of oxidation of BA in the soil slurry, the amounts of oxidant (HP) consumed (in moles) in order to oxidize one mole of BA were calculated. The initial amount of BA was 0.2 mg or 0.0016 mmol, therefore the amount of BA removed was calculated by multiplying the starting amount with the final $\frac{w_i}{w_0}$ value, Equation 5.1.

$$\mathrm{BA_{oxidized}(mmol)} = \mathrm{BA}_{start}\mathrm{(mmol)} * \frac{w_{end}}{w_0} \tag{5.1}$$

Next, the theoretical maximum amount of HP available was calculated. Since the CP peroxide used consisted for 65% of actual CaO_2 and for 35% of $Ca(OH)_2$, the actual amount of CP powder used in the batch reactors needed to first be multiplied by 0.65.

In addition, not all of the CaO_2 was transformed in HP, therefore a yield% value from the literature was assumed at the respective pH: the HP yield (in moles) from actual CP is 74% at a pH of 7 [12]. Combining the two numbers determining the HP from the amount of 65% CP powder used Equation 5.2 is obtained. First, the amount of CP powder was converted into the amount actual CaO_2 in mmol. Lastly, the assumed amount of HP in mmol was calculated using the molar yield value from the published data. These calculations were performed under the assumption that all of the CP is dissociated into HP at the end of the 14 days reaction time [12, 22].

$$\text{HP(mmol)} = \frac{\text{CP(mg)} * \mathbf{0.65}}{\mathbf{72.076}} * \mathbf{0.74} \tag{5.2}$$

The efficiencies are given in Table 5.2. As was expected, the efficiency of CCP was better compared to CHP: using equal concentration of oxidant, the efficiency for CCP was around half of that of CHP. However, it should be noted that the oxidant concentration was high compared to the contaminant, causing scavenging reactions to play an important role during the oxidation processes. Using multiple addition of oxidant or continuous addition might be more effective in both cases. An additional comparison can be performed using lower dosages where the degradation will not come close to complete degradation. This would allow for more accurate quantification of the oxidant efficiency between CHP and CCP since the contaminant will be depleted at a slower rate compared to the higher ratios used in these experiments.

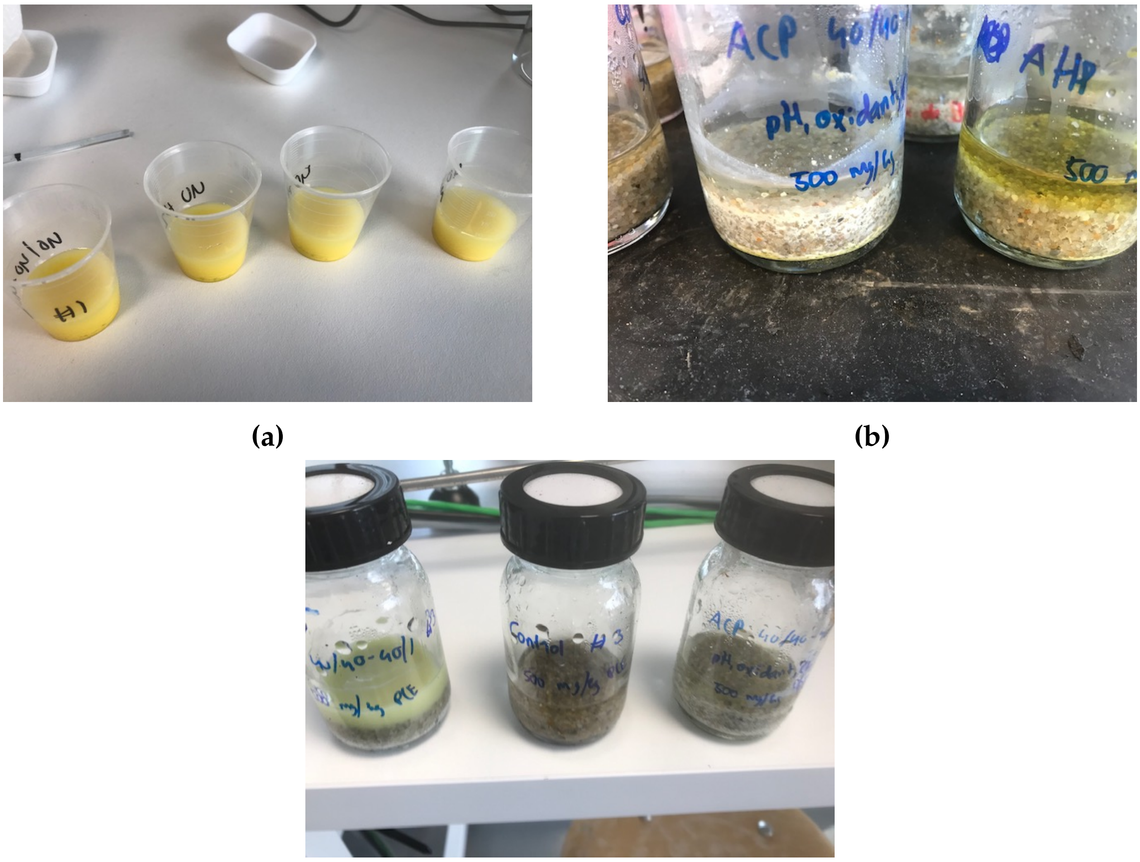
Table 5.2: Oxidant efficiency for the degradation of BA in a soil slurry.

Experiment	HP yield (mmol)	BA removal (mmol)	Efficiency ($\frac{\text{mol HP}}{\text{mol BA}}$)
CCP (66/66-66/1)	$4.92*\mathbf{10^{-2}}$	$1.54*\mathbf{10^{-3}}$	31.93
CCP (99/99-99/1)	$7.38*\mathbf{10^{-2}}$	$1.56*\mathbf{10^{-3}}$	47.31
CHP (99/99-99/1)	$15.3*\mathbf{10^{-2}}$	$1.52*\mathbf{10^{-3}}$	100.66

5.4 II-B: Soil slurry experiments with PCE contamination

In this stage the source of contamination was changed from BA to PCE. The experiments consisted of two batch tests, the conditions and operating parameters that were used are given in Table 4.6. The results from both tests will be presented and discussed separately.

The catalyst and OA were added to the separate buffer made from drinking water in the first round. In Figure 5.6a, the chelated Fe(II) in the buffer solution is illustrated, which had a strong yellow colour and was turbid, likely due to the increased concentration of OA and Fe(II) compared to the previous experiments. Figure 5.6b and Figure 5.6c show the contents of the reactor directly after oxidant addition and after 28 days of reaction time respectively. As can be seen, the CHP system remained yellow of colour after addition of the oxidant while the CCP system consist mostly of white precipitation and a colourless aqueous phase. After the reaction was stopped, the CHP system consists of a milky yellowish solution, while the CCP system consisted of a clear dark yellowish aqueous phase with a white precipitation in the soil phase indicating again precipitated $Ca(OH)_2$. After the reactions were quenched by placing them in ice, 2 replica's of each reactor were shipped off for analysis on their PCE content, while the 3^{rd} replica was used to measure any residual oxidant, the pH and the Cl^- content of the aqueous phase.



