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Diplomarbeit

# Laboratory Scale Experiments for the Development of an Electrokinetic in-situ Soil Remediation Method Using Diamond Electrodes

erstellt am

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# EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre an Eides statt, dass ich die vorliegende Diplomarbeit selbständig und ohne fremde Hilfe verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzten Quellen wörtlich und inhaltlich entnommenen Stellen als solche erkenntlich gemacht habe.

# Kurzfassung

## Laborversuche zur Entwicklung einer elektrokinetischen in-situ Bodenbehandlung mit Einsatz von Diamantelektroden

Diese Magisterarbeit präsentiert eine Literaturstudie und Laborversuche, die die Grundlage zur Entwicklung einer neuartigen elektrokinetischen in-situ Bodenbehandlungsmethode zur Eliminierung von organischen Schadstoffen darstellen.

In Österreich sind ca. 93 % der Altlasten mit organischen Schadstoffen kontaminiert, wobei für 40 % des Schadens Mineralöle und Phenole verantwortlich sind. Bislang steht in Österreich keine adäquate in-situ Methode zur Behebung dieses Problems zur Verfügung. Die hier zu entwickelnde Bodenbehandlung sieht die chemische Oxidation von Phenol und Diesel im Boden mittels Peroxodisulfat vor. Das Oxidationsmittel wird elektrochemisch an bor-dotierten Diamantelektroden aus einer Sulfatlösung synthetisiert. Danach wird es elektrokinetisch in der kontaminierten Bodenzone mit Hilfe von Feldelektroden unter einem elektrischen Gradienten verteilt, um zum Schadstoff zu gelangen.

Das Ergebnis dieser Laborstudie sagt aus, dass die Eliminierung von Diesel und Phenol in Altlasten mittels dieser Methode möglich ist. Produktionsversuche an einer bipolaren mechanisch implantierten Diamantelektrode ergaben eine linear verlaufende Synthesefunktion von Peroxodisulfat mit einer Steigung von 1,1 (Ah/l gegen mmol/l) bei 200 mA/cm². Somit können 54 mmol des Oxidationsmittels in ca. 16 Stunden generiert werden. Diese Menge ist notwendig, um ein mmol Natriumphenolat (0,1 g) in sandigem Lehm innerhalb von vier Wochen mit zweiwertigem Eisen als Katalysator zu 99 % zu oxidieren. Ein mmol Diesel (0,2 g) kann bis zu 84 % in zwölf Wochen durch 285 mmol katalysiertes Peroxodisulfat zersetzt werden. In elektrokinetischen Transportversuchen in gesättigtem lehmigen Sandboden gelang es, das Oxidationsmittel unter einer Feldspannung von 4 V/cm mit einer Geschwindigkeit von 4 cm/h von der Kathode in Richtung Anode wandern zu lassen. Dieses war das beste Ergebnis aus diversen Versuchsreihen, die Bodentexturen von reinem Ton bis zu reinem Sand inkludierten.

Somit lassen alle Ergebnisse der Teilversuche darauf schließen, dass eine Kombination derselben zu einer erfolgreichen in-situ Bodenbehandlung zur Eliminierung von Diesel und Phenol führen kann. Es besteht allerdings Potential zur Verbesserung der Elektrosynthese von Peroxodisulfat. Zudem sollte das Abbauverhalten von organischen Schadstoffen, besonders Diesel, unter oxidativen Bedingungen besser untersucht werden. Einzelne Dieselkomponenten könnten dafür individuell abgebaut und analysiert werden.

# Abstract

## Laboratory Scale Experiments for the Development of an Electrokinetic in-situ Soil Remediation Method Using Diamond Electrodes

This master thesis presents a review of literature experiences and the outcome of laboratory pre-assays leading to the development of a new electrokinetic in-situ remediation method for elimination of organic compounds in soil.

About 93 % of Austria’s contaminated land is affected by organic pollutants out of which diesel oil and phenol account for 40 %. Up to the present day, no effective in-situ remediation method exists (in Austria) in order to mitigate the damage. Thus, there is a need for a new treatment technology. The method to be developed aims to chemically oxidize phenol and diesel in soil with peroxodisulfate. The oxidant is generated in an electro synthesis process with diamond electrodes from a sulfate solution. The peroxodisulfate rich solution is then distributed electrokinetically within the contaminated area by means of an electric gradient generated by field electrodes in order to reach the pollutant.

The overall outcome of the laboratory study suggests that the elimination of diesel and phenol in soil matrix by means of this technique is possible. Electro synthesis experiments with a bipolar mechanically implanted diamond electrode at 200 mA/cm² resulted in a linear peroxodisulfate production curve with a slope of 1.1 (Ah/l vs mmol/l). Under these conditions, 54 mmol of the oxidant can be generated in about 16 hours. This is the amount needed to eliminate one mmol sodium phenolate (0.1 g) to over 99 % in sandy loam soil during four weeks in presence of bivalent iron as catalyst. One mmol of diesel oil (0.2 g) can be decomposed up to 84 % in twelve weeks with 285 mmol of catalyzed peroxodisulfate. As for the oxidant’s electrokinetic distribution different soil compositions have been tested (from pure clay to only sand) with loamy sand yielding the best result. Under the influence of an electric gradient of 4 V/cm, peroxodisulfate can travel 4 cm/h from the cathode towards the anode in this soil texture.

Thus, all investigated components of the new treatment method yield results suggesting that a combination of them can lead to an effective in-situ remediation technology for diesel and phenol elimination in contaminated soil. However, for further improvement, the oxidant production should be enhanced and the oxidative elimination of organic compounds, especially diesel oil, needs to be understood more clearly. Therefore, single constituents should be degraded and analyzed individually.

# Resumen

## Ensayos de escala de laboratorio para el desarrollo de un método in-situ de electrorremediación de suelos utilizando electrodos de diamantes

En esta memoria de título se presenta un estudio de literatura y se exponen resultados de pre-ensayos a escala de laboratorio que llevan al desarrollo de un nuevo método de electroremediacion in-situ de suelos para la eliminación de diesel y fenol.

En Austria, 93 % del suelo contaminado está afectado por compuestos orgánicos de los cuales diesel y fenol son los responsables de un 40 % de la contaminación. Hasta ahora no existe ningún método in-situ adecuado en Austria para la mitigación de este daño. El tratamiento a desarrollar se basa en la oxidación de diesel y fenol químicamente con peroxodisulfato. El agente oxidante se sintetiza con electrodos de diamantes a partir de una solución de sulfato. A continuación el oxidante se distribuye en el area contaminada por un gradiente eléctrico para llegar a estar en contacto con el contaminante.

El resultado integral de este estudio lleva a la conclusión que la eliminación de diesel y fenol en suelo mediante éste método es posible. Los ensayos de electrosíntesis de peroxodisulfato con electrodos de diamantes bipolares de implantación mecánica resultaron en una producción lineal a 200 mA/cm² con una pendiente de 1.1 (Ah/l contra mmol/l). Bajo éstas condiciones se producirían 54 mmol del oxidante en 16 horas. Esta cántidad se necesitará para una eliminación de 99 % de un mmol fenolato de sodio (0,1 g) en un suelo arenoso durante cuatro semanas en presencia de fierro bivalente como catalizador. Un mmol de diesel (0,2 g) se oxidará hasta un 84 % durante doce semanas con 285 mmol de peroxodisulfato catalizado. En cuanto a los ensayos de distribución electrocinética del oxidante en un suelo arenoso se logró una velocidad de 4 cm/h de migración desde el cátodo hacia el ánodo bajo un gradiente eléctrico de 4 V/cm. Se efectuaron ensayos con varias composiciones de suelo empezando con 100 % arcilla y terminando con solo arena.

Por lo tanto, los resultados obtenidos de cada subsistema del método sugieren que una combinación de éstos llevará a un nuevo tratamiento de suelo in-situ para la eliminación de diesel y fenol. Sin embargo, la electro síntesis del peroxodisulfato disponde de un potencial de mejoramiento. Además, la eliminación oxidativa de compuestos orgánicos, especialmente del diesel, debe investigarse más a fondo. Por ende, componentes particulares del diesel podrían degradarse y analizarce de manera individual.

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# 1 Introduction

This master thesis has evolved in the course of the development of a new electrokinetic remediation method for sites contaminated with organic compounds conducted at the Institute of Sustainable Waste Management and Technology, University of Leoben. It includes theoretical considerations on the new technology and a selection of results from laboratory scale experiences. As the development of the remediation technique will continue at larger scales, this thesis can only present preliminary results.

## 1.1 Problem Identification

In Austria, for the year 2006, 40,438 old industrial sites have been localized, whereas organic pollutants account for 93 % of the contamination. Out of the 93 % more than 40 % of the sites are affected by mineral oil and phenol. There are about 6,000 gas stations in Austria declared as contaminated land. [1, p. 13, 16], [2, p. 694]

Soil affected by organic pollutants poses a threat to the environment and human health for various reasons. Volatile organic compounds escape from top soil layers into the air, where they can be inhaled by animals or humans. Soluble organics, such as phenol, are highly mobile in soil and are destined to reach aqueous media. This can lead to groundwater contamination and spoil potential sources of drinking water [3, p. 24]. Lipophilic (gr. fat loving) substances, which accumulate in animal and human fat, are immobile in soil due to their hydrophobicity (not soluble in water). However, they tent to gather as non-aqueous phase liquids (NAPLs) above or below the water table according to their density, thus representing a source of constant groundwater contamination [4, pp. 2], [5, p. 30]. Mineral oils are one typical example for NAPLs.

There are several in-situ methods designed to treat soil contaminated with organic substances. However, each one of them has crucial drawbacks. Soil vapor extraction only serves to remove volatile compounds in non-clayey soils. Pump-and-treat is an inefficient method for NAPL removal and works only in high permeability soils. In-situ soil flushing is more effective than pump-and-treat considering lipophilic organic contaminants due to the application of surfactants and/or cosolvents. Nonetheless, the flushing solution will form canals in the soil system leaving out areas of lower permeability. Thus the method cannot clean-up a contaminated site completely. If bioremediation methods are applicable, they need long times for soil treatment. Ex-situ technologies are able to treat soils affected by NAPLs and other organic compounds. However, they always imply excavation of the contaminated ground, which means great distortion of the area and additional expenditures for heavy machinery, treatment and disposal fees. [6, p. 192], [7, pp. 158]

Thus, taking into account the number of contaminated sites and the disadvantages of existing remediation technologies, it is necessary to work on the development of a new in-situ treatment technique designed to clean-up soils affected particularly by organic compounds. The approach taken at the Institute for Sustainable Waste Management and

Technology combines two innovative remediation methods. This is for one electrokinetic treatment (EK) and for another in-situ chemical oxidation (ISCO). This combination promises to overcome the major shortcomings of the above mentioned established methods, which are the difficulty of treating low permeability and inhomogeneous soil and the removal of NAPL. EK guarantees a homogeneous coverage of all soil zones during the treatment and ISCO chemicals are able to deplete NAPLs and a great variety of other organic compounds [8, p. 35], [9, p. 4]. A description of the new remediation technology is presented in Chapter 1.3.

## 1.2 Goals and Targets

This master thesis aims to

1. describe the methodological approach to the development of the new electrokinetic remediation technique, i.e. clearly present crucial steps taken,
2. work out important parameters for all subsystems of the new technology based on literature and conducted experiments and
3. discuss the preliminary results and recommend further points of investigation to enhance the method.

## 1.3 Electrokinetic Remediation with Diamond Electrodes

The Institute for Sustainable Waste Management and Technology aims to develop a new method of electrochemical in-situ soil remediation. This technique shall be applied to soils contaminated with organic pollutants. For this work, phenol and diesel have been chosen as exemplary pollutants, because the new technology is meant to primarily remediate old gas stations and sites containing hydrocarbons and phenol.

The principal of this remediation approach is the production of oxidizing agents in an electrolysis cell. From there they are conducted into the soil driven by an electric field which is generated by electrodes placed in the soil. These force the oxidants to migrate through the contaminated soil material towards the field anode. The electrochemical cell will be operated with a diamond electrode provided by the company pro aqua Diamantelektroden Produktion GmbH. Diamond electrodes are especially apt to produce strong oxidants (see Chapter 8.2.1). The electrolyte is then conducted into a compartment which is subjected to an electric field produced by a stainless steel cathode and anode. The oxidants enter the soil system near the negatively charged cathode and are forced to move towards the anode. The fluid compartment is separated from the soil by a membrane which retains the electrolyte from entering the soil and allows only the ionic reagents to travel into the remediation site. Within the soil, the negatively charged oxidizing agents react with organic pollutants and decompose them, ideally to $CO_2$ and $H_2O$, on their way to the anode. Intermediate species will be formed during the degradation process. Figure 1 shows a preliminary scheme of the remediation technology.

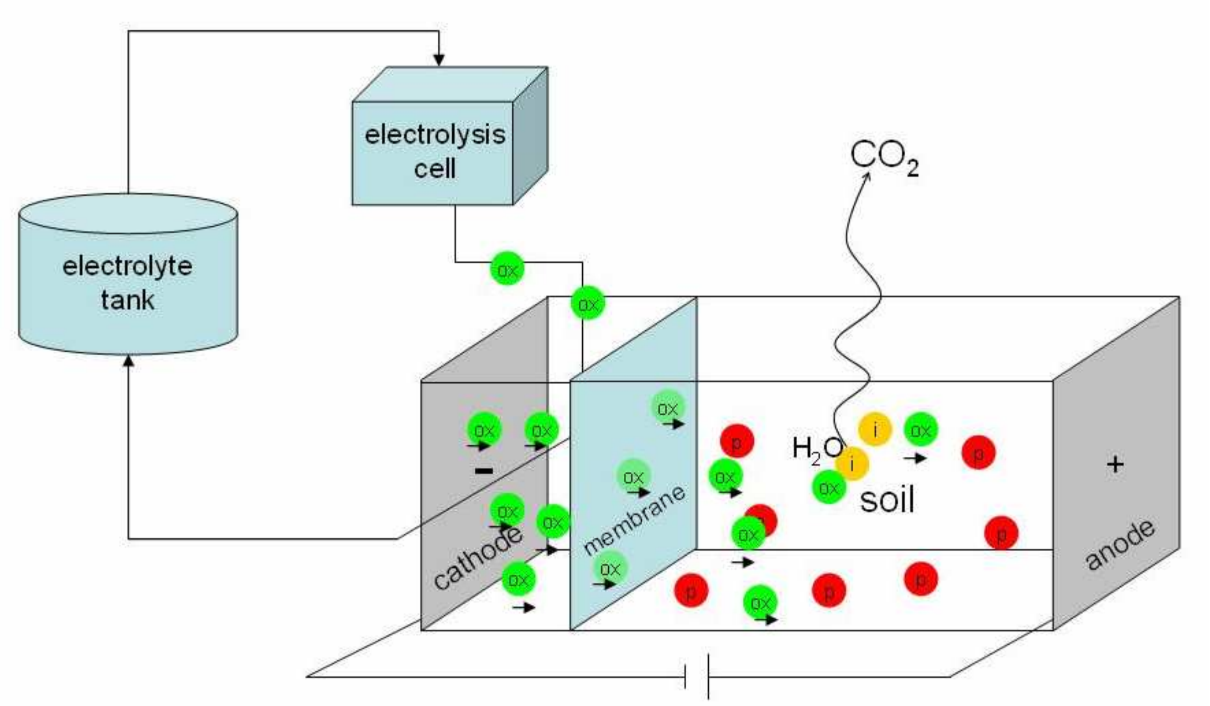

Figure 1: Preliminary scheme of the in-situ electrokinetic remediation technology
(ox = oxidant, p = pollutant, i = intermediate species)

The technology consists of three main components which have to be investigated separately before unifying the entire system. These three areas of investigation are:

1. electro synthesis of oxidizing agents with diamond electrodes,
2. degradability of organic pollutants in soil by the electro generated oxidants and
3. transport of charged oxidants in the soil by an electric gradient.

Peroxodisulfate has been chosen as reagent due to its strong oxidizing potential, its relatively long life time and its ability to form free radicals [9], [10]. These can be generated from sulfate containing electrolytes on diamond electrodes. Therefore, experiments have been conducted in order to optimize the production of peroxodisulfate with diamond electrodes. Furthermore, the degradation of phenol and diesel in soil with peroxodisulfate and the transport kinetics of the oxidant in different soil types have been investigated.

# 2 Background Information on Contaminated Sites in Austria

There is a need for innovative in-situ remediation techniques to cope with difficulties not yet overcome. Thus, this chapter aims to give an overview on the issue of contaminated sites in Austria in order to position the development of a new remediation technology into an overall context consisting of legal, statistical and technical components.

## 2.1 Legal Background

The Austrian legal framework on contaminated sites is partly subjected to European legislature, in this context mainly to directives. European directives need to be transformed into national laws. Those EU directives dealing with the issue of contaminated sites concern mostly water resources (drinking water, groundwater) and environmental liability. However, there is no directive especially addressing the problem of contaminated sites in Europe.

Austrian's national legislature includes several laws, ordinances and standards for the management of contaminated areas, i.e. old industrial sites and abandoned landfills. Table 1 gives an overview of applicable laws and their basic concerns. The according standards include the S series from 2085 until 2089 and 2091. A detailed list can be found in Appendix 1 – Contaminated Sites in Austria.

Table 1: Austrian laws on contaminated sites

| **Legal Document** | **Concern** |
|---|---|
| Water Act (Wasserrechtsgesetz) | The water act is the most important legal basis for the execution of soil remediation or containment, influencing as well site investigation measures. According to its concern of keeping water resources clean, especially groundwater, legal authorization is needed for the treatment of contaminated sites. |
| Law for the Clean-up of Contaminated Sites (Altlastensanierungsgesetz) | This law represents the foundation for financing the treatment of contaminated sites. Furthermore, it manages the national registration of potentially contaminated areas and the assessment of their potential hazard. If this evaluation confirms an environmental hazard the status from a potentially contaminated site turns into a registered contaminated site, which is entered into the Austrian atlas of contaminated land. All entries are assigned to priority classes for clean-up measures. |
| Trade Law (Gewerbeordnung) | The Austrian trade regulations oblige owners of enterprises to take environmental precautions when closing operative areas. They need to assure, that there is no danger to human life and health and no impact on the quality of water resources. |
| Waste Management Act (Abfallwirtschaftsgesetz) | This law is the legal representation for the principle of sustainability and obliges to take care of resources and only deposit waste free of hazardous potentials for following |

| | |
|---|---|
| | generations. It also rules the closedown of landfills. Landfill operators have to take measures in order to avoid negative environmental impacts. These measures include site investigation, sampling and even containment or remediative actions. |
| Law for the Promotion of Environmental Measures (Umweltförderungsgesetz) | This law regulates the financial aid for measures of environmental protection. Considering contaminated sites, these measures include containment and remediation. The financial means are raised by financial contributions regulated by the law for the Clean-up of Contaminated Sites. |

### 2.1.1 Definitions

For the technical context of this master thesis several terminological definitions should be considered according to ÖNORM S 2089 (1 to 6) and S 2088 (7 to 11):

1. remediation: elimination of the hazard’s origin and effects
2. containment: inhibition of the emission of pollutants hazardous to human health and the environment
3. on site: treatment of contaminated material directly in the area of the affected site
4. in-situ: treatment of contaminated sites without moving any polluted material
5. ex-situ: treatment of contaminated material after excavation
6. off site: treatment of contaminated material after excavation in another place than the contaminated site
7. critical value (Grenzwert): minimum or maximum value of a parameter determined in a legal document
8. benchmark (Orientierungswert): concentration of a substance serving as a comparative value for the assessment of site risks, it is the basis for local assessment of individual cases
9. reference value (Referenz- and Hintergrundwert): measured values of a substance considering regional geogenic and anthropologic impacts
10. inspection value (Prüfwert): if the inspection value is surpassed further investigation has to be conducted
11. intervention value (Maßnahmen-Schwellenwerte): if the intervention value is surpassed containment or remediation measures have to be taken.

### 2.1.2 Threshold Values

In the Netherlands, a precursor in the management of contaminated sites in Europe, standards distinguish three values according to the Risk-Based Assessment of Soil and Groundwater Quality:

1. target value: below this value the soil is considered clean
2. intervention value: above this value the site is seriously contaminated and
3. intermediate value: the contaminant concentration ranges between the target and intervention value causing a slight contamination. [11]

Thus, the technology to be developed described in this thesis is an *in-situ remediation* technology. Its remedial success can be measured by the ability to reduce the concentration of a pollutant in the first place below the intervention value and in the second place below the inspection value. For real site clean-up, remediation goals have to be determined beforehand according to the mentioned standards in order to be able to evaluate the treatment success.

Inspection or target and intervention values for hydrocarbons and phenol, the contaminants chosen for this study, are the following according to ÖNORM S 2088-1 and the Netherlands's standard (see Table 2):

Table 2: Inspection and intervention values for hydrocarbons and phenol according to ÖNORM S 2088-1 and the Netherlands's standards [11]

| **Value** | **Medium** | **Hydrocarbons (hydrocarbon – index)** | **Phenol (phenol - index)** |
|---|---|---|---|
| **Target value (NL)** | soil | 50 mg/kg | 0.05 mg/kg |
| | groundwater | 50 µg/l | 0.2 µg/l |
| **Inspection value (AUT)** | soil | 100 mg/kg | - |
| | soil eluate | 2 mg/kg | - |
| | groundwater | 60 µg/l | 30 µg/l |
| **Intervention value (NL)** | soil | 5000 mg/kg | 40 mg/kg |
| | groundwater | 600 µl/l | 2000 µg/l |
| **Intervention value (AUT)** | soil | 500 mg/kg | - |
| | groundwater | 100 µg/l | - |

The comparison shows, that the Dutch target values are below the Austrian inspection values but that the Austrian intervention values are stricter than the Netherlands's ones. The inspection value for soil eluate is only foreseen in Austria. However, the Netherlands' have a more complete list including in every category concentrations for phenol.

## 2.2 Statistics

By January 1, 2006, 45,207 contaminated sites (4,769 abandoned landfills and 40,438 old industrial sites) have been localized in Austria. It is estimated that about 65 % of the abandoned landfills and 55 % of the old industrial sites have been reported. This would result in a total of 80,860 contaminated sites only for Austria. While more than half of the total number has been reported, only 2,030 have been registered as potentially contaminated sites, whereas 1,796 sites account for abandoned landfills. Within the number of registered sites, 81 % pose a threat to groundwater, 10 % to air, 8 % to surface water and 1 % to soil. Out of the number of registered sites only 162 areas form part of the contaminated land atlas. 18 of them are in the process of remediation, 25 are being contained. In Appendix 1 – Contaminated Sites in Austria more detailed Austrian statistics on registered contaminated sites, potentially contaminated areas and the status of remediative actions for the year 2006 are presented. [1]

In order to estimate the relevance of the new remediation technology for phenol and hydrocarbon contaminated sites' treatment, it is necessary to know about the probability of occurrence of these pollutants in old industrial sites. Diesel oil will mainly be found in old gas stations, refineries and scrap yards for vehicles. Gas stations make up almost 6,000 contaminated sites in Austria [1, p. 16]. Phenol can be found in a number of sites of industrial activities, such as mineral coal mining, gas production, refineries, oil treatment facilities, polymer, paint and varnish production and wood treatment facilities [12]. Figure 2 shows the kind of branches that account for Austria's contaminated sites.

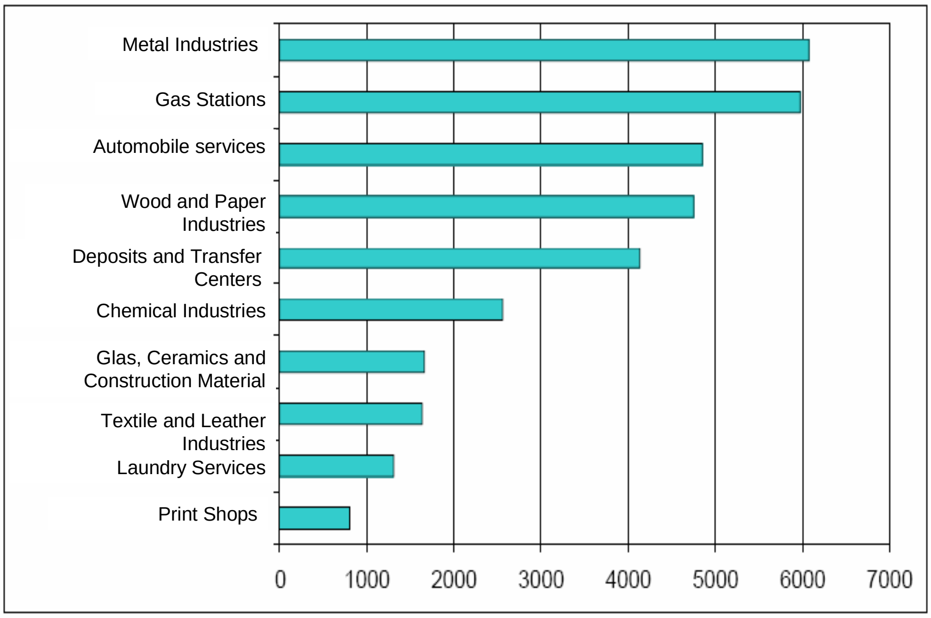

Figure 2: Branches accounting for contaminated sites in Austria adapted from [1, p. 16]

According to the State of the Environment Report [2, p.694], phenol and mineral oil make up about 38 % of contamination in sites, which are registered in the contaminated land atlas (see Figure 3).

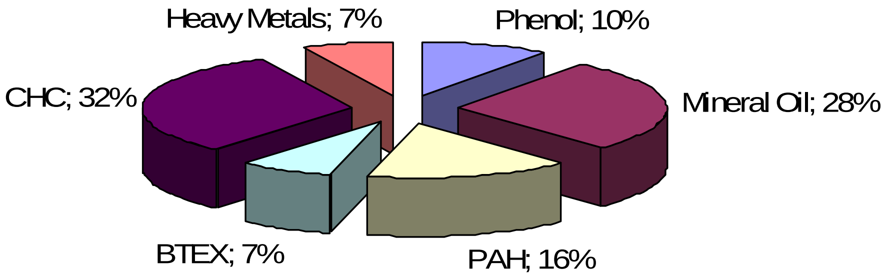

Figure 3: Occurrence of pollutants in declared contaminated sites in Austria [2, p. 694]

Thus, a necessity for a remediation method for phenol and hydrocarbon contaminated land is given.

## 2.3 Common Remediation methods

The following list presents briefly designated remediation technologies according to the Austrian standard ÖNORM S 2089 (not mentioning containment measures).

- Sorting: Sorting includes manual or mechanical sorting of contaminated site material for further treatment.
- Deposition: Treatment residues or untreatable sorting residues can be deposited in landfills.
- Extraction: The contaminated material is washed and the pollutants are extracted, thus the matrix of the contaminant is transferred from solid to liquid. This procedure is recommended for mineral oil affected soil.
- Microbial Processes: Micro organisms are used for decomposition of organic pollutants. This procedure can be applied in-situ or ex-situ in reactors or heaps and is recommended for hydrocarbon contaminated land.
- Thermal Treatment: The contaminated soil is heated in order to oxidize (classical waste incineration) or immobilize the pollutants (sintering). It is applied to hydrocarbon affected soils.
- Pneumatic Processes: There are three pneumatic procedures considered in the standard. By means of soil vapor extraction volatile organic pollutants present in the

vadose zone are removed. Active degassing collects gaseous residues from microbial decomposition processes. This technology is mainly applied to landfills. Active aeration is used in order to foster microbial activity in soils.

- Pump and Treat: This active hydraulic process extracts soil- and groundwater via wells from where it is conducted to a water treatment facility. The treated water can be re-injected into the groundwater, another receiving water course or a sewage system. Pump and treat is applied in the case of mineral oil contaminated groundwater.

There is no electrokinetic or in-situ oxidation remediation technology mentioned in the Austrian legal framework.

# 3 Soil Characteristics and Contamination

When developing an electrokinetic soil remediation method it is necessary to know about soil systems and their parameters, which are responsible for the success of the treatment method. Additionally, the behaviour of pollutants in the soil matrix has to be studied in order to be able to target them effectively. This will be discussed in more detail in Chapter 4.

Principally, soil consists of mineral particles originating from weathered rocks, organic matter such as humic and fulvic acids, water and its solutes and air. Thus, it constitutes the so called pedosphere, a 3-phase system composed of solid, liquid and gaseous constituents. Soil is characterized by a large surface, which interacts constantly with the surrounding environment. Matter and energy enter and leave the open system as they are transferred into the groundwater, surface water, atmosphere, plants, animals and food, while the pedosphere operates as storage, filter, buffer and transformation system. Central European soil presents pH-values between 3 and 8, whereas aging soil is getting more and more acid. Its content of organic matter varies between 5 and 500 mg/l for agricultural soils and 30 to 500 mg/l for wood soils. Electrical conductivity ranges from 0.1 to 1.8 mS/cm² and 0.2 to 1.6 mS/cm² respectively. [13, p.3]

## 3.1 Soil Parameters

This chapter will describe several soil parameters which are important to the electrokinetic remediation technique involving chemical in-situ oxidation.

***Soil Particles***

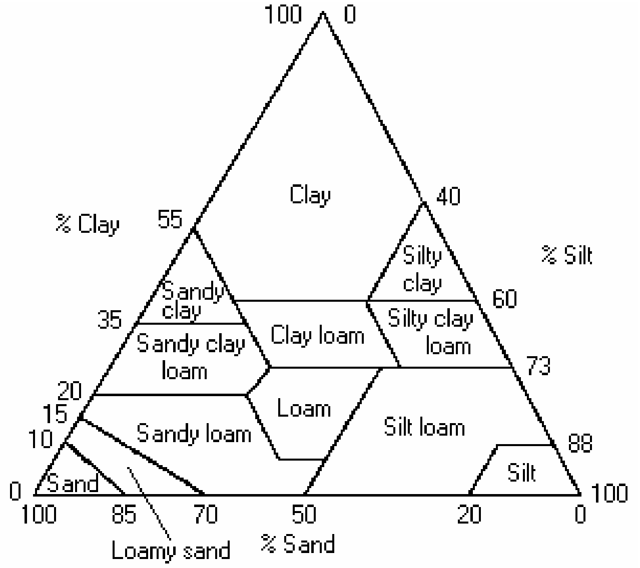

Figure 4: Soil types according to the US Soil Taxonomy [13, p. 158]

Particles of different minerals and sizes compose the soil. According to the content of different particle sizes, soil < 2 mm is called sand (2 mm to 63 µm), loam (63 µm to 2 µm) or clay (2 µm to 0 µm). Figure 4 shows the internationally used pyramid of US Soil Taxonomy.

### *Porosity and Water Content*

Dependent on its type soil is characterized by a certain porosity and pore water content. The size of the pores varies with the size of the soil grains. The smaller the particles the smaller will be the pores. However, three types of pore sizes are distinguished: 1) transmission pores (> 50 µm diameter), 2) storage pores (0.5 – 50 µm) and 3) residual pores (< 0.5 µm). The last type of pore is always filled with water even when the soil seems to be dry. Due to the small size of residual pores, gravity is not strong enough to force the water to percolate into the groundwater. Storage pores retain water after rainfall for a certain amount of time. When there is no more water input, the water gradually moves downwards and the pores are emptied. Transmission pores are not able to retain water for longer periods of time. A soil is called water saturated when all pores are filled, which occurs after heavy rainfalls. The field capacity describes the state of humidity when all gravitational water left the soil and is measured in volume %, the water capacity is measured in mass %. Thus, when the water content exceeds the field capacity, the soil is called saturated. [14, p. 20], [15, pp. 37]

The soil's pore space (ps) can be calculated from the ratio between the bulk density and the particle density (see Eq. 1):

Eq. 1: $$ps = \left(1 - \frac{\rho_{bulk}}{\rho_{particle}}\right) * 100\%$$

The particle density usually ranges between 2.6 and 2.7 g/cm³. [14 , p. 19]

### *Hydraulic Conductivity*

The above described porosity has a direct influence on the permeability of soil, an important parameter for the electrokinetic remediation. The smaller the particles, i.e. the less porous the soil, the lower the hydraulic conductivity will be. Sands present a permeability of $10^{-3}$ m/s, clayey soils of $10^{-9}$ m/s. Conventional methods, such as pump-and-treat can be applied only to soils with high hydraulic conductivity close to the permeability value of sand. Soil flushing still works at $10^{-5}$ m/s, whereas EK remediation promises to treat clayey soils as well. [13, pp. 248]

### *Thermal conductivity*

The most important mechanism of heat conduction in soil is water vapour transport beside convection and thermal conductivity. It is unusual to find isothermal conditions in soil. However, the closer to the soil surface the stronger the temperature gradient will be. In more profound depths temperature will vary less. At 1 m depth, temperatures range between 3 and

15℃ during the year in Central Europe, at 7 m depth, temperature is almost constant at 8℃. [13, pp. 257]

## 3.2 Soil Contamination

Considering only organic soil pollution, the tendency shows that the increasing production of organic chemical compounds poses a threat to soil conservation. Today about 300 million tons of organic substances are yearly produced world wide and about 1000 new compounds are invented each year [15]. A pollutant's behavior in soil depends on its characteristics. However, these are known well only for very few substances. The most important parameter is the contaminant's persistence. Persistence depends on physical properties such as vapour pressure, solubility, adsorption and desorption characteristics in soil. Generally, the sum of the substance's specific toxicity, its concentration and persistency result in the observed effect. [13, p.392]

Before considering in detail what happens to a pollutant in soil, basic paths from soil into the surrounding environment shall be mentioned. These are presented in Figure 5.