(a) **(b)**

(c)

Figure 5.6: Illustrations of reagents and reaction mixtures **(a)**: Chelated Fe(II) **(b)**: CCP (left) and HCP (right) reaction mixture **(c)**: Left to right: CHP, control and CCP reaction mixtures after 28 days.

The theoretical amount of PCE in each reactor was 16.4 mg when taking a soil phase contamination of $510\,mg\,kg^{-1}$ and assuming a groundwater PCE concentration of $150\,mg\,L^{-1}$. However, due to the high volatility of PCE (see Figure 4.1.1) volatilizing of the contaminant in the headspace was expected to influence the results [2,3]. Table 5.3 lists the results obtained for the first round of experiments.

Table 5.3: Results for reactors #1 - #3. The amount of PCE and Cl^- denote the average amounts for each reactor. The pH of the buffer was 7.10 with a strength of 0.25 M.

Reactor	PCE (mg)	TCE (mg)	Cl^- (mg)	pH final
Control	6.2	0.0495	1.09	7.11
CCP	1.45	$<5*10^{-4}$	12.05	3.31
CHP	1.845	$<5*10^{-4}$	5.71	1.68

Results for the control reactors showed and average amount of PCE of 6.2 mg per reactor, indicating that approximately 62% of the PCE was volatilized over the course of the experiment. The amount of PCE in the control reactors were taken as baseline concentrations for the the other reactors. The amount of TCE found in the reactors was small for the control while the TCE content for the CCP and CHP reactors were below the detection limit of <0.5 µg. The effectiveness of CCP and CHP was compared by comparing the PCE removal and extend of mineralization, illustrated in Figure 5.7.

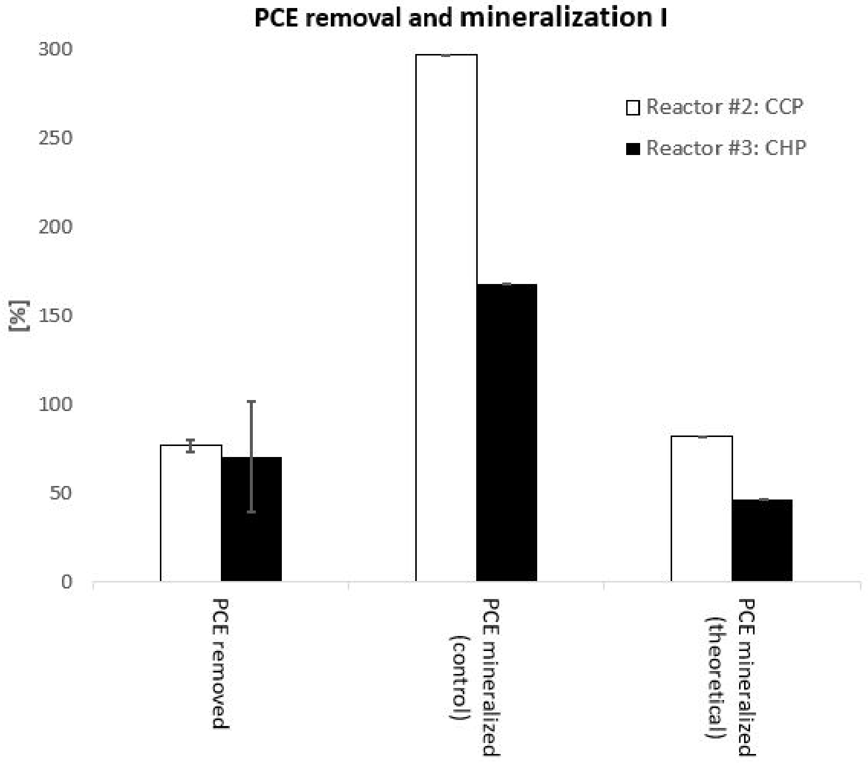


Figure 5.7: Results for the first round of batch experiments. The amount of PCE removed and the amount of PCE mineralized in relation to the control (reactor #1), or the theoretical amount of PCE, are given in percentage.

From Figure 5.7, the CCP reactor appeared to have degraded slightly more PCE than the CHP reactor: 77% compared to 70%, indicating a more efficient removal of PCE by CCP compared to CHP. However, the standard deviation in the case of CHP was significantly higher than in the case for CCP and the control reactors, using ANOVA results in $p = 0.80$, indicting the difference is not significant. Reason for this might be due to differences in volatilization of the contaminant during the experimental procedure which was shown to have a large impact on the result when looking at the control reactors. Additionally, the pH significantly dropped to acidic pH indicating the buffer capacity was not strong enough to maintain neutral pH. The measured pH values were 3.31 and 1.68 for CCP and CHP respectively, the slightly higher pH in the case of CCP can be attributed to the release of $Ca(OH)_2$. In general, the acidic pH would increase the effectiveness of both CCP and CHP systems by increased Fe(II) availability and less decomposition of HP [12, 39]. Moreover, the amount of HP released from CP increases with decreasing pH indicating increasing ROS generation and consequently more effective degradation of PCE [12, 22, 50]. It has also been shown that the addition of organic acids, including CiAc and OA, increases the stability of HP at neutral pH, these effects are potentially less noticeable at acid pH due to higher HP stability [49]. In this case, addition of the OA can also cause decrease in degradation efficiency. The lower pH indicated that the addition of the CA would not increase the Fe(II) availability by any significant amount. Moreover, the OA itself could still compete with PCE of the ROS generated in the system effectively acting as a ROS scavenger due to an excess of OA used (40/1 excess) despite the reaction rate of OA with HO· being significantly lower than the reaction rate between HO· and PCE (3.8*10^6 and 2.6*10^9 M^-1s^-1 respectively).

For the degree of mineralization it was assumed that all of the PCE that was removed from the system was completely degraded and no intermediate degradation products are present resulting in 4 moles of Cl^- from each mole of PCE degraded. From Figure 5.7, it became evident that the amount of PCE that was vapourized in the 3^{rd} replica of the batch reactors was less compared to the 1^{st} and 2^{nd} replicas. The degree of complete mineralization corresponded to 297% and 168% of the amount of PCE present in the control reactors for CCP and CHP respectively. Taking the amount of PCE that was initially added to the reactor and assuming again a PCE concentration in the groundwater of $150\,mg\,L^{-1}$ the degree of mineralization were 82% and 46% for CCP and CHP respectively. The values obtained in the second case correspond to the amount of PCE removed from the reactors as illustrated Figure 5.7 and to the results obtained by Jiang et al. [20]. The actual amounts of complete mineralization could potentially be higher than the measurement suggested. From Table 2.3, it can be seen that the second order rate constant for Cl^- with HO· is 4.3*10^9. This reaction rate is slightly higher than the second order rate of PCE with HO·: 2.6*10^9. Therefore the presence of Cl^- can scavenge the HO· radicals and at the same time decrease the amount of Cl^- in the system.

The oxidant efficiencies were calculated in identical fashion as for the BA batch tests. However, due to the lower pH Equation 5.2 was slightly modified resulting in Equation 5.3 where the amount of HP yield from CaO_2 was changed from 74% to 82% [12].

$$\mathrm{HP(mmol)} = \frac{\mathrm{CP(mg)} * 0.65}{72.076} * 0.82 \tag{5.3}$$

For CCP and CHP the oxidant efficiencies were 113 mol HP / mol PCE and 138 mol HP / mol PCE respectively. Compared to the values given in Table 5.2, the oxidant efficiency in the case of PCE was significantly lower compared to BA despite a lower oxidant/contaminant ratio and lower degree of contaminant destruction. This was in line with the expectation, the presence of contaminants forming DNAPL phases increases the total oxidant demand [26].