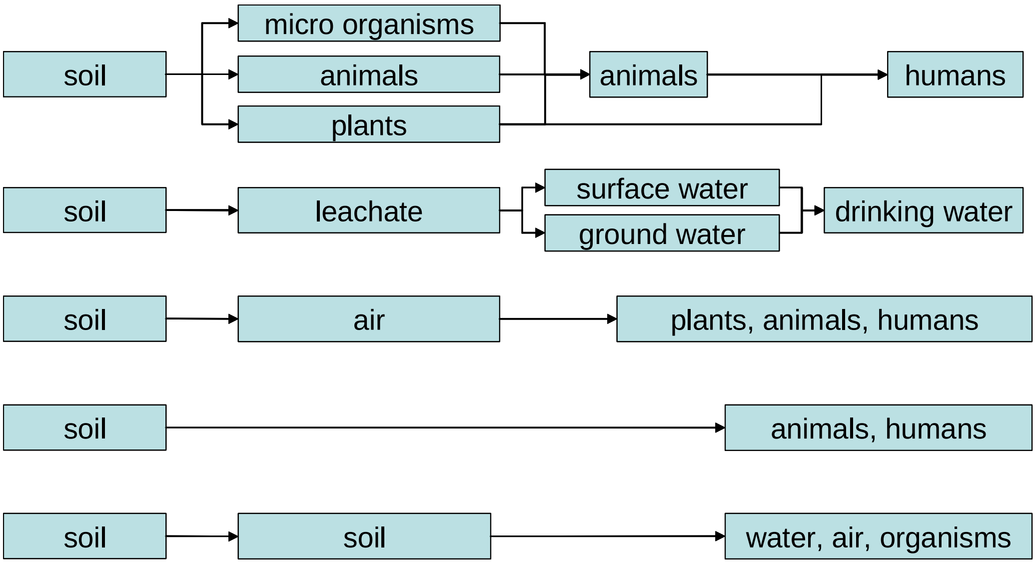

Figure 5: Possible pathways of soil pollutants into the surrounding environment [13, p. 360]

Once a pollutant gets in contact with soil, there are several pathways to enter other environmental compartments: the first option in Figure 5 shows that micro organisms and small animals, which live in the soil or on its surface, as well as plant roots can take up pollutants. These are then transferred to animals superior in the food chain and finally to humans. This is called bio magnification. Secondly, the pollutant can also be accumulated in the leachate if it is water soluble and can so reach surface- or groundwater, which is naturally transformed into drinking water. Thirdly, the pollutant can be re-transported into the air by soil air movement and be incorporated by plants, animals and humans. Also, a direct uptake is possible, especially for playing children. Last, if polluted soil is excavated and transferred to another place, i.e. deposited, it can initiate the same four mechanisms as described above. [13, p. 360]

Considering more in detail what may happen to the soil's pollutants there are six mechanisms they are subjected to:

1. Volatilization: Pollutants of low molecular weight and little affinity (little adsorption) to soil particles leave the soil via the air path especially in areas prone to erosion.
2. Leaching: Water soluble compounds leave the soil with the percolating water and are not retained by soil particles.
3. Adsorption: Organic pollutants have an affinity for organic soil particles where they can be adsorbed. The higher the organic content of the soil and the smaller the soil particles are, the better pollutants are adsorbed. Adsorption can happen in two phases: 1) during minutes up to a few days a balance between the soil solution and the solid phase can evolve or 2) in a process called aging, where during several years the pollutant is bound in a covalent manner to humic substances or diffuses into the soil matrix. Only if the rate of adsorption is higher than the rate of biological degradation, there will be an accumulation of pollutants.
4. Biological absorption: Pollutants which are available for plants and soil animals can be accumulated biologically.
5. Microbial degradation: The soil's micro organisms do not distinguish between organic pollutants and organic soil matter as nutrients, so the pollutants might be transformed into metabolites or even mineralized in micro biological processes. However, this is only the case if the pollutant is not toxic to the bacteria or does not appear in toxic concentrations.
6. Chemical degradation: By means of hydrolysis, oxidation, precipitation or exposure to light contaminants can be chemically degraded or immobilized. [13, pp. 365], [15, p.166]

# 4 Pollutants

As mentioned in Chapter 3, chemical and physical characteristics of a pollutant determine its behavior in soil. Thus, it can be localized in different zones in the soil. Roughly, soil can be divided in the water saturated and vadose (unsaturated) zone. Thus, considering only the pollutant's solubility and density it is possible to make an approximation about its residence area in soil. Volatile organic compounds (VOC), such as gasoline, have temperatures of ebullition in the range of 60 to 250 ℃ according t o the WHO. Those are often present in pore air in the top soil layers from where they escape gradually by volatilization. In these cases, site clean-up can be realized by soil vapor extraction. However, VOCs with lower vapor pressure migrate into deeper zones of soil. In the case of non-polar organic liquids like fuel oils, which have low solubility in water, a separate phase apart from water is formed in the soil pores. Therefore, they are called non-aqueous phase liquids (NAPLs). They are divided into LNAPLs (low-dense NAPLs) and DNAPLs (dense NAPLs). LNAPLs have a density inferior to water and thus form a pool above the water table. DNAPLs are denser than water and consequently accumulate just above the impermeable stratum in the groundwater. NAPL contaminated sites are difficult to treat with conventional methods: soil vapor extraction does not remove all constituents of NAPLs, pump-and-treat will have little success due to the insolubility of the contaminant in water. Only enhanced soil flushing with surfactants and/or cosolvents seems to be able to remove the pollutants, beside the option of excavating the contaminated soil [4, p. iii]. The emerging technology of in-situ chemical oxidation promises to remediate NAPLs contaminated sites, which are a continuous source of contamination plumes in groundwater [5, p. 30], [9, p. 4]. Polar organic contaminants, such as phenol, are able to dissolve in water. Therefore, they are more mobile and migrate with the soil's pore water until reaching the groundwater. Thus, they can be found alongside the entire soil depth above the impermeable stratum [3, p. 8]. Figure 6 shows a schematic view of the distribution of different kinds of pollutants in soil. The yellow pictured VOCs with high vapor pressure escape from soil by volatilization. Polar organic carbons (OC) are shown to distribute throughout the entire soil system and finally moving on with the groundwater flux. LNAPLs are shown to form a plume of contamination, in which volatile and liquid molecules are present. Near the water table the liquid forms a pool. DNAPLs sink to the ground, where they also spread by forming plumes in the groundwater flow.

The two contaminants chosen for this study are phenol and diesel. Latter was chosen because of its relevance to Austrian contaminated sites (23 % are contaminated with hydrocarbons from mineral oil according to [2, p. 694]), its hydrophobicity and complex composure, being a representative for alkanes, alkenes, cyclic and polyaromatic compounds. Additionally, it is easy to handle and does not pose a mayor health threat when using gloves and respiratory masks, while handling during soil spiking. Phenol was selected due to its hydrophilic character and representation in Austria's affected soils (9 % are contaminated with phenols according to [2, p. 694]). When working with phenol, special attention needs to be paid to dermal uptake and inhalation.

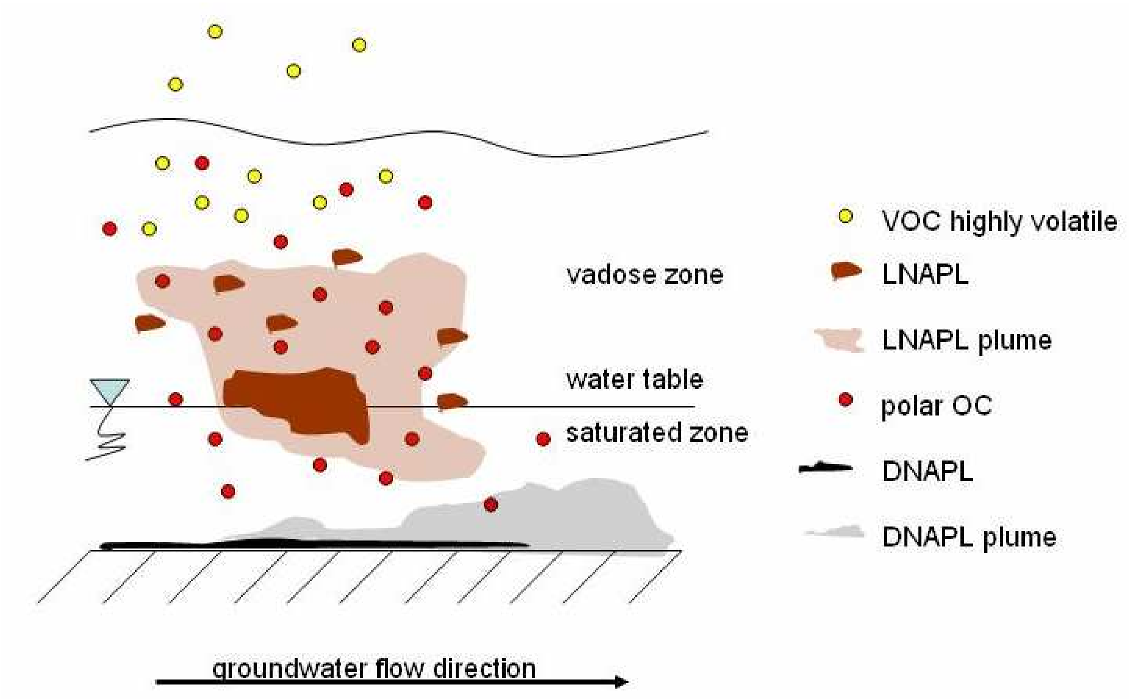

Figure 6: Distribution of different types of contaminants in soil

## 4.1 Phenol

Phenol is a water soluble, 84 g/l at 20 ℃, aromati c organic compound and thus highly mobile in soil and slightly acid in solution [3, p. 8]. The compound is a hazard to groundwater and drinking water. The final destination of phenol contamination is the aquatic medium. Its fish toxicity is $LC_{50}$ 5.4 mg/l in 96 hours. It is easily micro degradable under aerobic and anaerobic conditions, if its concentration does not exceed the toxicity level for microorganisms, which is about 0.5 g/l [16]. Therefore, it is estimated that phenol's half live in soil ranges between a few days up to 300 days, whereas in water it ranges between 10 to 100 days [3, p. 12]. At room temperature, phenol is a solid forming clear to white crystals. It is mainly uptaken by inhalation and dermal resorption. The maximum allowable concentration at work places (MAC) is 19 ppm. Oral intake of 1 g phenol and dermal intake of 10 g can be lethal for humans. Chronic intoxications lead to changes in blood constituency and harm the kidney. Phenol is used in the production of resins, medicine, pesticides, lubricants, softeners and others. [16]

Contaminated sites resulting from mineral coal mining, gas production, refineries, oil treatment facilities, polymer, paint and varnish production and wood treatment facilities amongst others most probably show presence of phenol together with other contaminants [12]. Beside contamination by spill in predestined areas as mentioned above, phenol also enters the environment by vehicle exhaust [3, p.9]. When localized in soil, it needs to be taken into account that it is a natural constituent of coal tar and a frequent intermediate product in organic matter decomposition.

In chemical analysis phenol and its derivates can be determined by the phenol-index, which is a spectroscopic method.

## 4.2 Diesel Oil

Diesel can be characterized as LNAPL as it is hydrophobic. Its solubility in water is 0.01 g/l, and it has a lower density (810 - 860 kg/$m^3$ at 15 °C) than water [17]. It is composed of various constituents such as alkanes, isoalkanes, cycloalkanes, alkenes and polyaromatic hydrocarbons [18, p. 212]. According to the Austrian ÖNORM S 2088-1 diesel has an average carbon length of $C_{10}$ – $C_{21}$. The $LD_{50}$ value is 2000 mg/kg for rats. The compound is also toxic to fish. It is adsorbable in soil, almost not biodegradable, but bio accumulative and non-mobile [17]. It belongs to the petroleum-based hydrocarbons and therefore to the priority pollutant group defined by the US EPA and EU [13]. Diesel contamination can be found basically in all places, where fuels are used and spilled. This refers mainly to gas stations, refineries and scrap yards for vehicles. As it is a very heterogeneous compound, its behavior in soil is difficult to characterize. Nevertheless, it can be estimated that the short carbon-chained constituents are volatile and leave the soil via the air path. The long chained components are mainly hydrophobic and remain over the water table as LNAPL. Aromatic compounds with polar characteristics might enter the groundwater and pose a threat to drinking water sources. Therefore, diesel or heating fuel contamination is difficult to handle. In order to find an appropriate treatment technology, it is important to understand the behavior of diesel in soil.

The behavior of hydrophobic organic compounds (HOCs) in soil depends on both the contaminant’s and the soil’s characteristics. Interaction between HOCs and soil can be described by sorption phenomena, meaning adsorption and absorption. HOCs are adsorbed to organic or mineral surfaces. They are absorbed mainly into organic matter and microporous minerals. Absorption into soft organic matter can happen within minutes, while absorption into hard organic matter can take up to weeks. It is believed that the binding between hydrophobic particles and soil depends on the soil’s organic matter. Binding mechanisms are versatile (interaction of functional groups, protonation, van der Waals interactions etc.). Additionally, the percentage of fine soil particles (clay and silt) seems to be crucial to HOC binding due to their large surface areas. Clay-sized soil particles present surface charges, which might provoke the effect that they, when water wetted, repulse hydrophobic organic matter, which then tends to accumulate in soil organic matter (SOM). [7, pp. 137]

Considering the concentration gradient of diesel in soil depth, it needs to be taken into account that NAPLs co-exist in pore spaces with water. As the soil becomes more saturated with water, the pores will rather be filled with water than with diesel, thus its concentration will decrease with depth in soil [19]. Thus sorption to soil particles and soil organic matter will equally decrease with depth. Figure 7 shows a schematic view of the presence of a non-wetting and a wetting NAPL in pore space.

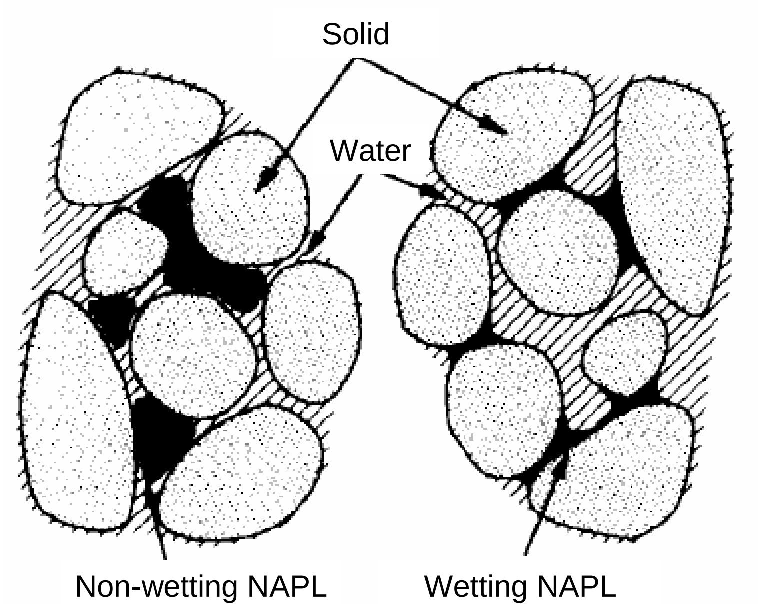

Figure 7: Characteristics of the presence of NAPL in pore water (adapted from [19])

The common analytical parameter for diesel oil detection in contaminated sites is the hydrocarbon index. This parameter measures the concentration of all carbon chained molecules between $C_{10}$ and $C_{40}$ by means of gas chromatography.

# 5 Spiking Methodology

In order to be able to measure the success of decontamination, the soil needs to be spiked with the pollutant. As the homogeneous distribution of the substance is the basis for any interpretation and conclusion drawn from the decomposition results, the spiking methodology is crucial. It needs to be efficient in order not to spread the pollutant into the surroundings and reproducible for high confidence in the results. Generally, a spiking method is considered valid and statistically sound if the coefficient of variance is below 20 %. For example, a coefficient of 10 % implies that the homogeneity is about 90 %, which means that any analytical measurement following the spiking is submitted to 10 % of variability [20, p. 401]. Thus, the coefficient of variance is a parameter of precision. Soil spiking with water soluble pollutants is less complicated, as the contaminating substance can be dissolved in water, and will thus not be discussed in detail. However, several organic contaminants are little water soluble, e.g. diesel oil. In most scientific reports on synthetically contaminated soil treatment, there is no description of the applied spiking method. Thus, the confidence for the final results after treatment is not given, due to the lack of information on the homogeneity of contamination. Brinch et al. [21, p. 1808] suggest that the pollutant can be dissolved in a hydrophobic solvent and added to the soil sample. Two methods have been investigated: a) spiking a fraction of the sample, evaporate the solvent and add the rest of the sample or b) spiking the entire sample and evaporate the solvent. As the solvent can be a disturbance for the following experiments, method a) seems more suitable, because the solvent's remains were less. Watts et al. [18, p. 213] spiked soil with diesel and BTX dissolving equimolar amounts of each pollutant in pentane, adding the solution to the soil until obtaining a concentration of 15 mmol/kg. Pentane was then allowed to evaporate. However, there is no comment on the completeness or extent to which pentane evaporated. Doick et al. [20, p. 400] suggest adding the entire spike to a fraction of the sample and while mixing aggregating the rest of the specimen. A Waring blender, an adapted bench drill and a stainless steel spoon were applied as mixing instruments. Table 3 presents the results obtained for a contamination of 1 % of transformer oil.

Table 3: Different spiking methods and their efficiencies and variances [20, p. 402]

| **Waring blender** | | **Bench drill** | | **Stainless-steel spoon** | |
|---|---|---|---|---|---|
| efficency [%] | CV | efficency [%] | CV | efficency [%] | CV |
| 102.8 | 35.0 | 72.2 | 10.9 | 75.4 | 6.0 |

CV = coefficient of variance

Thus, mixing with a spoon provides the highest homogeneity but a lower efficiency as the blender. This might be due to the thorough contact of spoon and soil while mixing, so the transformer oil could evaporate easier. However, the focus should be on the achieved homogeneity of spiking as this is deciding for the interpretation of the results obtained after soil treatment.

# 6 Electrokinetic Soil Remediation

Electrokinetic (EK) soil remediation refers to the application of a direct current via electrodes, which are implanted into the soil of a contaminated area. Low intensity currents in the range of mA/cm² cross sectional area or low electrical gradients such as 1 V/cm length are applied [22, p. 2638]. This remediation approach is an innovative method for the in-situ treatment of soils contaminated with a number of different pollutants. The process is apt to treat species such as heavy metals, radioactive elements, nitrates, sulfates, cyanides, polar and non-polar organic contaminants, halogenated hydrocarbons and mixtures of the mentioned pollutants [23, p. 103]. The main advantage of EK remediation is that it is able to treat small grained soil in-situ, particularly with high clay content and low hydraulic conductivity ($10^{-9}$ m/s), where traditional techniques such as pump-and-treat have no or incomplete effects [8, p. 35]. The low hydraulic conductivity is of advantage because the soil can retain water and therefore the pore liquid can conduct the electrical current [7, p. 160]. Until now, it has been difficult to treat such soils in-situ with little distortion. EK methods can also be applied to sandy and unsaturated soils [23, p. 108]. Within EK remediation, there is a variety of mechanisms involved. For one, EK processes such as electroosmosis, electromigration and electrophoresis will take place and for another, a number of physicochemical reactions such as sorption, precipitation, dissolution, oxidation and reduction determine the effect of the applied technique [6, p. 192], [22, p. 2638], [24, p. 498], [25, p. 117]. In the following chapter these theoretic aspects will be explained in more detail.

A typical EK remediation system is shown in Figure 8, where the electrodes are inserted via wells in the soil. The area between the electrodes is subjected to EK processes. Two main phenomena occur: one, the transport of contaminants via electromigration (migration of ionic species in an electric field) or two, via electroosmosis (water flux induced by an electric field) which takes dissolved contaminants with it to the cathode [25, p. 117]. The method which is being described in this work, however, takes a different approach to EK remediation. The contaminant, in this case an organic compound, shall not be flushed to either one of the electrodes but shall be oxidized directly in the soil. Thus, oxidizing agents are introduced into the electric field and travel into the soil driven by electromigration and electroosmosis.

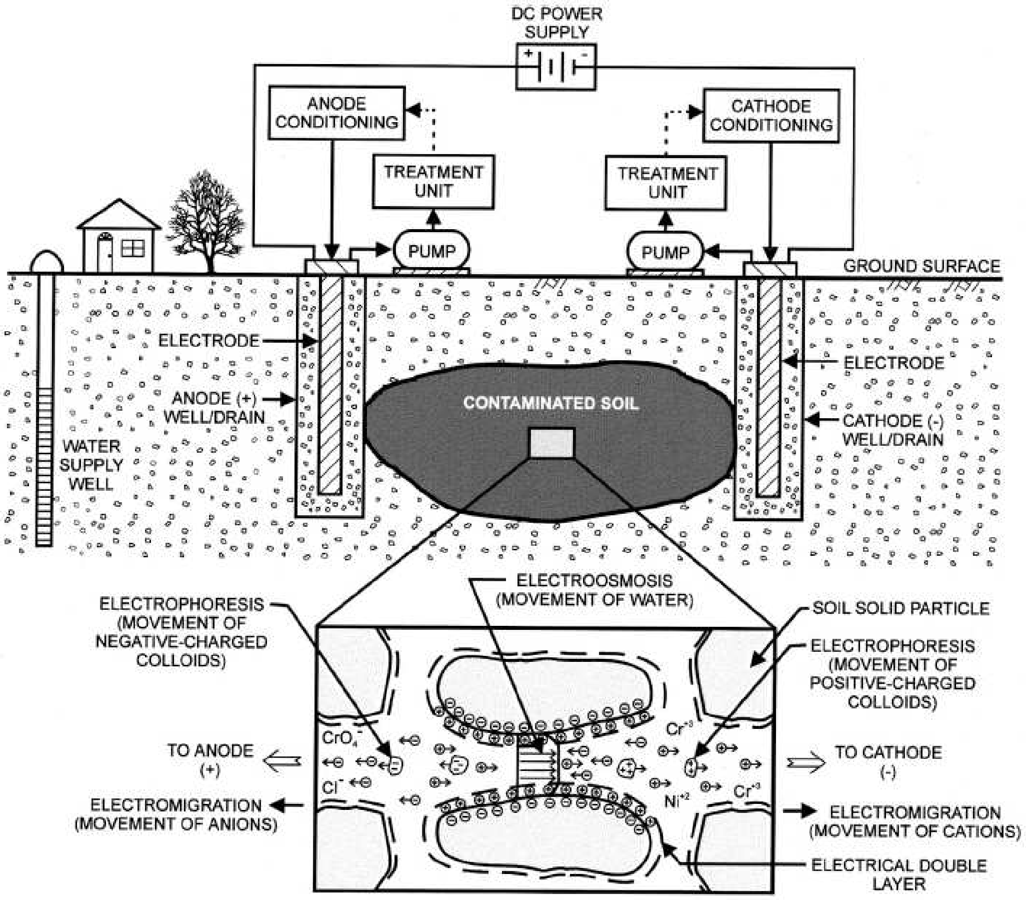

Figure 8: Schematic EK soil remediation set-up [7, p. 161]

## 6.1 Theoretical Considerations

When employing electrokinetics to soil, four major phenomena will occur, i.e. electroosmosis, electromigration, electrophoresis and electrolysis. These will be described in this section. Other processes occurring during EK application due to soil characteristics, such as complexation, dissolution, sorption, precipitation etc., are not discussed in this context as they are not subject of investigation in the project. Also diffusion has been found to be only a minor contribution to EK remediation processes [26, p. 317]. Therefore it will not be discussed here.

### *Electroosmosis*

Electroosmosis describes the flow of pore fluid and its solutes relatively to a stationary charged surface [24, p. 498]. As charge-neutrality has to be maintained in the soil-liquid system, the outer pore fluid layer, 1 to 10 nm thick, adopts the contrary charge of the soil particles. Usually soil particles, especially clays, dispose of a negative charge. The charge density increases in the following order as reviewed by Acar et al. [25, p. 119]: sand < silt < kaolinite < illite < montmorillonite. So as soil particles are negatively charged, the pore water is charged positively near the soil. Due to the drag interaction between the outer pore fluid layer and the inner bulk water, the entire pore water is moved by the electric field to the negative cathode [24, p. 498]. A maximum flux of $10^{-4}$ ($cm^3/s*cm^2$) can be achieved at 1 V/cm electric field gradient in low activity clays with high water content and low conductivity (100 µS/cm) according to Acar et al. [25, p. 120]. However, electroosmotic flow can cease when the counter flow driven by a hydraulic gradient is equal to electroosmosis or when the surface charge of soil particles is zero [25, p. 118].

Considering that the electric field is homogeneous even in heterogeneous soils, transport of ions and organic compounds due to electroosmotic advection will occur in every region of the targeted treatment area. This is an advantage over soil flushing techniques, where the flushing liquid will take the path of lowest resistance in heterogeneous soils, i.e. areas of bigger pores [24, p. 498].

### *Electromigration*

The term electromigration refers to the transport of charged ions in solution in the electric field. They are responsible for the current conduction. In contrast to electroosmosis, migration is not dependent on soil charge; therefore, it occurs as well in sandy as in clayey soils. Generally, ion velocity is proportional to the ion charge number and the field strength [24, p. 498]. However, on the one hand, movement of ions is subjected to their concentration in the soil solution, which again depends on interactions with the soil such as sorption, ion exchange, complexation and others. On the other hand the movement depends on their velocity in the pore liquid, when they are not engaged in any other reaction, which is then a function of the electric potential gradient and the ion concentration gradient amongst others. The latter factor is not soil dependent, except for advection by electroosmosis [26, pp. 316, 318]. Due to the number of factors, which interfere with the theoretical ion velocity, the effective ion mobility is important for EK remediation. This effective mobility is a function of soil porosity, ion charge and ion diffusion coefficient. It is measured in $cm^2/Vs$. Multiplication with the electric gradient V/cm leads to the actual ion velocity [22, p. 2641].

Comparing the influence of electromigration and electroosmotic advection on ion transport, Acar and Alshawabkeh [22, p. 2643] came to the conclusion that transport by migration is about 10 times higher.

### *Electrophoresis*

Electrophoresis describes the movement of charged particles relative to a stationary liquid (mirror process of electroosmosis). It is only of relevance if surfactants are used in order to mobilize hydrophobic pollutants for an electroosmotic advection [22, p. 2642], [24, p. 498].

### *Electrolysis*

At the anode and cathode water electrolysis reactions take place (Eq. 2 and Eq. 3).

Eq. 2: Anode: $2 H_2O \rightarrow 4 H^+ + 4 e + O_2$

Eq. 3: Cathode: $2\ H_2O \rightarrow H_2 + 2\ OH^-$

Thus, the area around the anode becomes acid and around the cathode basic. As the protons and hydroxyl ions are subjected to the electric field, they start to migrate into the opposite direction. However, as the proton is about 1.8 times faster than the hydroxyl ion due to its smaller radius, the system is dominated by an acid front moving towards the cathode, where it neutralizes the basic front. The final acidity of the soil depends on its buffering capacity which is linked directly to its cation exchange capacity. The pH-value can drop to about two near the anode and rise to 12 near the cathode [8, p. 9], [22, p. 2640]. It is possible to enhance EK remediation by neutralizing the electrolytes near the anode and cathode in order to save soil from acidification or alkalinization and to inhibit adverse chemical reactions due to extreme pH-values.

## 6.2 Methods and Studies on Electrokinetic Remediation

Electrokinetic remediation techniques have not been applied before the late 1980s. Since then, a variety of approaches has been investigated and put into practize. This chapter will give an overview of important technologies and studies on EK remediation.

As conventional methods did not succeed in remediating low hydraulic conductivity soils without greater distortion of the area, the necessity for the development of in-situ EK processes rose. Methods, such as pump-and-treat, work in soils with higher hydraulic conductivity and can clean the soil only from soluble contaminants. Also soil vapour extraction does not present satisfying results in clayey soils. Soil washing implies the excavation of contaminated material, which then can be treated in solution containers, where good cleaning results are obtained. The pollutant is transferred from the soil to the water matrix which can be treated by regular waste water technology. Another method, in-situ soil flushing, an enhanced version of pump-and-treat, works with cosolvents or surfactants which mobilize hydrophobic organic contaminants and is applicable to soils with hydraulic conductivities as low as $10^{-5}$ cm/s [4, p. 5]. Bioremediation processes do not succeed either, if conditions are more difficult. Low temperatures, the lack of nutrients and too high concentrations of contaminants which are toxic to the micro organisms let microbiological techniques fail. Pure heat treatment, with the soil as resistor to electric current, has also been employed, rising the soil’s temperature up to 100 °C in order to extract vaporized and volatilized contaminants from soil air. This method, however, is biologically not sound and the captured gases need to be treated externally. [6, p. 193], [7, pp.158]

Having a look at the evolution of EK techniques, it can be observed that by the late 80’s the first EK method was patented in the Netherlands. In the early 90’s in the USA, the Lasagna group started to develop the “Lasagna Process” for the removal of organic compounds. At the same time in Germany, “Geooxidation” was fostered. In the late 90’s, interest rose in Asia, Japan and South Korea, and thorough investigation on EK remediation started. In the following, relevant methods which have been put into practize are briefly presented. [6, pp. 192]

### *Electro-Bioreclamation*

This technique has been developed by a Dutch company for volatile and semi-volatile organics, NAPLs, heavy fuel oils, PAH and others. AC or DC current is applied for Joule heating. The soil itself is the resistor and is heated up to 90 °C. At this phase soil vapour and groundwater are extracted via wells placed between the two electrodes. In a second phase, thermophilic bacteria inherent to the soil start degrading the organic compounds. As temperatures decrease the fauna of bacteria changes and continues to decompose the pollutants. Meanwhile, nutrients are inserted by using the electrical field. [6]

### *Lasagna Process*

This process is focused on removing heavy metals and soluble organic compounds from low permeability soils. It was applied first in 1995 in the US. The name is derived from the position of treatment zones between the electrodes, which are placed horizontally into the soil. For shallow zones, not deeper than 15 m, a vertical placement of electrodes is also possible. Sorbents, catalytic reagents, buffering solutions and oxidizing agents are introduced into the soil to create treatment zones. Electric current is applied which drives the contaminants into the designated areas by electromigration and electroosmosis. These electrokinetic effects have advantages over traditional hydraulic methods, because the electric field spreads homogeneously and thus all zones of the contaminated field can be treated equally. The polarity of the electrodes may be switched in order to force the pollutant to travel several times through the treatment area. The cathodic effluent can be recycled into the anode compartment neutralizing the pH-value at the same time. However, a disadvantage of this process is the difficulty of establishing a good electrical contact with the electrodes and the entrapment of gases, which evolve in the electrolysis at the electrodes. [23, pp. 109], [27]

### *Electro-Klean Process*

This process has also been developed in the US. The method can remediate several types of soils, from permeable to low permeable, and treat heavy metals, radionuclides and certain volatile organics. A DC current is applied directly to the soil via two electrodes. For enhancement, mostly acid fluids are added for better heavy metal solubility. The drawback of this technique is its low efficiency of application in high buffering capacity soils and its poor applicability to organic compounds. [23, pp. 110]

### *Electrokinetic Bioremediation*

Via an electric field nutrients are inserted into the area of remediation, where they can be dispersed homogeneously or be directed to a certain point. These nutrients will foster microorganisms' growth and their metabolism. The activated microbiological fauna can then decompose organic pollutants. However, as all methods involving micro organisms, the concentration or the metabolized species of the contaminant may surpass the microbial tolerance and thus inhibit the remediation process. [23, p. 111]

### *Electrochemical Geooxidation*

An electric field is applied to the soil. Soil particles are supposed to act like anodes and cathodes, thus each promoting oxidation and reduction processes on their surfaces. The method is supposed to remediate sites from organic and inorganic species. However, the success of this method has never been proven and remediation times are long. [6, 193], [23, p. 111]

### *Sandia Method - Electrochemical Ion Exchange*

Electrodes are placed into porous but conductive ceramic castings in the soil in order to keep the electrolyte from infiltrating the soil and taking pollutants with it into deeper soil zones. When current is applied, ionic contaminant species, e.g. heavy metals, move to the electrode compartment of opposite charge due to electromigration. There they are trapped in the circulating electrolyte in the ceramic casting, which leads the pollutant through an ion exchange facility. As the concentration of the ionic contaminant is very low in the electrolyte the treatment of the effluent becomes very expensive. [23, pp. 111]

### *Electrosorb*

Via electromigration, ionic species move to the electrodes, where they are trapped in a polymer matrix. This matrix is impregnated with pH-regulators and surrounds the cylindrical electrodes, which are placed into the soil. Until now, there has not been observed any disadvantage to this method applied in the US [23, p. 112]. However, it is unable to treat soil contaminated with non-polar species.