In the second round of PCE batch experiments, the buffer strength was increased in order to maintain a near neutral pH. This was achieved by creating the phosphate buffer directly in the groundwater and increasing the buffer strength. As can be seen, the aqueous phase is a clear yellow solution. However, not all of the Fe(II) was dissolved before addition. This could be explained by the fact that OA is shown to form complexes with Fe(II) in stoichiometry of 3 to 1, $[\mathrm{Fe(II)}(C_2H_2O_4)_3)]^{2+}$ [39].

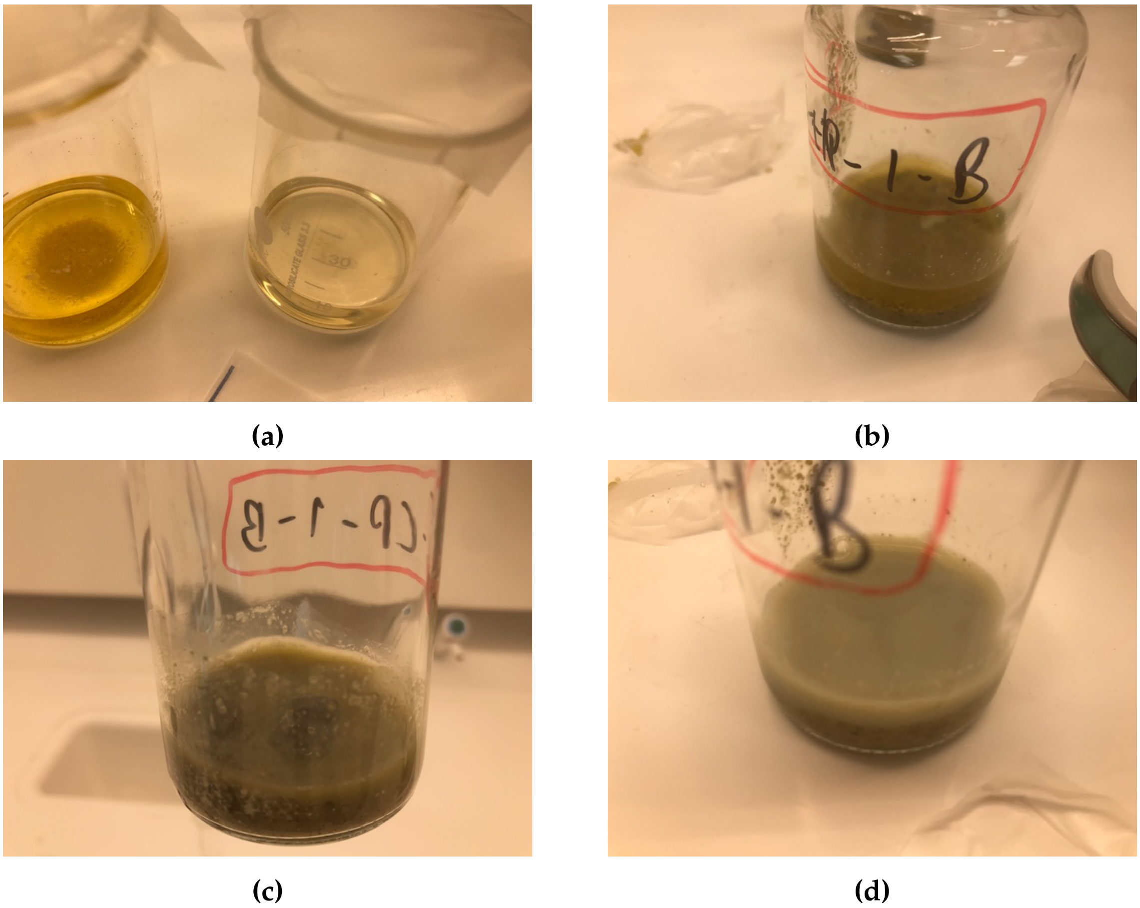
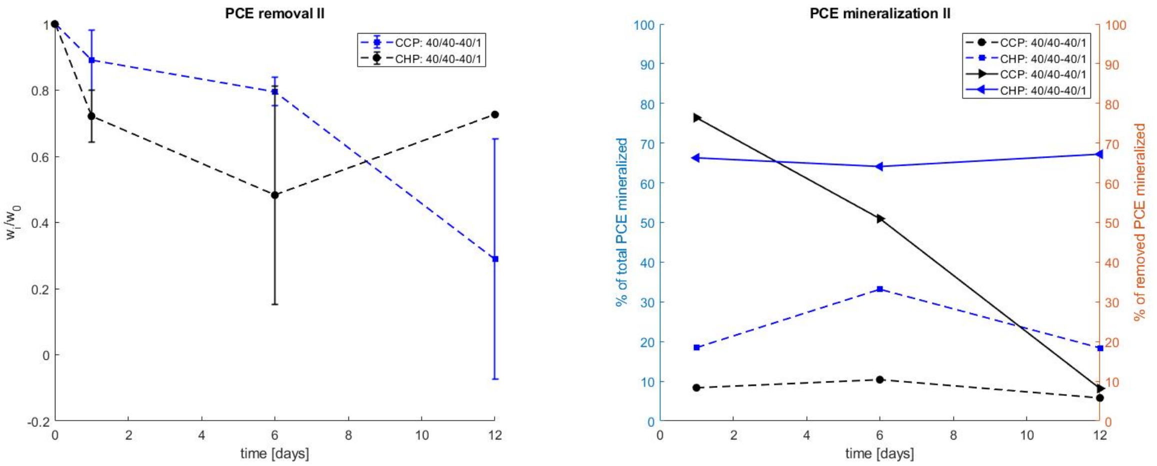

(a)
(b)
(c)
(d)

Figure 5.8: Second round of PCE batch test. **(a)**: Chelated Fe(II) in GW (left) and GW buffer **(b)**: soil and catalyst mixture **(c)**: mixture after CP addition **(d)**: mixture after HP addition.

The results for the second round of PCE batch experiments are presented in Figure 5.9.



(a) **(b)**

Figure 5.9: Results form the second round of PCE batch experiments showing **(a)** the % of PCE removed compared to the control and **(b)** the % of PCE mineralized (dotted line = left axis, solid line = right axis) . Both plots are based on the control. Average PCE in control $= \mathbf{10.05 \pm 1.34}$ grams. The system ratio is 20/20-20/1 for both CHP and CCP.

During this round, the PCE removal for the two systems were determined at different time intervals over a period of 28 days. The goal of this sampling strategy was to investigate the difference in oxidant efficiency between adding liquid directly or adding CP as a slow HP releasing compound similar to what is discussed in section 5.3.

From Figure 5.9a it can be seen that the amount of PCE gradually decreases over time. Initially, the CHP system degraded the PCE at a faster rate than the CCP system. After 1 day, the PCE content in the CCP reactors decreased with 11% compared to a decrease of 28% in the CHP reactor. The CHP system removed 52% of the PCE after 6 days, while after 12 days the amount of PCE removed is 27%. However, the standard deviation of the 6 day measurement is relatively large compared to the measurements of the CHP system. The CCP system showed 20% PCE removal after 6 days and 71% after 12 days, indicating a larger PCE removal after 12 days compared to the CHP system. Again, however, the standard deviation for this measurement was large. The large deviations in the measurements can be attributed to the volatalization of PCE. The experimental procedure was performed in the exact same fashion for each of the reactors trying to minimize the exposure of the PCE to air. This was achieved by adding the aqueous phase as quickly as possible. One factor that might have affected the soil contamination with PCE is the particle size of the Kærgård soil. The bigger particle size reduced the surface area of the soil and consequently reduces the area where the pure PCE that was added to soil can absorb to.

In Figure 5.9b, the percentage of PCE mineralized are given. The percentage of the removed PCE that was mineralized is given on the axis to the right of the figure. This value appears to be constant for the CHP system at 66% at 1 day and 67% at 12

days. For CCP, there is a significant decrease in the amount of PCE that is completely mineralized. After 1 day, 76% of the removed PCE was mineralized, after 6 days this percentage was found to be 51% and after 12 days only 8% of the removed PCE was completely mineralized. This could be a result of the deviation between the PCE content in the reactor itself, which can vary significantly as is seen by the standard deviations in Figure 5.9a and Figure 5.7. This large standard deviation can potentially be caused by the difference in organic contents of the soil (section 8.4), where B3312 soil was used in preparation for part of the day 6 and day 12 reactors, increasing the total oxidant demand for these reactors.
However, as expected due to a lower oxidant and catalyst dosage the amount of PCE mineralized is less compared to the previous experiment. The lower amount of full mineralization also implies a higher concentration of reaction intermediates present in the reactor.

During this round of experiments, the buffer strength was increased significantly in order to maintain a neutral pH. The pH measurements are given in Table 5.4. This round, the pH is near neutral for all of the reactors. As was seen in previous round, the pH is slightly higher for CCP due to formation of $Ca(OH)_2$. Due to the near neutral pH, Equation 5.2 is used in the calculation of the oxidant efficiencies for the CCP systems of which the results are documented in Table 5.4.

Reactor	pH	Oxidant efficiency (mmol HP/ mmol PCE)
Control	7.10	-
CCP 1 day	6.51	-
CHP 1 day	6.10	-
CCP 6 days	6.72	-
CHP 6 days	6.14	-
CCP 12 days	6.64	13.43
CHP 12 days	6.34	72.36

Table 5.4: Measured pH values and calculated oxidant efficiencies

The oxidant efficiency was calculated for the final measured PCE removal after 12 days. For CHP the oxidant efficiency was 72.36 mmol HP/ mmol PCE. CCP had an oxidation efficiency of 13.43 mmol HP/mmol PCE, indicating a larger oxidant efficiency when the HP is added to the system in the form of CP powder compared to direct addition of liquid HP.

5.5 III: Continuously operated column studies

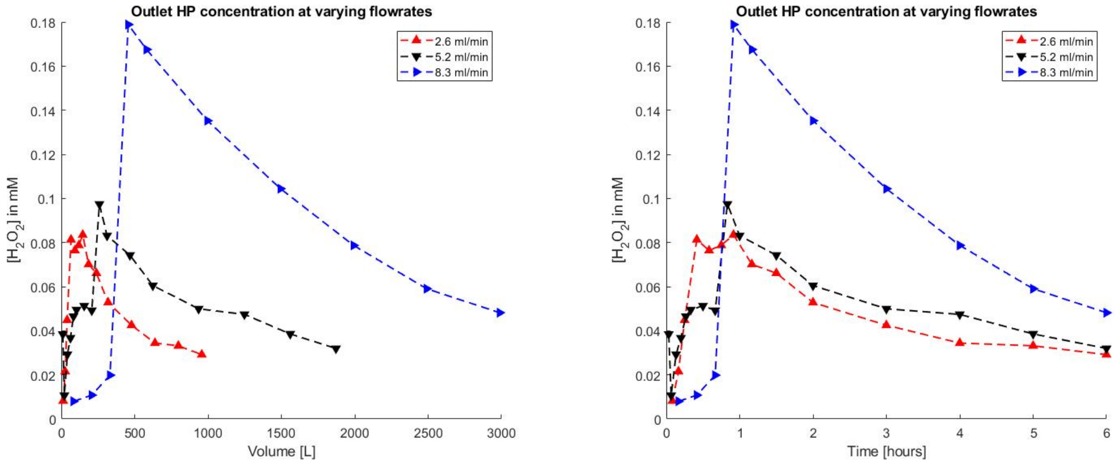
The column studies were performed in two stages. The first stage was the investigation of the CP dissolution into HP in continuously operated column studies. The effects of temperature, pH and flowrate were investigated. In stage III-B, BA was degraded using the same set-up.

5.5.1 III-A: Oxidant delivery and CP dissolution

The column was operated by pumping drinking water or buffer solution through the column from top to bottom. The oxidant was added to the top of the packed bed. After addition, the CP distributed itself over the top layer of the packed bed and remained there over the course of the entire experiments. This is illustrated in Figure 5.10 where the pores in the packed bed contain a white powder similar to the powder added to the column. Preliminary experiments performed showed clogging of the filter in the outlet of the column when the packed bed height was 5 cm. Therefore, it is indicated that the CP powder distributes further down than 5 cm and the minimum packed bed height used in the experiments was 9.5 cm to avoid clogging of the filter.

Figure 5.10: CP distribution in the soil packed bed.

The first three runs were performed with 0.15 g of CP and 50 g of sand in the column resulting in a bed height of 17.5 cm. This resulted in a pore volume of 13.33 mL. The flowrates used in the experiments were 2.6 mL min^{-1},5.2 mL min^{-1} and 8.3 mL min^{-1} resulting in retention times of 5.12 min, 2.56 min and 1.61 min respectively. Drinking water that did not contain any buffer capacity was used as the feed solution. The experiments lasted 6 hours. Figure 5.11a and Figure 5.11b presents the results obtained for the first 3 column runs.



(a) **(b)**

Figure 5.11: Measured HP concentration in outlet versus **(a)**: volume pumped through column **(b)**: time. $CP_0 = 2\,\text{mmol}$.

The general shape of the graphs obtained were similar. The HP concentration was low initially, as would be expected, and reached a maximum point, after which the concentration decreases gradually. This shape was in line with the expectation based on literature where the CP dissolution takes up to several days [12,22,50]. Therefore it can be expected that time required to fully deplete the CP in the column studies would also be in the range of around 6 days. This is confirmed by the observation that the slope of the graphs is decreasing as time is progressing beyond the 1 hour mark.

From Figure 5.11a it was seen that the highest HP concentration was reached at a higher volume pumped through the column when the flowrate was increased. This was expected because of the lower retention time at higher flowrates. From Figure 5.11b however, it can be seen that the flowrate had little influence on the rate of CP dissolution and the maximum HP concentration was reached at the same time point for each of the three flowrates investigated.