### *Studies*

Beside these applied technologies mentioned above, there are several new methods being investigated.

Acar et al. [25] succeeded in removing phenol from kaolinite clay soil by electromigration and electroosmotic advection. As phenol is a polar organic compound, it can protonate in acid media and therefore travel as any other ion. Removal rates reached up to 95 %. In the same study, a non-polar organic compound, hexachlorbutadiene, could not be removed without surfactants (enhanced EK remediation). So it was concluded that successful EK remediation was only viable for water soluble contaminants.

Yang and Long [28] combined the effects of electrokinetics and the Fenton reaction in order to mineralize and remove organic contaminants, in that case phenol. The soil was spiked with a concentration of 200 mg/kg phenol. Experiments lasted 10 days. Near the anode a permeable wall of iron powder was constructed and hydrogen peroxide was introduced into the electric field via the electrolyte. $H_2O_2$ reacts with the iron powder, which functions as a catalyst and produces hydroxyl radicals - strong oxidizing agents. In a sandy loam soil sample it was found, that for a decontamination efficiency of 99 % about 32 % resulted from in-situ oxidation, whereas 67 % were due to ion migration or osmotic advection. However, the blank experiment without oxidizing agents resulted in 99.8 % removal.

In later studies Yang and Liu [29] used basically the same set-up for trichloroethylene (TCE) removal. It was found that TCE can be removed up to 89 % in loamy sand, whereas half the removal is ascribed to in-situ mineralization by hydroxyl radicals. In sandy loam, up to 60 % of oxidation can be achieved.

Park et al. [30] confirm these results. A sandy soil sample was spiked with phenanthrene and iron (Fe(II) and $Fe^0$). Hydrogen peroxide was introduced via osmotic advection into the system from the anode. It was found, that up to 82 % of phenanthrene could be removed of which only 31 % accounted for osmotic flow.

In Austria, as part of the INTERLAND project [31] within the scope of the subproject of “In-situ Generation of Oxidative Substances”, a new approach to EK remediation was tested (see Figure 9). The cylindrical production anode (a diamond electrode, which is known to be able to produce strong oxidizing agents, see Chapter 8.2.1), was placed in a hydrocarbon contaminated area and fed by an electrolyte in order to produce OH° (black point). The generated oxidants are transported by the electrical field to the field anodes (red points in Figure 9). On their way they oxidize organic contaminants. The green points represent sampling points for chemical analysis. Results from laboratory experiments (50 kg soil material) show that after a period of 256 days, applying the analytical method of the hydrocarbon-index (HC-index), about 23 % of the organic pollutant were mineralized. However, in the blank experiment, about 12 % of the original contaminant concentration was lost, which results in only 11 % degradation. For another experiment, hydrocarbon contaminated soil has been treated electrochemically during 20 weeks. Final analyses showed that according to the hydrocarbon-index 56 % and according to the TOC 48 % of the original pollutant have been eliminated, whereas the blank experiment lost 28 % (HC-index). In the field experiment, during one month, a reduction of 17 % of the total TOC could be achieved [31, pp. 538 - 542]. This leads to the conclusion that further experiments have to be conducted in order to obtain reliable results and to enhance homogenization of the spiked soil and analysis methods.

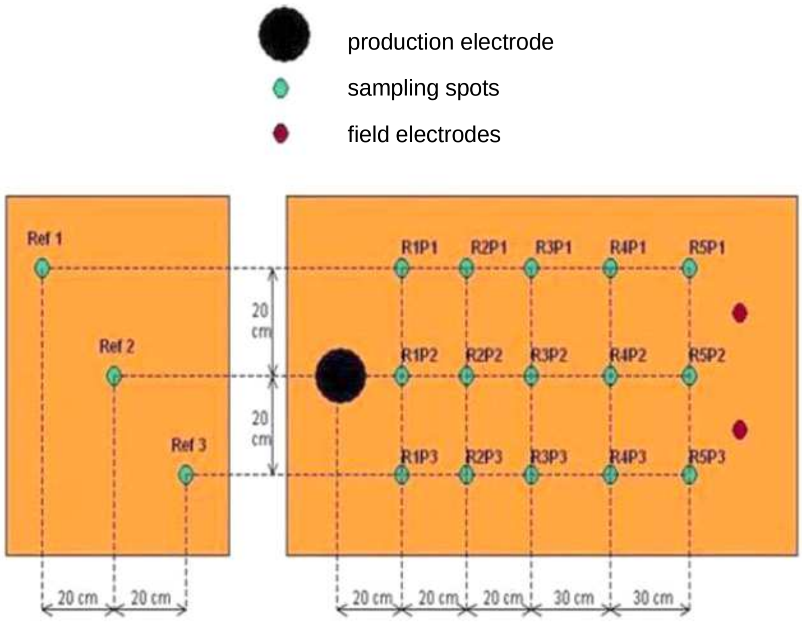

Figure 9: Schematic set-up of electrodes for the in-situ generation of oxidizing agents and their transport through the contaminated soil in the Interland project [31, p.470].

In this study, the basic scheme of the remediation method is different from the methods and studies mentioned above. It has already been presented in the introduction. An external production unit, composed of an electrolysis cell with a diamond anode, will produce peroxodisulfate ions, which are strong oxidants. These will be introduced into the electric field by circulating the electrolyte between the field cathode and the soil protected by a membrane. The anionic oxidants are repelled from the cathode and will migrate in the electric field towards the anode. On their way the peroxodisulfate or its free radicals will oxidize the organic pollutants, phenol and diesel oil. The supposed advantage of this method is that it is not dependent on the type of soil. First, the removal of contaminants does not rely on a strong osmotic flux, because they will be decomposed directly in the soil. Secondly, high buffer capacity soils will not be of disadvantage, as the method shall be independent of the soil's pH-value. Thirdly, the soil may be coarse grained or fine grained as the principal mobilization of the oxidizing agent will occur by electromigration, which works in both types of soil. Effects in the vadose and saturated zones have to be explored as above mentioned studies almost completely focused on saturated soils.

## 6.3 Considerations and Conclusions for Laboratory Scale Experiments

Before conducting EK soil remediation experiments, a number of parameters have to be considered. The specification of parameters depends on the type of EK method being applied and the kind of contaminant. In the following, some common parameter determinations for the treatment of organic pollutants with electroosmosis, electromigration and integrated in-situ oxidation shall be presented.

I) **Soil Type:** Soil is very versatile and therefore its selection will determine an important number of parameters. First, it should be decided if the soil sample shall be real soil, including the uncertainty of the exact substances of content, scavengers etc., or a synthetic soil, which can be described precisely but is only a model of real soil and might exclude difficulties, which later appear in field experiments. The soil type is also crucial for factors like permeability, particle size, buffer capacity, sorption reactions, cation exchange capacity, types of minerals present (and the chemical reactions they might be involved in), pore volume, and content of organic matter amongst others. All these factors have an influence on the mobility and chemical reactions of the pollutant in soil. In representative studies, real soils have been used including kaolinite, sandy loam and loamy sand [23], [25], [28], [29], [30].

II) **Water Content:** Mostly saturated soil has been used, as on the field water can be added easily [25], [28], [29], [30]. However, this could result in a flushing effect. Therefore, investigation for the vadose soil zone is necessary.

III) **Specimen Conditioning:** After having decided on a soil type and water content, the laboratory sample needs to be conditioned before application. This includes mainly pretreatment of real soils, such as drying, sieving and spiking. Spiking procedures have been presented in Chapter 5 in detail.

IV) **Electrical Parameters:** Electrical parameters include the type of current, DC or AC, and the applied current density in mA/cm$^2$ cross sectional area or electrical gradient in V/cm length. Normally direct current is chosen, but changing poles of electrodes at slow frequencies can contribute to the system’s equilibrium (water content). As for the electrical gradient, usually, 1 V/cm is applied [25], [28], [29].

V) **Field Electrode Material and Integration:** The electrode should be inert and stable, especially the anode. Graphite, platinum, gold, silver but also titanium and stainless steel meet the requirements [23, p. 100]. There are basically two possibilities of integrating the electrodes into the soil system. The first one is to simply insert the electrodes into the soil sample, the second one is to build an electrode compartment. When using an electrode compartment, the electrolyte can be circulated and effluent withdrawn. It is necessary to protect the soil from the electrolyte, which implies the usage of a membrane or low permeable barriers. Bentonite has been employed [30] or glass fiber filters sandwiched between nylon clothes [28], [29]. Furthermore, the electrodes can simply be placed opposite from each other. In field experiments a variety of arrangement can be tested.

VI) **Reactor Arrangement:** The experiments can be conducted in one or two dimensional systems. A one dimensional system would take into account e.g. only the length, while a two dimensional system would include length and depth. The system can be open or closed. Both types have been used. Yang and Long [28] and Yang and Liu [29] used a closed system with cylindrical acylic glass, i.e. a soil column, while Acar et al. [25] and Park et al. [30] worked with open boxes. The size of a test cell can vary from 10 cm to about 100 cm in length, which implies at the same time shorter or longer experimental periods. All revised literature reported horizontal arrangements.

VII) **Analysis:** Also the analytical method after conducting the experiments has to be chosen carefully. First of all, a blank run is always necessary in order to estimate removal effects which are not ascribable to the remediation method (e.g. vaporization, microbial degradation if microorganisms are present, chemical reactions with soil substances). Furthmore, the content of soil organic matter has to be determined beforehand. Many authors having conducted respective experiments with hydrocarbon and phenol contamination have used gas chromatography in combination with a flame ionization detector [18], [28], [32], [33]. Acar et al. [25, p. 126] propose to slice the soil into segments and analyze each part. Thus, it is possible to conclude, where along the length of the cell the remediation method succeeds after a certain time.

As for the experiments conducted in the course of this thesis, different soil types have been chosen. Degradation assays have been conducted separately with synthetic sandy loam while transportation of ions has been tested on several points of the textural triangle, also using synthetic samples. The soil’s water content was adjusted near the field capacity. Two stainless steel electrodes have been placed directly onto the soil. Horizontal and vertical arrangements have been tried. Analysis has been conducted by slicing the soil into 1 cm pieces.

# 7 In-situ Chemical Oxidation

In-situ chemical oxidation (ISCO) is a relatively new approach to soil and groundwater remediation, whereas it has been a long established waste water treatment. Oxidizing agents, aqueous or gaseous, are introduced into soil and/or groundwater at the source of contamination. These decompose the pollutants, ideally, to water and carbon dioxide or to less nocuous compounds. The major oxidants used for ISCO are permanganate, ozone, hydrogen peroxide and peroxodisulfate. As in soil systems a great number of reactants and conditions can be found, several reactions might take place, amongst which acid/base reactions, adsorption/desorption, dissolution, hydrolysis, ion exchange, oxidation/reduction and precipitation are common [9, p. 4]. Pollutants, which can be treated with ISCO chemicals are: benzene, toluene, ethylbenzene, xylene (BTEX), methyl tert-butyl ether (MTBE), petroleum hydrocarbons, chlorinated solvents, polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), chlorinated benzenes, phenols, organic pesticides and munitions constituents [34, p. 1], [35, p. 3]. ISCO's main advantages are: It does not produce great amounts of residues to be treated, it is a relatively quick method with treatment times of months up to one year, it can be applied to a variance of different pollutants and works best at hot spots. Its drawbacks are soil conditions (matrix, soil organic matter and permeability), low contaminant concentration in large polluted areas, contaminant mixtures, delivery problems and short-lived oxidants [9, p. 4], [10, p. 5], [34, pp. 1]. Other common methods for treatment of soil and groundwater contaminated with organic pollutants (as mentioned in Chapter 4) imply more complicated technical measures. These result, both, in a greater impact to the contaminated area, even in case of on-site or in-situ treatment, and in higher expenses. The alternative of bioremediation is often not sufficient due to the toxicity of the contaminant. But it is ideal for subsequent application to a previous ISCO treatment. Thus, ISCO seems to be the method with less impact to the site to be treated. Furthermore, few devices are needed, which saves costs. It is also estimated that remediation times are short.

This chapter will introduce the applied chemicals, their reaction mechanisms, advantages and disadvantages, experiences and recent studies and the available ISCO technology. ISCO is relevant to this work, as the electrochemically synthesized oxidants are distributed via an electric field into the soil matrix, where they will oxidize organic pollutants. The method described in this work only differs from classical ISCO by the electrokinetic distribution of the oxidants and their electro synthesis with diamond electrodes.

## 7.1 ISCO Chemicals

ISCO chemicals have first been applied in waste water treatment. Therefore, chemical reactions and the applicability to certain pollutants has already been investigated. In Table 4 the standard oxidation potentials of strong oxidizing agents are presented.

Table 4: Standard oxidation potential of ISCO chemicals [9, p. 2], [34 p. 2]

| **Chemical Species** | **Standard Oxidation Potential (Volt)** |
|---|---|
| Hydroxyl radical/Fenton's reagent ($OH^\circ$) | 2.8 |
| Sulfate radical ($SO_4^{\circ -}$) | 2.6 |
| Ozone ($O_3$) | 2.1 |
| Peroxodisulfate ($S_2O_8^{2-}$) | 2.0 |
| Hydrogen peroxide ($H_2O_2$) | 1.8 |
| Permanganate ($MnO_4^-$) | 1.7 |

Until present day, only permanganate oxidation has been applied in a number of field applications for remediation. Fenton's reagent, ozone and peroxodisulfate including the sulfate radical are emerging technologies in experimental stage. [9, p. 2]

In the following, chemical reactions of hydrogen peroxide and peroxodisulfate are presented. Additionally, advantages and disadvantages of the application of these two ISCO chemicals are discussed. In Appendix 2 – Additional ISCO Chemicals the same information is given for permanganate and ozone.