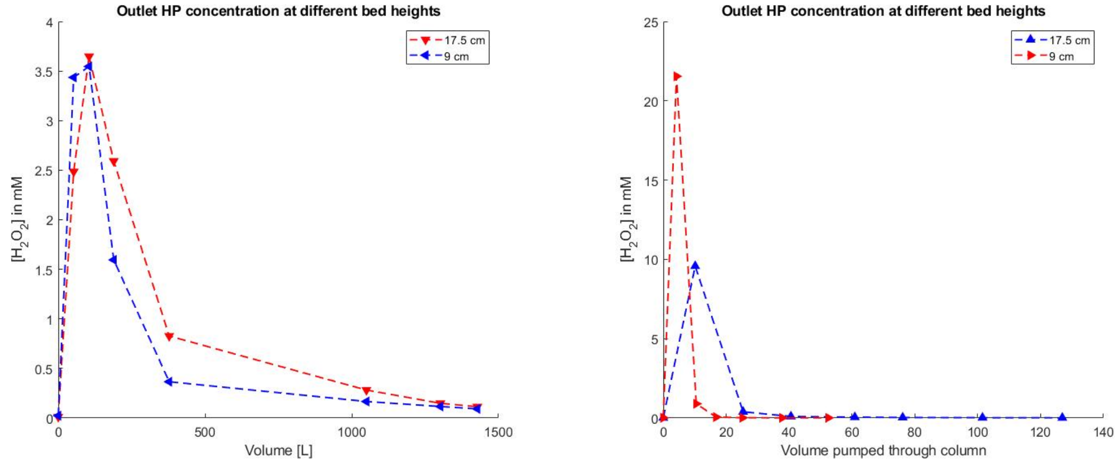
For the higher flowrates, the HP concentrations appeared to be higher compared to the lower flowrates. This observation was possibly caused by the decreased retention time of the HP at higher flowrates. This was in line with results obtained by Baciocchi et al. where a decrease in HP concentration was observed when the retention time increased as a result of an increase in bed height in the column. HP dissociation increased with increasing retention times [51]. During the experiments the pH of the outlet was measured at specific time intervals ranging over the full reaction time, the results are documented in Table 5.5.

Table 5.5: Measured pH values of the column outlet at different time points. The average pH at $t = 0$ was 9.13.

Experiment	**pH** (10 min)	**pH** (1 hour)	**pH** (3 hours)	**pH** (6 hours)
2.6 mL min^{-1}	11.64	11.20	11	10.70
5.2 mL min^{-1}	11.98	11.19	10.89	10.58
8.3 mL min^{-1}	11.80	11.41	11.02	10.70

The pH increased significantly in the beginning of the experiment. This can be attributed to the fast dissolution of the $Ca(OH)_2$ present in the added CP powder which makes up 35w% of the powder and has been shown to increase the pH upon formation and dissolution [12, 22, 50]. Over time, the pH seemed to gradually decrease. This was expected since the amount of HP formed decreases over time. From Equation 2.1 it follows that the amount of $Ca(OH)_2$ formed decreases in identical amounts causing a decrease in the pH. The pH is not significantly influenced by the flowrate.

The next runs were performed at two different bed heights: 17.5 cm and 9.5 cm with pore volumes of 13.33 mL and 6.67 mL respectively. The flowrate was set to 2.1 mL min^{-1} for each of the runs resulting in retention times of 6.35 min (17.5 cm) and 3.17 min (9.5 cm). The feed solution consisted of a 0.025 M phosphate buffer made in drinking water (pH of 7.15). A comparison was made between direct addition of HP and CP in order to see the difference between the lifetime of the oxidant in continuously operated column studies. Figure 5.12a and Figure 5.12b present the results obtained during these runs.



(a) **(b)**

Figure 5.12: Measured HP concentration in outlet at different bed heights for **(a)**: CP addition and **(b)**: direct HP addition.

From Figure 5.12a it can be observed that the influence of bed height was minimal when looking at the maximum concentration of HP measured at the outlet when CP was added to the column. However, after the 1 hour mark the difference between the heights was larger. The concentration for the higher bed height appeared to be higher compared to the lower bed height. This did not confirm the expectation. It was expected that the lower bed height would have a higher concentration at the outlet because the retention time in this case was shorter compared to a higher bed height. As a result, more HP decomposition was expected. In the case of direct HP addition, the maximum concentration was higher, a maximum of 22 mM compared to a 3.6 mM maximum. Additionally, the maximum concentration of HP measured was 22 mM in the case of the lower bed height compared to 9.5 mM in the case of the higher bed height. This was in line with the expectation and with the literature [51]. The first factor that might influence this decrease the concentration is again the decomposition rate of the HP due to a longer retention time in case of the higher bed height. The second factor could be diffusion of the HP in vertical direction: the diffusion will be larger when operating with a bed height of 17.5 cm compared to 9.5 cm.

In Table 5.6 the measured pH of the outlet is measured. Due to limited reaction time in the case of HP, only 1 pH measurement has been documented.

Table 5.6: Measured pH values of the column outlet at different time points. The average pH at $t = 0$ was 7.30.

Experiment	**pH** (30 min)	**pH** (1.5 hours)	**pH** (3 hours)	**pH** (8 hours)
CP 9 cm	7.8	7.49	7.36	7.34
CP 17.5 cm	7.8	7.44	7.33	7.31
HP 9 cm	7.33	-	-	-
HP 17.5 cm	7.31	-	-	-

The pH and buffer capacity of the feed solution influenced the HP formation significantly, the maximum concentration in the case of non-buffered feed solution was found to be 0.18 mM compared to a maximum concentration of 3.6 mM in the case of a buffered feed solution at neutral pH. This has been observed and illustrated in published literature and previous research, where the rate of HP formation from CP decreased with increasing pH up to a point where the HP formation is negligible (pH > 12) [12, 22]. Moreover, addition of phosphate to HP systems has been proven to stabilize HP in both aqueous and soil studies increasing the HP lifetime [51]. Therefore, the phosphate buffer might have had a stabilizing effect on the HP in both direct HP addition and in the CP addition.

$$2CaO_2 + 2H_2O \rightarrow 2Ca(OH)_2(s) + O_2(g) \tag{5.4}$$

At increased pH, the formation of oxygen, shown in Equation 5.4, is more dominant than the formation of HP. The increased oxygen formation was observed during the experiment through the continuous formation, migration and disappearing of bubbles in the bed and in the aqueous phase on top of the bed, Figure 5.13 shows an illustration of these bubbles captured on camera. At neutral pH the formation of bubbles was observed to a lesser extent. However, CP is not the only source of oxygen in this system since oxygen is one of the reaction products in the decomposition of HP, Equation 2.3.