### 7.1.1 Hydrogen Peroxide/Fenton's Reagent

The reaction mechanisms of hydrogen peroxide are complex due to numerous side and competing reactions. Until now, a detailed field study of in-situ oxidation with hydrogen peroxide or the Fenton's reagent is lacking. With iron activation hydrogen peroxide can increase its oxidation potential by forming a hydroxyl radical according to Fenton's reaction (see Eq. 4). Best conditions involve acidic pH-values. [34, pp.9]

Eq. 4: $H_2O_2 + Fe^{+2} \rightarrow OH^- + OH^\circ + Fe^{3+}$

The radical is very short-lived, can migrate only nanometers and its concentration is therefore very low. This results in the difficulty of having to provide hydrogen peroxide, a catalyst, and the contaminant in the same place at the same time for successful oxidation [9, p. 9]. Furthermore, $OH^\circ$ is an unspecific oxidant and thus prone to scavengers. In soil these are typically carbonates. Also, the same Fe(II) initiating the activation reaction of hydrogen peroxide can function as a scavenger (see Eq. 5).

Eq. 5: $OH^\circ + Fe^{2+} \rightarrow OH^- + Fe^{3+}$

In order to avoid the scavenging effect of iron ions, assays have been conducted with chelated iron, which promises better success [36, p. 1226].

The radical can initiate chain propagating reactions, in which several radical species are formed. The organic pollutant (RH) is also subject of the radical reactions. Terminating reactions can involve iron as mentioned above or the reaction of two radicals (see Eq. 6 till Eq. 9).

Eq. 6: $OH^\circ + H_2O_2 \rightarrow HO_2^\circ + H_2O$

Eq. 7: $HO_2^\circ \rightarrow O_2^{\circ -} + H^+$

Eq. 8: $OH^\circ + RH \rightarrow R^\circ + OH^-$

Eq. 9: $R^\circ + H_2O_2 \rightarrow ROH + OH^\circ$

When applying hydrogen peroxide, special attention has to be paid to heat and gas evolution. Volatile compounds may escape with the evolving gas into the environment. Therefore, gas monitoring and extraction is necessary. On the other hand, controlled exothermic reactions might desorb or dissolve organics and NAPLs and make them available for degradation. However, DNAPLs can be mobilized as well, resulting in a groundwater contamination plume. Hydrogen peroxide’s advantages are the high oxidation potential and the potential to treat mixtures of contaminants. [9, p. 20], [10, pp.6], [18, p. 210], [34, pp. 9 - 14]

### 7.1.2 Peroxodisulfate/Sulfate Free Radical

Peroxodisulfate in non-activated and activated form is the newest oxidant in ISCO applications. Peroxodisulfate has a stability of one to two weeks in soil. Even though, this is an asset, it has to be considered that $S_2O_8^{2-}$ is kinetically slow in reacting with organic contaminants [37, p. 1]. Usually, sodium peroxodisulfate is used for in-situ remediation as it is sufficiently soluble in water and does not produce ammonia like ammonium peroxodisulfate [9, pp. 19]. Its reactions vary with pH conditions (see Eq. 10 till Eq. 13) [34, p. 7]:

Eq. 10: $S_2O_8^{2-} + 2\,H_2O \rightarrow 2\,HSO_4^- + 0.5\,O_2$ (for pH 7)

Eq. 11: $S_2O_8^{2-} + 2\,H_2O + H^+ \rightarrow 2\,HSO_4^- + H_2O_2$ (for pH 3 – 7)

Eq. 12: $S_2O_8^{2-} + 2\,H_2O + H^+ \rightarrow 2\,HSO_4^- + HSO_5^-$ (for pH < 3)

Eq. 13 : $S_2O_8^{2-} + OH^- \rightarrow HSO_4^- + SO_4^{2-} + 0.5\,O_2$ (for pH > 13)

When heat, UV radiation or a catalyst (mostly $Fe^{2+}$) is applied, the peroxodisulfate anion produces sulfate free radicals (see Eq. 14 and Eq. 15) [9, p. 19]. A radical disposes of an unpaired electron and is therefore highly reactive. The existence of the sulfate free radical has been proven by absorption spectra. The adsorption wave length is about 450 nm [38, p. 533]. The sulfate free radical is comparable to the hydroxyl radical in oxidative strength and in reaction velocity which results from its electrophilicity [39, p. 163].

Eq. 14: $S_2O_8^{2-} \rightarrow 2\,SO_4^{\circ -}$ (for > 40 °C)

Eq. 15 : $Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{\circ -} + SO_4^{2-} + Fe^{3+}$

Other catalysts can be Ag >> Co > Cu, Fe, > Pt listed according to their efficiency [35, p. 4]. Chain propagating reactions are as follows (see Eq. 16 till Eq. 18) [34, p. 8], [37, p. 2]:

Eq. 16: $SO_4^{\circ -} + RH \rightarrow R^{\circ} + HSO_4^{-}$

Eq. 17: $SO_4^{\circ -} + H_2O \rightarrow OH^{\circ} + HSO_4^{-}$

Eq. 18: $SO_4^{\circ -} + OH^{-} \rightarrow OH^{\circ} + SO_4^{2-}$ (for alkaline pH)

$OH^{\circ}$ reacts with the organic compound as shown in Eq. 8. Eq. 17 has a very low rate constant in comparison to the sulfate radical reaction rate with organics (reviewed by [37, p. 2]). Both radicals, $OH^{\circ}$ and $SO_4^{\circ -}$, can be responsible for the decomposition of organics. Which one predominates depends on the pH-value. As reviewed by Liang et al. [37, p. 2] the sulfate radical predominates under acidic conditions, while the hydroxyl radical prevails in an alkaline environment. Radicals react by three mechanisms with organics: 1) hydrogen abstraction, 2) hydrogen addition and 3) electron transfer. Sulfate radicals are known to react rapidly with aromatic compounds and with higher selectivity than $OH^{\circ}$. This suggests that $SO_4^{\circ -}$ reacts rather by an electron transfer mechanism than hydrogen addition or withdrawal [37, p. 2], [39, p. 163].

The equations above show that the sulfate free radical can initiate a number of radical reactions, which can lead to the effect that theoretically less than the stoichiometric amount of peroxodisulfate is needed for pollutant oxidation. Chain terminating reactions take place between two radicals, in Eq. 19 self decay is presented [38, p. 533], or with the same iron catalyst as shown in Eq. 20 [34, p. 8]. Thus controlling the amount of the catalyst is paramount for good oxidation efficiency. This can be achieved by sequential addition of the catalyst or by chelating it [36, p. 1232], [40, p. 1214].

Eq. 19: $SO_4^{\circ -} + SO_4^{\circ -} \rightarrow S_2O_8^{2-}$

Eq. 20: $SO_4^{\circ -} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+}$

The half life of the sulfate free radical is reported to be about 4 seconds [40, p. 1214]. If $Fe^{2+}$ is used as catalyst, acidic conditions are needed in order to keep the ion in solution. However, it also functions as a scavenger. A disadvantage of peroxodisulfate usage is the drop in pH when peroxodisulfate is degraded. This unbalances the soil system. As peroxodisulfate is corrosive the equipment material should be chosen carefully [34, pp. 8]. An advantage of peroxodisulfate over permanganate is that it can oxidize benzene and is therefore apt to treat BTEX and fuel spill contaminated sites. Furthermore, peroxodisulfate seems to react to less extent with soil organic matter. Another plus for peroxodisulfate is its ability to form free radicals, however, the same factor can be a drawback as the administration of the right mixture of peroxodisulfate and catalyst might be difficult. Furthermore, information on soil remediation with peroxodisulfate is very rare, and its application to vadose soil zone has not been reported. [9, pp. 20]

## 7.2 Requirements and Applications

In order to be able to oxidize a pollutant the oxidant needs to get in contact and react with it. Thus, a critical factor is the distribution of the oxidant and its reactivity with the specific contaminant. It needs to be considered that there are several factors of influence which can reduce the oxidant's effectiveness as presented in Table 5.

Table 5: Factors of influence on ISCO [10, pp. 10 – 12], [34, p. 4], [35, pp. 1 – 5], [37, p. 2]

| **Parameter** | **Influence** |
|---|---|
| Temperature | Reaction kinetics and heat catalyzed formation of radicals are dependent on temperatures. |
| pH-value | Depending on the oxidizing agent neutral, alkaline or acidic conditions are advantageous. |
| Presence of metals | Easy oxidizable metals can act as scavengers, multi valent metals such as iron, copper, cobalt and manganese can act as catalysts and scavengers. |
| Soil organic matter (SOM) | SOM may act as scavenger. |
| Oxidants | Depending on the oxidant, different concentrations for administration are necessary. Save storage needs to be considered. Taking into account the reaction velocity, highly reactive and unspecific oxidants can travel only short distances. |
| Availability of pollutants | Bonding between soil minerals or SOM and pollutants can reduce their availability. Also pollutants' characteristics such as density and hydrophobicity may complicate the oxidant's access to their prevailing residence area. |
| Soil characteristics | Permeability, homogeneity, texture, hydrogeological conditions and SOM amongst others are of importance. |

Considering soil parameters, the distribution of oxidants is the better, the more porous the matrix. This means that sandy soils are better apt than low particle soils for ISCO applications. If the permeability is very low, diffusion will play an important role in the oxidants' distribution, therefore they need to be long-lived. This is the case for permanganate and peroxodisulfate. Radicals are too short-lived for low permeability soils. However, applying electrokinetic distribution, as in this study, makes these disadvantages less severe. Good distribution also occurs in low water conductivity soils. As far as the saturation of the soil is concerned, peroxodisulfate and permanganate are more convenient in the vadose zone than radicals. The best option would be ozone, which, however, is costly and has the lowest performance in the saturated zone. For groundwater remediation, radicals are more efficient for higher current velocities of groundwater. For lower velocities permanganate and peroxodisulfate are appropriate. [10, pp. 10] So, in theory, peroxodisulfate and the sulfate free radical complement each other perfectly for all kinds of soil and groundwater conditions. Peroxodisulfate is stable enough to migrate longer distances to reach the pollutant and local activation by catalyst guarantee good oxidation success [41, p. 419].

Table 6 shows the applicability of different oxidants to diverse pollutants. Peroxodisulfate and the sulfate free radical together are able to oxidize a wide range of contaminants. Only ozone can top the theoretical success.

Table 6: Applicability of oxidants to certain pollutants [9, p. 3], [10, p.10]

| **Pollutant** | **$MnO_4^-$** | **$S_2O_8^{2-}$** | **$SO4^{\circ -}$** | **Fenton's Reagent** | **$O_3$** |
|---|---|---|---|---|---|
| alkane | - | - | + | + | + |
| alkene | + + | + + | + + | + + | + + |
| BTEX | + + | ? | + + | + + | + + |
| benzene | - | + | + + | + + | + + |
| phenols | + | + | + + | + + | + + |
| chloro-phenols | + | - | + + | + + | + + |
| nitro-phenols | - | - | - | ? | ? |
| PCE, TCE | + + | + | + + | + + | + + |
| toluol | + + | + + | + + | + + | + + |
| ethylbenzene | + + | + + | + + | + + | + + |
| PAH | + | + | + + | + + | + + |
| PCB | - | - | - | - | + |
| MTBE | + | + | + + | + | + |

++ = very good efficiency, + = good efficiency, -= poor or no efficiency, ? = no data available

However, when applying any oxidant, the organic pollutant might not be oxidized completely. Therefore, an evaluation of metabolites has to be conducted in order to assure their innocuous nature. Also, the migration potential of metals can be elevated by oxidation. So possible heavy metals such as As, Ba, Cd, Cr etc. should be monitored. Last, the concentration of sulfate in groundwater needs to be checked [10, p. 12]. According to ÖNORM S 2088-1 sulfate concentration must not exceed 150 mg/l.

## 7.3 Literature Experiences with Fenton’s Reagent

Fenton’s reagent has been investigated more thoroughly than peroxodisulfate for its application in in-situ soil remediation. Even though this project does not focus on hydrogen peroxide, experiences from scientific research shall be mentioned here (Table 7). In contrast to peroxodisulfate studies hydrogen peroxide has been tested not only in water but also in soil matrices. This provides valuable information for the investigation conducted for this thesis. Additionally, petroleum and diesel degradation has been tested, whereas, almost exclusively, VOCs have been oxidized with peroxodisulfate in scientific studies.

Table 7: Summary on contaminant elimination with hydrogen peroxide

| **Contaminant** | **Elimination** | **Initial contaminant concentration** | **Hydrogen peroxide amount in ml/g soil and concentration** | **Catalyst** | **Catalyst concentration** | **Soil type** | **Reaction time** | **Ref.** |
|---|---|---|---|---|---|---|---|---|
| diesel | 99 % | 1000 mg/kg | 1 (1.5 M) | iron (III) perchlorate | 25 mM | silty loam | 1 h | [18] |
| diesel & kerosene | 70 % | 1000 mg/kg | 1 (35 %) | magnetite | 5 wt% | silica sand | 192 h | [32] |
| BTX | 95 % | 15 mmol/kg | 1 (2.5 %) | iron (III) sulfate | 12.5 mM | loamy sand | 2 h | [42] |
| nonane | 37 % | 15 mmol/kg | 1 (2.5 %) | iron (III) sulfate | 12.5 mM | loamy sand | 2 h | [42] |
| decane | 7 % | 15 mmol/kg | 1 (2.5 %) | iron (III) sulfate | 12.5 mM | loamy sand | 2 h | [42] |
| dodecane | 1 % | 15 mmol/kg | 1 (2.5 %) | iron (III) sulfate | 12.5 mM | loamy sand | 2 h | [42] |
| TCE | 40 % | 19.5 g/kg | 1.33 (3 %) | iron present in sand | 0.04 g/kg | sand slurry | 1 h | [5] |
| TCE | 42 % *) | 3 g/kg | - (3 %) | iron present in sand | 0.04 g/kg | sand | -**) | [5] |
| transformer oil | > 80 % | 17.4 g/kg | 1 (0.7 %) | iron present in sand | 4.52 g/kg | sand | 72 h | [43] |
| transformer oil | 60 % | 19.0 g/kg | 20 (0.08 %) | iron present in peat | 2.64 g/kg | peat | 72 h | [43] |

*) 100 % minus TCE remaining in the sample and in the effluent; **) 5 pore volumes at a velocity of 8.5 cm/h

All assays have been conducted at near neutral pH-value and room temperature

Referring to Watts et al. [42] the outcome of the study is that the more toxic compounds of diesel, namely BTX, have been destroyed and the health risk is reduced significantly, while the less toxic aliphatic constituents, i.e. nonane, decane and dodecane, can hardly be oxidized. Thus, the authors suggest treating only the aromatic part of gasoline contamination in order to save time and money while revising the applied threshold value and the analytical method for evaluating the potential danger of gasoline contaminated sites. Two further studies revealed additional information. Yeh et al. [33] investigated the effect of soil organic matter (SOM) for the oxidation of chlorophenols with catalyzed hydrogen peroxide in loamy sand soil. An oxidation – desorption – oxidation scheme is proposed where initially part of the SOM is oxidized, which leads to desorption of the contaminant, which then is oxidized by the remaining reagent. Ferguson et al. [44] found that in-situ chemical oxidation of diesel contaminated Antarctic soil with hydrogen peroxide is not an appropriate technology to solve the problem. The low temperatures and permafrost soil inhibit successful chemical oxidation. Activation by heating is not recommendable due to possible melting of the permafrost soil and the potential spread of the contaminant into deeper soil layers. Thus, ISCO is restricted for temperate climate zones.

Resuming the outcomes of these studies the following aspects should be considered for ISCO treatment:

1. Natural occurring iron minerals, such as goethite and magnetite, can enhance the oxidation process by peroxygen (i.e. hydrogen peroxide) compound activation.

2. When treating multi component contaminants such as gasoline, attention should be paid to intermediate products; often the more toxic compounds (aromatic hydrocarbons) are oxidized almost completely reducing the sites hazardous potential, while the legal threshold value can not be met due to little depletion of aliphatic less hazardous compounds.

3. SOM should be determined beforehand, as it has great influence on the oxidation success and efficiency.

4. DNAPLs can be treated, however, solubilization by partial oxidation needs to be considered and additional groundwater treatment might be necessary.

5. ISCO seems to be inadequate for permafrost regions and extreme cold climate zones.

## 7.4 Literature Experiences with Peroxodisulfate

Among the number of oxidants used in soil remediation, peroxodisulfate is the chemical less investigated [45, p. 552]. In this chapter a number of studies shall be reported (see Table 8) in order to obtain an overview of peroxodisulfate's strengths and successful laboratory application.

Table 8: Summary of peroxodisulfate application for contaminant elimination

| **Contaminant** | **Purpose of study** | **Elimination** | **Initial contaminant concentration** | **Oxidant concentration** | **Catalyst** | **Medium** | **Reaction time** | **Ref.** |
|---|---|---|---|---|---|---|---|---|
| MTBE | influence of pH-value, temperature, oxidant concentration | 96 % | 0.06 mM | 43.3 mM | heat, 40 °C | water,<br>pH 7 | 3 h | [41] |
| phenol as constituent of creosote | degradation of creosote components in water with peroxodisulfate | 97 % | 0.98 µg/l | $8.9*10^{-8}$ mol/l | $Fe^{2+}$,<br>$7.1*10^{-8}$ mol/l | water,<br>pH 2 | 2 d | [46] |
| TCE | examination of iftransition metals can activate peroxodisulfate to produce sulfate free radicals | 66 % | 0.45 mM | 9 mM | $Fe^{2+}$,<br>6.8 mM | water,<br>pH 5 | 10 min | [40] |
| TCE | examination of conditions under which transition metals can activate peroxodisulfate to produce sulfate free radicals | 99.6 % | 0.45 mM | $S_2O_8^{2-}/S_2O_3^{2-}$<br>9/2.3 mM | $Fe^{2+}$,<br>2.3 mM | water,<br>pH 5 | 20 min | [40] |
| TCE | oxidation of TCE in water and soil slurry systems with peroxodisulfate and chelated iron(II) catalyst | 100 % | 0.45 mM | 9 mM | $Fe^{2+}$/citric acid<br>4.5 mM/0.9mM | water,<br>pH 2.8 | 20 min | [36] |
| TCE | oxidation of TCE in water and soil slurry systems with peroxodisulfate and chelated iron(II) catalyst | 100 % | 0.45 mM | 9 mM | $Fe^{2+}$/citric acid<br>4.5 mM/0.9 mM | soil slurry<br>83 % water | 3 h | [36] |
| VOCs | treatability of 59 VOCs with thermally activated peroxodisulfate at 20, 30 and 40 °C | 90 – 100 % (for 37 VOCs) | 100 µg/l each | 21 mM | heat, 40 °C | water | 72 h | [45] |
| TCE | influence of pH-value at 10, 20 and 30 °C | 100 % | 0.46 mM | 23 mM | - | water,<br>pH 7 | 50 h | [37] |
| PCE,<br>TCE,<br>cis-DCE | part of the US EPA Superfund program, testing of peroxodisulfate ISCO application in spiked groundwater/soil matrices | 74 % (PCE)<br>86 % (TCE)<br>84 % (cis-DCE) | 8 mg/l (PCE)<br>8 mg/l (TCE)<br>26 mg/l (cis-DCE) | 1.0 g/l | - | groundwater/ soil matrix | 120 h | [47] |

if not stated otherwise, reaction temperature was 20 °C

With respect to the study conducted by Huang et al. [41], it was found that increasing pH and ionic strength slow down degradation, whereas higher temperature and oxidant concentration speed up the reaction. Near neutral pH the half life of MTBE at 50 ℃ was found to be 0.3 hours, whereas it is 14.8 hours at 20 ℃. The formed MTBE metabolites were tert-butyl formate, tert-butyl alcohol, acetone and methyl acetate, which are all degradable by peroxodisulfate. However, results in groundwater were less successful than in synthetic solutions, probably due to the presence of scavenger carbonates. It is suggested to do further testing on this oxidation technology for groundwater and soil systems. Huang et al. [45] revealed that compounds with carbon – carbon double bonding and benzene rings attached to functional groups were degraded more rapidly. In contrast, saturated hydrocarbons and halogenated alkanes were difficult to deplete. According to Liang et al. [37] best degradation occurs at pH 7. Half lives of TCE at 10, 20 and 30 ℃ are 116, 35 and 6 h respectively. Thus, the influence of temperature is evident. Furthermore, the reduction rates slow down with increasing and decrasing pH-values. If not controlled, pH will drop due to the nature of the peroxodisulfate reaction. A prior study realized by Balasz [35] tested several transition metal catalysts for degradation of ethylene glycol, 1,3-dichloro-2-propanol, 1,1,1-trichloroethane and tributyl-phosphate with peroxodisulfate. The aqueous solution was acidified. Experiments were run at 80℃. It was found that the following metals are apt for catalysis: Ag >> Co > Cu, Fe > Pt. The authors recommend applying an oxidant concentration of at least 0.5 M for optimal efficiency for treatment of chlorinated organics.

Concluding from the findings of the above mentioned studies, the following aspects should be considered for the in-situ oxidation with peroxodisulfate:

1. The influence of temperature needs to be taken into account. Laboratory experiments were conducted in a range of temperatures between 80 and 10 ℃, finding that the half life for TCE is 21 times longer at 10 ℃ than at 30 ℃. Temperature conditions in soil are likely to be around 10 ℃.

2. Both, increase and decrease in pH diminish the performance of peroxodisulfate remediation. Due to the nature of peroxodisulfate reactions, the pH-value will decrease. Thus, it is recommendable to control pH conditions.

3. As for hydrogen peroxide, the same difficulty with catalysts applies: the same ion, i.e. Fe(II), which serves as catalyst, can turn into a scavenger. The solution of chelated iron complexes does not seem to be as successful in soil application according to Dahmani et al. [47, p. 139]. Also carbonates in groundwater impede good performance of peroxodisulfate remediation.

4. The pollutants tested in the above mentioned studies include mainly chlorinated compounds and VOC. The oxidation of aliphatic pollutants and contaminants with a variety of organic compounds, such as diesel, has not been investigated yet.

5. Apart from the mentioned field application, there is almost no scientific base for peroxodisulfate performance in soil.

## 7.5 Available Peroxodisulfate ISCO Technology

According to the EPA, peroxodisulfate remediation technology is only in the state of development. Neverthless, there are several companies already offering ISCO remediation with peroxodisulfate. Most of the companies are located in the US. However, there are also internationally active firms. Table 9 presents a selection of ISCO peroxodisulfate technology offering companies.

Table 9: Companies providing ISCO technology with peroxodisulfate

| **Company Name** | **Contaminants** | **Method and Experiences** | **Ref.** |
|---|---|---|---|
| ISOTEC$^{SM}$ | petroleum spill, BTEX, MTBE, chlorinated alkenes (PCE, TCE), chlorinated alkanes (TCA), PAH | sodium peroxodisulfate catalyzed by heat, hydrogen peroxide or chelated iron complexes producing sulfate free radicals, individual application or together with Fenton's reagent or permanganate | [48] |
| FMC Corporation | chlorinated compounds, PAH, petroleum hydrocarbons, BTEX and MTBE | application of activated peroxodisulfate product named Klozur$^{TM}$<br>application in over 30 states of the USA | [49] |
| Redox Tech, LLC | MTBE, BTEX, naphthalene, chlorinated alkenes and alkanes | application of peroxodisulfate in solution activated by steam injection, hydrogen peroxide or iron-EDTA<br>operation of two pilot scale experiments, an underground petroleum storage tank and an EPA superfund site | [50] |
| Geo-Cleanse International, Inc. | pesticide and TCE | the company is currently developing ISCO treatment with peroxodisulfate<br>experiences in three bench scale studies | [51] |
| Advanced Oxidation Technology, Inc. | chlorinated compounds, MTBE, TCE and phenols | ex-situ treatment with peroxodisulfate catalyzed by VTX, the company's proper catalyst | [52] |
| In-situ Technieken | - | provides ISCO remediation with fluoride, ozone, Fenton's reagent, hydrogen peroxide and permanganate<br>one of the very few companies offering ISCO in Europe | [53] |

A list of patents concerning peroxodisulfate ISCO remediation technology can be found in Appendix 3 – Patents.

## 7.6 Useful Information for Laboratory Scale Experiments

Learning from above presented scientific studies and commercial applications of peroxodisulfate chemical oxidation, it is obvious, that there is a great number of variables that influence treatment performance. Therefore, several parameters, which will not be changed during the laboratory investigation, have to be determined in advance in order to keep the number of assays reasonable. The following list will give an overview of aspects to consider.

- **Soil Characteristics**: In order to produce a wide spectrum of results that cover a large number of different soils and its characteristics the following important parameters have to be considered:
  1) Soil permeability and particle sizes are important for the administration of oxidants and the probability of contact between oxidant and pollutant.
  2) Soil organic matter has an influence on the strengths of sorption of organic pollutants to the soil and their availability for chemical oxidation. It also functions as a scavenger.
  3) On the one hand, metals can act as catalysts as in the case of iron, but on the other hand can function as scavengers. Additionally, heavy metals can be mobilized by oxidation or in an acidic environment.
  4) Treatment success in saturate and vadose conditions should be determined.

- **Temperature:** The influence of temperature on the reaction kinetics and therefore the remediation time needs to be taken into account. Therefore, simulating subsurface soil conditions would be adequate, i.e. working with temperatures around 8 to 15 ℃.

- **Pollutant:** According to the selection of pollutants it might be necessary to analyze intermediate species as in the case of diesel oil, where aromatic compounds are rather oxidized than aliphatic constituents, in order to determine the actual reduction of hazard potential.

- **pH-Value:** The development of pH conditions should be monitored as it is known that pH will drop decreasing the remediation performance.

- **Oxidant and Catalyst:** The concentrations of peroxodisulfate and its catalyst should be varied in order to find an optimal combination for a group of pollutants. It has to be kept in mind, that an overdose of catalyst might have adverse effects, namely the catalyst turning into a scavenger.

For the laboratory experiments of this study, it has been decided to work at a temperature of about 15 to 17 ℃ in a dark surrounding in order to avoid heat and UV catalysis. Furthermore, one cyclic and one multi component pollutant were chosen, namely phenol and diesel oil. The spiked soil was mixed directly with the oxidant in order to exclude the possible lack of contact between peroxodisulfate and pollutant. Likewise, the influence of soil organic matter is not considered as the chosen soil type does not dispose of any natural organic compounds. The water content was set at 20 % on a wet basis. Thus, in a first series of experiment only the concentration of peroxodisulfate and general presence of a catalyst were investigated.

# 8 Synthesis of Oxidants with Diamond Electrodes

This chapter will focus on several aspects concerning diamond electrodes. First, diamond electrodes will briefly be characterized and their advantages will be pointed out. Then, the specific electrodes used for this work and their development in the course of the project will be described. Finally, the production of oxidants, especially peroxodisulfate, is explained, before giving useful details for laboratory scale experiments involving diamond electrodes.

## 8.1 Diamond Electrodes

The first reports on diamond electrochemistry were written by the early 1980s, more thorough investigation was conducted from the 1990s on, when applications in electro analysis and electrochemical water treatment were fostered [54, pp. 3]. Boron-doped diamond electrodes (BDD) consist of a substrate, on which diamond crystals are implanted or deposited and resemble semi metallic conductors. By now, BDD are commercially used in electro analysis, waste water treatment and electro synthesis of inorganic and organic compounds.

### 8.1.1 Fundamentals and Characteristics of BDD

Diamond electrodes offer several advantages in comparison to other electrodes. Some of BDD electrodes' special characteristics are:

- extremely wide potential window of water stability,
- ability of synthesis of strong oxidizing agents,
- resistance from fouling and
- chemical stability in aggressive media. [55, p. 1950], [56, p. 1062], [57], [54, p.2], [58, p. 26]

BDD electrodes have shown advantages over several traditional electrodes and their applications. Titanium/metal-oxide electrodes (Pt, Sn, Sb, As, Nb, Zr, Pb) have been tested for the decomposition of organic pollutants and electro synthesis of oxidants. However, they present a number of disadvantages, such as the formation of chloro-organic compounds, low current efficiency and the inability of mineralizing organic species. Lead-dioxide electrodes decompose themselves during utilization by releasing lead ions into the electrolyte. Platinum electrodes are prone to corrosion and have also lower current efficiencies, especially in the application of oxidants' synthesis (see Figure 16). Graphite or carbon-based electrodes produce carbon dioxide during operation by decomposing themselves. Tinoxide electrodes present a limited service life and iridumoxide electrodes only provide selective oxidation of organic composites [59, p. 192], [60, pp. 24].

A further important advantage of BDD electrodes is their chemical inertness. They show high corrosive stability even in acidic fluoride media and dispose of an inert surface with low adsorption properties, which inhibits fouling [59, p. 192]. As far as reaction mechanisms on the diamond surface are concerned, two types have been described. The first is a direct electrochemical oxidation involving electron exchange between the BDD surface and the reactant. The second process is an indirect oxidation, where oxidative species formed at the anode, i.e. hydroxyl radicals, oxidize the reactant [59, p. 192].

### Potential Window

The main advantage and most important characteristic of diamond electrodes is the wide potential window, which implies a high overvoltage for oxygen and hydrogen evolution. The purer the diamond surface, the wider is the potential window of the electrode. This can have a range of up to 4 V [58, pp. 28]. As diamond electrodes have poor surface adhesion qualities, the evolution of gas bubbles, such as oxygen, is suppressed until reaching a certain potential, which is the reason for the high overvoltage for water stability. This also leads to the supposition that electrolyte species (anions, organic/inorganic pollutants) do not react directly with the electrode, which can extensively inhibit fouling [61, p. 209]. Figure 10 shows a representative potential window of BDD electrodes. BDD electrodes, produced by chemical vapor deposition (CVD) have overpotentials up to 2.8 V on the anodic and -1.3 V for the cathodic side. Considering the potentials for the generation of oxygen (1.30 V), peroxodisulfate (2.01 V), ozone (2.07 V) and the hydroxyl radical (2.80 V), all of these powerful oxidants can be generated [62, p. 642].

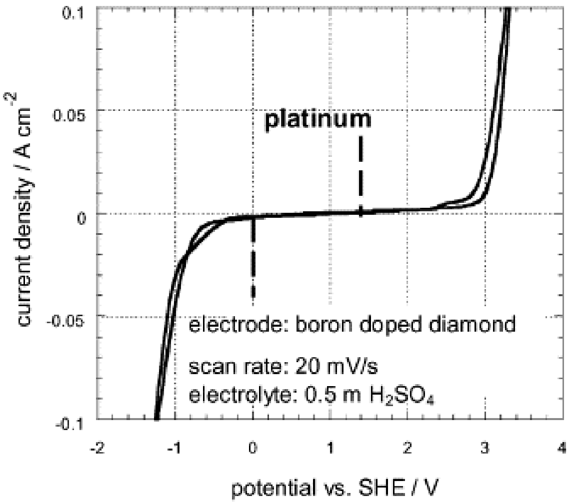

Figure 10: Potential window of CVD BDD electrodes [62, p. 642]

Figure 11[1] demonstrates the potential window of the mechanically implanted (MI) BDD electrode on titanium basis, which has been one model used in this study. The potential of oxygen evolution is marked. If the potential of the anode lies above the oxygen potential, oxygen will not be evolved until the current rises in the diagram. All oxidants having a lower

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[1] The actual measurement has been conducted in reference to SCE (standard calomel electrode). So 241 mV were added to the potential values as SCE vs SHE (standard hydrogen electrode) is 241 mV.

generation potential than this point can be produced. Even though, the MI electrode's anodic potential is lower with > 2000 mV than the CVD electrode's potential with > 2500 mV, it suffices for the electrochemical generation of peroxodisulfate, ozone and hydrogen radicals at higher currents.