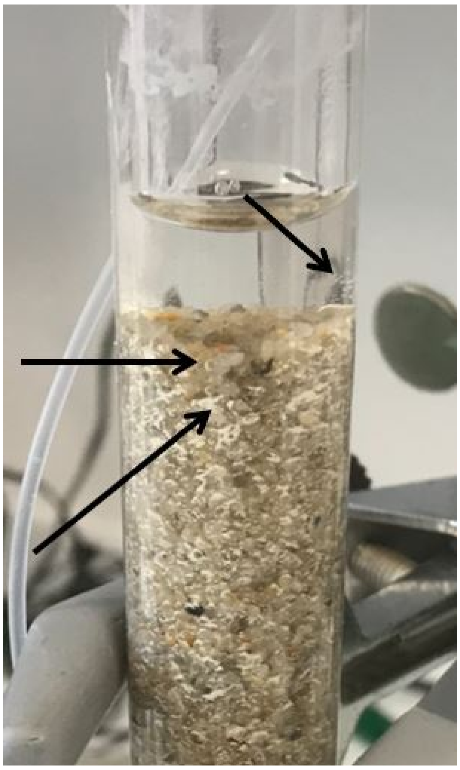
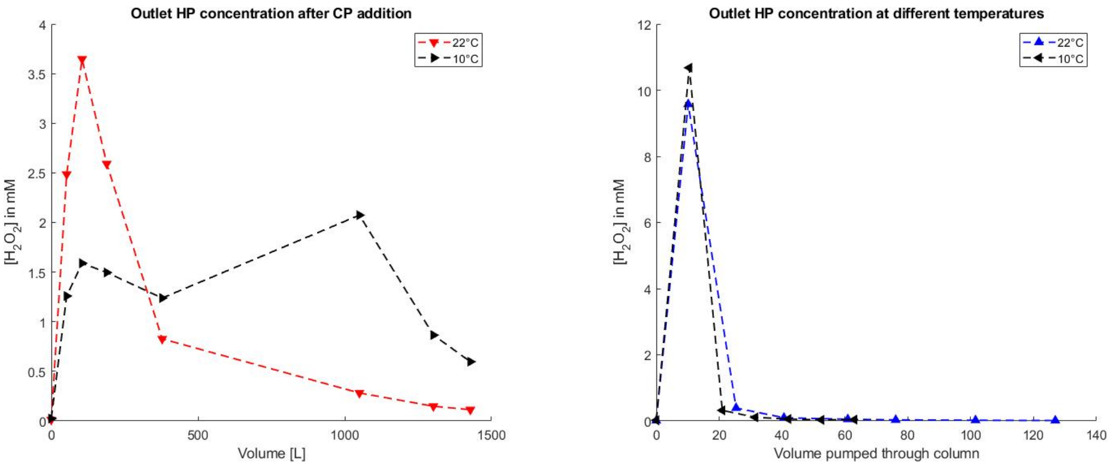


Figure 5.13: Bubble formation during the CP dissolution column studies at pH > 10. Arrows indicating the bubbles mentioned.

The last factor investigated was the temperature. The previous runs were operated at room temperature (22 °C). For both CP and direct HP addition the temperature was decreased to around 10 °C in order to simulate the subsurface temperature conditions. This was achieved by refrigerating the buffer solution to 7 °C, placing the feed solution inside a cooling bag packed with a frozen ice pack. After every hour, the feed solution was filled up with refrigerated buffer solution of 7 °C. The temperature of the feed solution was monitored with a thermometer. The flowrate was 2.1 mL min^{-1} and the bed height was 17.5 cm, resulting in a retention time of 6.35 min, the operating time was 8 hours for CP addition and 30 minutes for direct HP addition. The results are presented in Figure 5.14.



(a) **(b)**

Figure 5.14: Measured HP concentration in outlet at different temperatures for **(a)**: CP addition and **(b)**: direct HP addition.

Figure 5.14b shows the results for the direct HP addition. The maximum measured HP concentration was 10.6 mM at lower temperature compared to 9.6 mM at room temperature. This difference cannot be considered significant without repeating the measurements and obtaining an average and standard deviation for both cases.

In the case of CP addition, however, the difference was more significant. The maximum concentration measured was significantly higher at room temperature than at the lower temperature. but the decrease in HP concentration over time was lower. Therefore, the total amount of HP formed during the experiment operated at 10 °C was larger compared to the experiment performed at room temperature. This was in line with the expectation, literature has shown that the amount of HP formed from CP dissolution is larger for lower temperatures [22, 50].

Table 5.7: Measured pH values of the column outlet at different time points. The average pH at $t = 0$ was 7.30.

Experiment	**pH** (30 min)	**pH** (1.5 hours)	**pH** (3 hours)	**pH** (8 hours)
CP 10 °C	10.30	7.76	7.50	7.33
CP 22 °C	7.8	7.44	7.33	7.31

The lower maximum concentration can be attributed to the pH, the measurements of which are given in Table 5.7. The pH in the start of the experiment quickly increased, indicating that the amount of Ca(OH)$_2$ that was dissolved increased the pH by a significant amount. This indicated that the CP dissolution rate was faster at the lower temperature, however the increased pH might hinder the CP dissolution as has been shown in literature [12, 22, 50]. As the rate of CP dissolution slowed down, the pH decreased and after 8 hours of reaction time the pH was almost equal to the pH of the buffer solution. This explanation could be tested by repeating both experiments using a stronger buffer solution in order to keep the pH in near neutral range (pH < 7.5).

5.5.2 III-B: Degradation of BA in continuously operated column

In this experiment, 50 grams of model soil was contaminated with 0.15 mmol (18.32 mg) of BA. In 250 mL buffer solution (0.25 M), 3 mmol of OA and Fe(II) is dissolved. After full addition, this results in a system ratio of 20/20-20/1. A control experiment was performed where no oxidant or catalyst was added. A flowrate of 5 mL min^{-1} was used resulting in a 2.67 min retention time. The results for this experiment are presented in Figure 5.15.

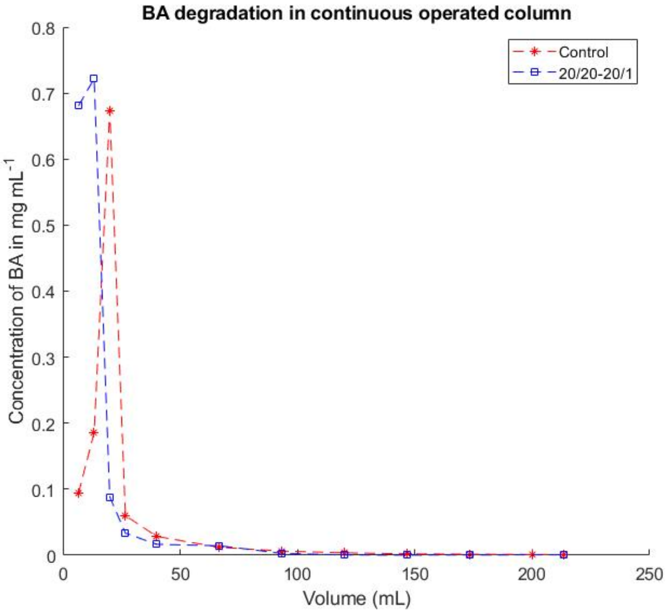


Figure 5.15: Results from the continuous degradation of BA in a soil packed column.

As can be seen from Figure 5.15, the concentration of BA increased significantly in the beginning of the experiment, reaching a maximum concentration of 0.72 mg mL^{-1} after pumping 1 pore volume (13.33 mL) through the column. For the control, this highest point was reached at 1.5 pore volumes. This difference is explained through an inconsistency in the experimental procedure where a technical difficulty in the column inlet caused there to be a delay in pumping. After this initial peak the concentration decreases drastically in both cases. When oxidant was added the concentration appeared to be slightly lower, but no significant difference was observed. This can be explained through the CP dissolution curves given in Figure 5.12a, where the amount of HP released reached a maximum after 50 minutes and the HP concentration in the first 5 minutes was almost negligible. In this experiment, the majority of the contaminant was flushed out of the column within this time and the BA concentration was negligible at the 50 minute mark.

It can be concluded that this method was not suitable for the determination of the degradation capacity of CP in continuous operated column studies. A better approach would be to perform the experiment in similar way to Sørensen [22]: mix the contaminant with the catalyst and CA and pump the solution through the column which contains CP packed soil. The BA concentration can be measured at the outlet. Another solution could be to contaminate the soil a high concentration of PCE to assure the formation of DNAPLs [51]. This way the CP could be added and the catalyst and CA can be pumped through the column as was performed in this experiment. The PCE dissolution rate and the solubility is most likely small enough to assure degradation of PCE occurs in the aqueous phase. Moreover, a slower flowrate should be used in order to limit the amount of contaminant that is flushed out of the column without reacting.

5.6 Summary and implications for CCP technology development

It has been shown that addition of CAs increases the HO· formation. A method was developed that was able to successfully quantify the radicals through the hydroxylation of BA to p-HBA. This method can be useful in future research not only on CCP systems but on other oxidation systems as well.

BA was successfully degraded with both CiAc and OA. OA appeared to degrade BA slightly more effective, but both of the CAs tested are viable for further development of this technology. The optimal ratio between CP/Fe(II)-OA was 1/1-1. Using this ratio and total dosage of 99/99-99/1, 97% of the BA was degraded in an aqueous system made with drinking water. In soil systems, 98% of BA was removed using a 66/66-66/1 ratio, indicating effective oxidation of water soluble organic contaminants by using CCP. The efficiency of the oxidation was better in the CCP system compared to the CHP system, where 47.31 and 100.66 moles of HP was needed for the degradation of 1 mole BA for CCP and CHP systems respectively.

PCE was successfully degraded in soil systems as well. The initial contamination was higher compared to the experiments using BA, but 77% of the PCE was removed from the soil slurry with a system ratio of 40/40-40/1 at acidic pH. With a system ratio of 20/20-20/1 at neutral pH, 71% of the PCE was removed after 12 days of reaction. This indicates that CCP can be used for chlorinated solvent source-zone remediation with higher oxidant efficiency than CHP, a method that has been used for this purpose before [29]. The efficiencies for the CCP system and CHP system were respectively: 13.43 and 72.36 mole HP per mole PCE degraded. This indicates that potentially that the desired degree of contaminant remediation can be achieved with a lower oxidant dosage when CCP is used compared to CHP. Nevertheless, more testing should be performed with CCP where it is compared to a larger variety of AOPs.

The column studies showed a remarkable lifetime of HP, where after 8 hours of operating the column, HP was still measured in the column outlet. This increased oxidant lifetime can be beneficial when applying ISCO for the purpose of plume remediation. It is shown that CP will only spread through the soil before it settles in the pore space of the soil, after which it dissolves and releases HP. Addition of catalyst would allow for ROS generation which can successfully degrade contaminants that migrate through the soil. This has been previously been demonstrated by Sørensen in the degradation of MCPA and MCPP. However, the batch studies showed effective PCE removal in batch studies. This shows the potential to use CCP to reduce the effects of back diffusion, where after ISCO has been used in a chlorinated solvent source zone the PCE concentration in the groundwater starts to increase due to the DNAPL dissolution (section 2.3) [29]. However, more research needs to be carried out before any conclusive statements can be made about this proposed system.

6. Conclusions

The main aim of this thesis was to investigate different operating parameters and their influence on the performance of CP based chemical oxidation in the oxidation various organic contaminants in both aqueous and soil systems. The focus was placed on two limiting factors in CCP and ISCO: system pH and the presence of contaminants forming DNAPL in soil systems. During the experiments comparisons have been made with CHP.

How do chelating agents affect the hydroxyl radical production of analytical grade CP activated by (chelated) Fe(II)?
The effect of CA addition to aqueous CCP systems (pH = 7) was tested by monitoring the formation of p-HBA by the hydroxylation of BA. This method allowed for the quantification of the amount of $HO\cdot$ formed during the process. It was shown that addition of CAs increased the hydroxyl radical production in both neutral (pH = 7) and acidic (pH = 4) systems.

Which chelating agent results in the most optimal degradation of the model contaminant?
During these experiments BA was degraded in aqueous systems at neutral pH. Using a system ratio (CP/Fe(II)-CA/BA) of 66/66-66/1, two CAs were tested in the systems performance in the degradation of BA. Addition of OA and CiAc both resulted in 83% and 77% BA removal, indicating that OA was a slightly more effective chelating agent compared to CiAc and this CA was used in further experiments. However, the difference in performance is small meaning that CiAc is also an effective CA that could be considered in application of CCP.

What is the most optimal oxidant/Fe(II)-CA/contaminant ratio for the degradation of the model contaminant?
In the next set of experiments, the system ratio was varied by changing the oxidant and catalyst ratio while keeping the total dosage constant. It was shown that the 66/66-66/1 ratio was most effective in degradation of BA in aqueous systems at neutral pH. Increasing the dosage to 99/99-99/1 resulted in 96% removal after 30 minutes.

How does the oxidant dosage affect the remediation of a contaminated soil slurry?
During the experiments performed using BA contaminated soil systems, two systems ratio's were investigated: 66/66-66/1 and 99/99-99/1. Both ratio's were successful in removing large amounts of BA from the systems over a period of 14 days. However, the difference in final degradation of was not significant and the main difference in degradation performance was observed within the first 8 days of the reaction. This indicated that the lower dosage of 66/66-66/1 was more optimal in the degradation of

BA in this soil system.

How does the presence of DNAPLs affect the oxidant efficiency of CCP and CHP?
After BA was used as contaminant in soil system and was successfully degraded, PCE was introduced to the soil system. The concentration of contaminants was increased in order to ensure the formation of DNAPLs. After 28 days, 77% of the PCE was degraded using CCP, whereas in the CHP system 70% of the PCE was degraded. Additionally, analysis of chloride content showed 82% and 42% PCE mineralization for CCP and CHP respectively indicating more effective treatment of PCE contaminated soil over a period of 28 days using CCP.

What is the difference in oxidant efficiency between CCP and CHP systems?
For both BA and PCE soil systems, the oxidant efficiency was calculated for both the CCP and CHP systems. In general it was observed that CCP had a larger oxidant efficiency compared to CHP. This was attributed to the slow HP release by the CP which reduces the decomposition of HP and increases the effectiveness of the system.

How does a continuously operated soil packed column affect the HP release of CP and the remediation of contaminated soil using CCP?
Column studies were performed to investigate the HP dissolution form CP under various circumstances. Additionally, comparisons were made with direct HP addition. It was shown that flow rate had little effect on the dissolution rate of CP. The highest HP concentration measured at the outlet was measured after 55 minutes of starting the experiment in each case. As expected the pH of the feed solution had a significant impact on the HP formation from CP dissolution. Using an unbuffered feed solution resulted in an increase in pH reaching values near a pH of 12, while a buffered feed solution of pH 7 resulted in a significant increase in HP formation. At neutral pH the HP concentration were around 20 times higher compared to the HP concentrations measured at alkaline pH. Decreasing the temperature to 10 °C has shown to increase the the overall yield of HP. However, no increase in the maximum HP concentration was measured but rather a decrease. Instead, the HP concentration decreased at a slower rate at the lower temperature resulting in increased overall HP yield.

Overall it has been shown that CCP is a viable method for the removal of organic contaminants from aqueous and soil systems at neutral pH. Additionally, it has been shown that this method is capable of significantly reducing contaminant concentration in severely DNAPL PCE contaminated soils using one addition at acidic and near neutral pH. The oxidation was more efficient in the CCP systems compared to the CHP system.

7. Recommendations for future work

The potential for CCP to remediate contaminated soil and groundwater has been shown in previous work and has been expanded upon in this work. It was shown that DNAPL PCE contaminated soil was more effectively treated with CCP compared to CHP using one oxidant addition. However, there was still a significant amount of PCE left inside the contaminated soil. Therefore, the process should be optimized through finding the optimal oxidant dosage. Additionally, the use of multiple additions has proven to increase the effectiveness and efficiency of CCP systems. Combined with the results obtained during the PCE batch studies showing the oxidation potential of CCP systems using a single oxidant addition, it indicates that using multiple additions could potentially benefit the oxidation capacity of CCP systems in severely DNAPL PCE contaminated soils.

In this work, Fe(II) was used as the catalyst. However, Fe(III) has been shown to increase the superoxide radical generation through HP catalysis. In turn, the superoxide radical is a ROS that is linked to an increase in DNAPL dissolution in DNAPL contaminated soil systems [24]. Therefore, using a combination of Fe(II) and Fe(III) as catalyst could potentially improve the remediation of DNAPL PCE contaminated soils by enhancing the DNAPL dissolution rate.

Activated persulfate is also an effective technique and has been shown to effectively remediate DNAPL contaminated soil in combination with CHP not only in laboratory studies but in full scale treatment at the Kærgård plantation as well. It has been shown recently that the CP/persulfate dual oxidant system is an effective oxidation system [35]. Development of CP based oxidation systems could benefit from the development of this dual oxidant system due to the high performance of persulfate/CHP systems.

The column studies that were performed in this work were incomplete and should be supplemented in future work, stage III-C was not completed but is an important step in the technology development of CCP for use in ISCO. The designed degradation system was shown to be ineffective in the degradation of BA due to high solubility of the contaminant. However, this method has more potential when used with DNAPL PCE contaminated soil. PCE has a significantly lower solubility in water compared to BA, therefore decreasing dissolution rate into the aqueous phase and therefore retention time in the column.

For the CP dissolution column experiments, the difference between one addition and continuous addition (in the form of a slurry) should be investigated. Continuous addition could improve the amount of HP that can be obtained from the CP. Comparative studies can be performed with HP, where a diluted diluted HP solution is fed to the column.

In this work, 65% CP powder was used. It was attempted to use technical grade (approx. 50%), but attempts to find a supplier able to deliver technical grade CP have been unsuccessful. As was suggested in previous work, the technology development of CP based ISCO would benefit from laboratory studies using technical grade CP, which consists typically of 50% CaO_2 and 50% $Ca(OH)_2$ [12].

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8. Appendices

8.1 Appendix A: HP analysis calibration data

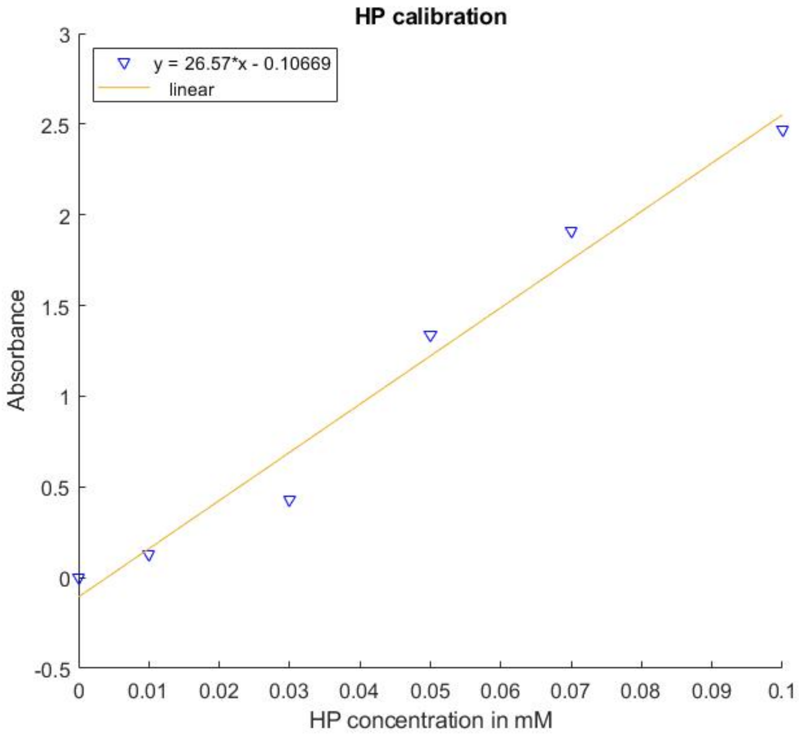

Figure 8.1: Calibration curve for HP measurements.

8.2 Appendix B: Model soil pore volume data

Table 8.1: Pore volume determination data. Average pore volume is 0.28 mL g^{-1}

grams of sand	Volume pumped (mL)	Pore volume per gram
10	2.8	0.28
12.5	3.3	0.27
30	8	0.29
37.5	11.9	0.32
51	13.6	0.267

/

8.3 Appendix C: Pump calibration

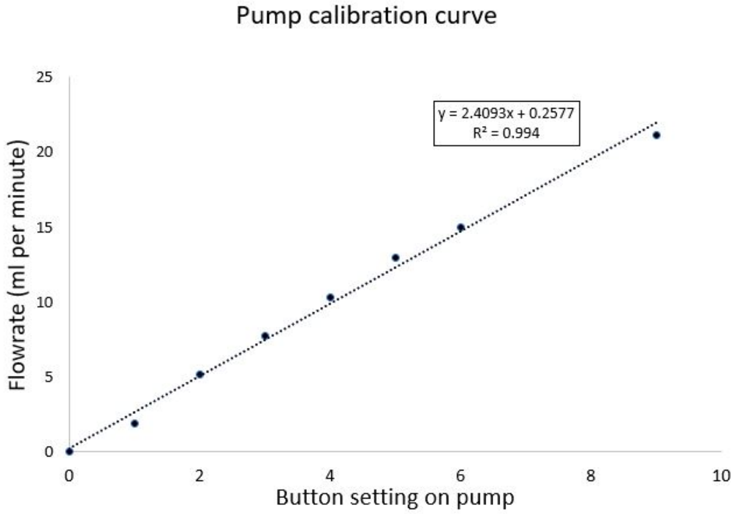

Figure 8.2: Calibration curve for the pump used in the column studies.

8.4 Appendix D: Kærgård plantation soil data

Table 8.2: Organic compound measurements for the Kærgård soil samples. (From Rambøll)

ID	Depth (mbg)	PCE (mg kg^{-1})	(C10 - C20) (mg kg^{-1})	(C6 - C35) (mg kg^{-1})
B3306	6	0.05	< 1	1
B3312	6	0.25	200	500
B3315	6	0.058	<1	1