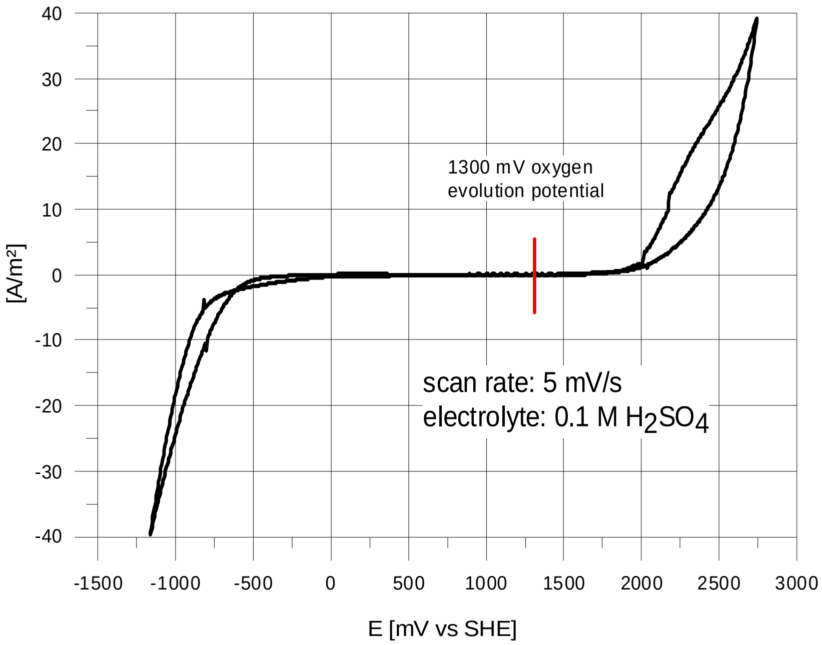

Figure 11: cyclic voltammogramme of an MI BDD electrode [63]

### 8.1.2 Fabrication Methods

Principally, there are two different ways of fabricating BDD electrodes, chemical vapor deposition (CVD) and mechanical implantation (MI). Latter type electrode has been used in this work and will therefore be explained briefly. Information on the CVD process can be obtained from Appendix 4 – Chemical Vapor Deposition Process.

#### Mechanical Implantation Process

Even though CVD BDD electrodes have many advantages (see Appendix 4 – Chemical Vapor Deposition Process) shearing stress and production cost have lead to the development of a new method for covering substrates with diamonds. This method is based on the mechanical implantation (MI) of premanufactured synthetic diamonds. MI electrodes are reliable for electro synthesis and waste water treatment applications. The advantages of MI BDD are:

1. low production cost
2. production of large surfaces
3. no carbide and stress generation due to lower temperatures
4. the surface density of diamonds is controllable [64, pp. 376].

The MI BDD electrode used in this study was produced by the company pro aqua Diamantelektroden Produktion GmbH. The fabrication process is as follows: The titanium substrate is treated about 30 min with boiling oxalic acid (10 %) in order to increase the surface's roughness and eliminate titanium oxide. Then the diamond crystals of 100 to 150 µm particle size are implanted mechanically by rolling. The non-covered areas of the substrate's surface are sealed with non-conductive silicon based coating, Tyranno coat ST-100 Standard. Then the electrode is heated up to 350 ℃ for 30 min for polishing with a grinding machine until the diamond crystals are visible, see Figure 12. The diamond covered area makes up about 25 +/- 5 % [64, pp. 375].

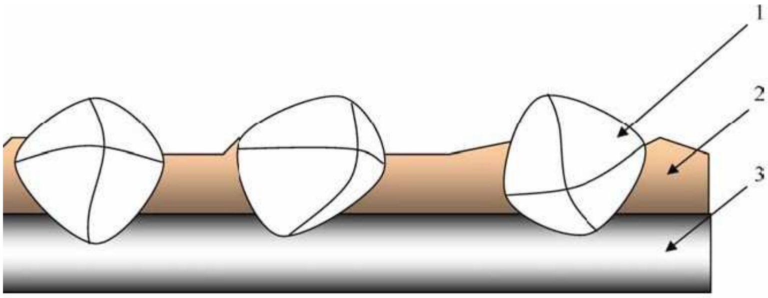

Figure 12: MI BDD electrode, 1) boron-doped diamond crystals, 2) non-conducting silicon based coating, 3) titanium substrate [64, p. 376]

The characteristics of MI BDD differ from the CVD electrodes. This is due to the different kinds diamond coatings. The MI diamond particles are bigger and dispersed over the electrode surface (see Figure 13). Therefore, MI BDD electrodes act rather like a number of micro electrodes. This might provoke inhomogeneities in local electrochemical activity. However, this does not impede applications in electro synthesis or electrochemical waste water treatment [64, pp. 378; 381].

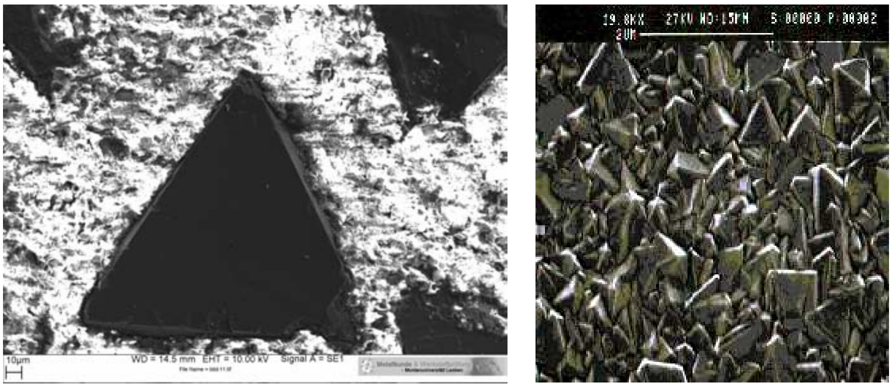

Figure 13: a) SEM picture of MI BDD electrode [65]  b) SEM picture of a polycrystalline BDD electrode [66]

Comparing Figure 13 a) and b), the difference in the diamond coating can be seen. While the CVD electrodes are covered completely with crystals, the MI electrodes are covered to less extent (25 %), while their diamonds are up to 10 times bigger.

### 8.1.3 Development of Diamond Electrode Models for the Soil Remediation Project

All information presented in this chapter has been given by the owner of the company pro aqua Diamantelektroden Produktion GmbH [67].

In the course of this study, the electrode has been modified several times and enhanced to meet better the requirements of the electro synthesis of peroxodisulfate. Experiments started with a monopolar titanium based model which was then transformed into a monopolar electrode on polymer basis. This model was sophisticated and resulted in a bipolar diamond electrode cell on polymer basis. The last two mentioned electrodes have especially been developed for integration in the soil remediation technology. They were thus prototypes which have continiously been enhanced on the basis of this study.

The first model was a titanium based MI BDD electrode as can be seen in Figure 14a. The diamonds were implanted as described above on a circular titanium base of 100 mm in diameter covering approximately 25 % of the surface [64, p. 377]. Afterwards 24 holes with a diameter of 8 mm were cut out. This provided a total area of 66 cm². The holes served transportation of the oxidants to the other side of the electrode. The shaft was used for contacting. The potential window of this electrode has been presented in Figure 11. Due to an increasing resistence of the electrode, voltages rose during experiments and the production behavior was instable. Therefore, a MI BDD electrode on polymer basis has been developed promising better stability. In order to contact the polymer foil with integrated diamonds, it had to be attached to a mixed oxide base. This was realized by simply compressing the foil and the metal base with cable binders as shown in Figure 14b.

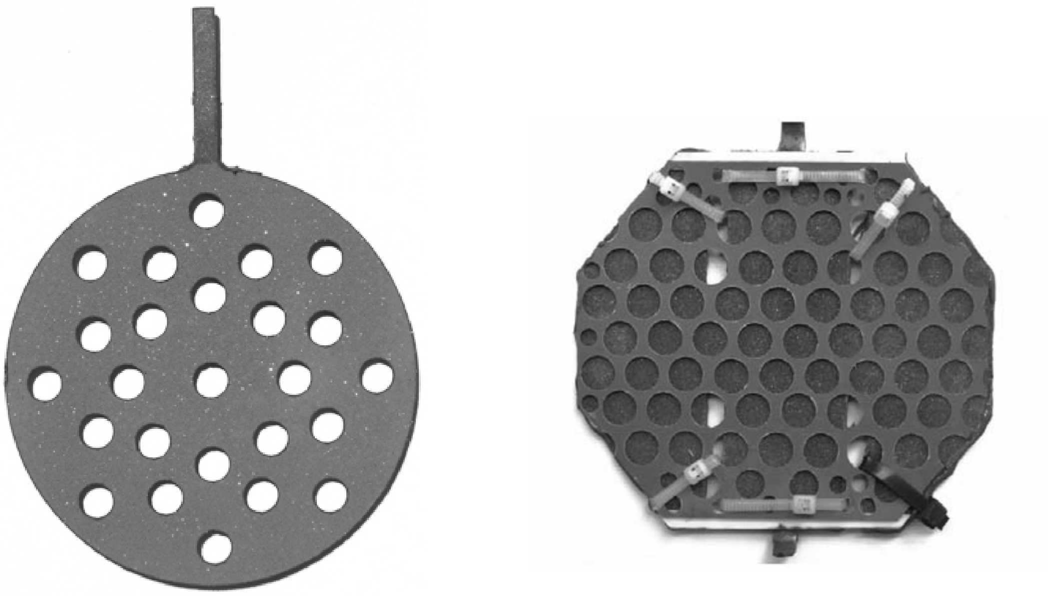

Figure 14:a) first model of a Ti MI BDD electrode, b) monopolar MI BDD on polymer basis

The area of the electrode was about 54 cm². This monopolar electrode worked according to the same principles as the Ti MI BDD electrode. However, as the performance on oxidant production was even lower, it was assumed that the bonding between the polymer foil and the mixed oxide was not strong enough and adverse reactions took place in between the materials, i.e. cathodic reduction [73]. So finally, a bi-polar electrode on polymer basis has been developed in order to avoid the contacting problem. Here, 40 % of the electrode surface were covered with diamonds [67]. This model was delivered in a cell with three electrode foils of 3 x 5 cm (i.e. 45 cm² in total). The electrodes were separated with glass fiber membranes embedded into silicon. The distance between two electrode foils was about 6 mm. Two mixed oxide plates were used as anode and cathode. Functioning in a bi-polar mode, each electrode foil has a cathodic and anodic side. A schematic set-up of the cell is shown in Figure 15.

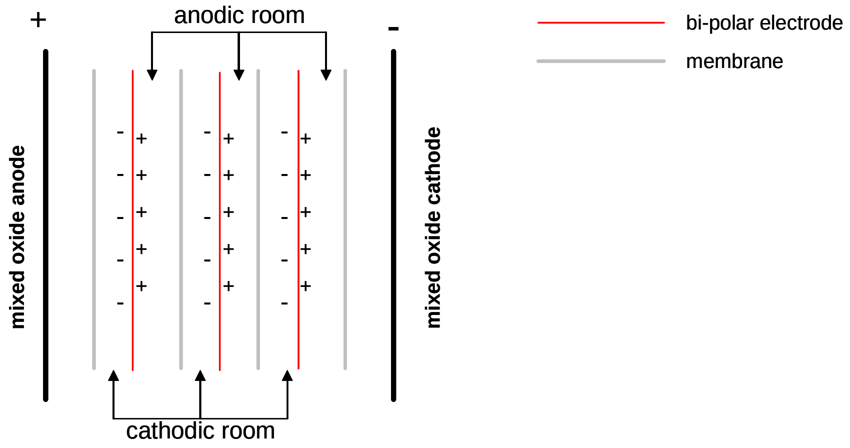

Figure 15: schematic set-up of the bi-polar MI BDD polymer electrode

## 8.2 Applications of Diamond Electrodes

A vast field of different application is being investigated recently. Known applications of diamond electrodes are:

- waste water treatment
- water disinfection
- inorganic and organic electro synthesis
- chemical and trace metal analysis [54].

Most efforts have been made in the area of waste water treatment and electro synthesis of oxidants. In thorough detail, water disinfection and industrial waste water treatment are reported in literature, because diamond electrodes are able to mineralize completely (toxic) organic pollutants. A brief literature review is given in Appendix 5 - Waste Water Treatment with BDD Electrodes, as operational parameters have been taken into account for the design of proper experiments. As far as electro synthesis is concerned, the production of strong oxidizing agents, such as hydroxyl radicals, peroxodisulfate and ozone amongst others, is being investigated. In the following, the most important aspects of electro synthesis for the generation of peroxodisulfate are explained.

### 8.2.1 Inorganic Electro Synthesis

When speaking of electro synthesis, the electricity driven generation of oxidizing reagents is referred to. BDD electrodes are ideal for this application due to their high overpotential for water stability. Mostly, hydroxyl radicals ($OH^\circ$), ozone ($O_3$), hydrogen peroxide ($H_2O_2$) and peroxodisulfate ($S_2O_8^{2-}$) are produced amongst others.

Advantages of electro synthesis with BDD electrodes over conventional synthesis are [59, p. 196]:

- Electricity driven synthesis does not have any need for extra chemical reactants, which are mostly hazardous, expensive in acquisition and disposal and difficult to handle,
- the electrochemical synthesis allows the precise control of reaction conditions and produces less side products and
- electro synthesis can reduce the overall number of process steps.

However, until now, electro generation (mainly $Na_2S_2O_8$, $KMnO_4$, $H_2O_2$, $O_3$ and metal ion redox species like $Ag^+/Ag^{2+}$) has not succeeded to be applied on industrial scale due to limitations in the availability and the stable performance of BDD electrodes [59, p.196].

In the following, general chemical reactions (Eq. 21 till Eq. 25) occurring during any kind of electro synthesis in aqueous media, are presented. According to Comninellis et al. [68, p. 469] hydroxyl radicals are generated directly at the surface of BDD electrodes:

Eq. 21: $BDD\,(H_2O) \rightarrow BDD\,(OH^\circ) + H^+ + e$ $E^\circ = 2.33\ V$

The hydroxyl radicals can then form hydrogen peroxide and ozone according to the following reactions [69, pp.485]:

Eq. 22: $2\,OH^\circ \rightarrow H_2O_2$ $E^\circ = 1.78\ V$

Eq. 23: $OH^\circ \rightarrow O^\circ + H^+ + e$

Eq. 24: $2\,O^\circ \rightarrow O_2$

Eq. 25: $O^\circ + O_2 \rightarrow O_3$ $E^\circ = 2.07\ V$

These species are therefore available in the electrolyte for oxidizing other compounds like sulfate to peroxodisulfate, on which will be put emphasis in this chapter as this oxidant shall be used for soil remediation.

### Generation of Peroxodisulfate

The main studies on peroxodisulfate generation with BDD electrode surfaces have been conducted by Comninellis et al. [68], Michaud et al. [70] and Serrano et al. [71]. Peroxodisulfate is used for cyanide oxidation, dye oxidation and fibre whitening amongst others. However, it has not been considered until recently for oxidation of organic pollutants. Comninellis et al. [68] state that BDD electrodes are more apt for peroxodisulfate synthesis than the traditionally used Pt electrodes (see Figure 16), because the electrochemical process is strongly dependent on the electrode material. Due to their resistance to corrosion and high over potential BDD electrodes meet the requirements better. Results show that high concentrations of sulphuric acid (7.5 M) and high current densities (200 mA/cm²) at 25 ℃ can achieve current efficiencies of 75 %. [69]

Serrano et al. [71] used circular CVD BDD anodes on Si substrate with a diameter of 90 mm. The distance between anode and zirconium cathode was 10 mm. The cell was fed with two circuits of anolyte and catholyte the flow rate being about 200 l/h, the temperature 9 ℃ and the applied current density 23 mA/cm². It has been found that electrolytes with higher concentrations of sulphuric acid (> 2M) result in a current efficiency of about 90 %. Lower concentrations (< 2M) result in efficiencies below 90 %. Serrano et al. [71, p. 431] suggest two reaction mechanisms for the generation of peroxodisulfate (see Eq. 26 till Eq. 32). As sulfuric acid is present in associated ($H_2SO_4$) and dissociated ($HSO_4^-$, $SO_4^{2-}$) forms, all compounds can be involved in the reaction mechanisms.

Eq. 26: $2\ HSO_4^- \rightarrow S_2O_8^{2-} + 2\ H^+ + 2\ e$ $E° = 2.12\ V$

Eq. 27: $2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e$ $E° = 2.01\ V$

The main side reaction is oxygen evolution, while a little ozone is generated, as well:

Eq. 28: $H_2O \rightarrow 0.5\ O_2 + 2\ H^+ + 2\ e$ $E° = 1.02\ V$

The second mechanism involves hydroxyl radicals generated through the anodic discharge of water:

Eq. 29: $H_2O \rightarrow OH° + H^+ + e$

Eq. 30: $HSO_4^- + OH° \rightarrow SO_4^{-°} + H_2O$

Eq. 31: $H_2SO_4 + OH° \rightarrow SO_4^{-°} + H_3O^+$

Eq. 32: $SO_4^{-°} + SO_4^{-°} \rightarrow S_2O_8^{2-}$

A competitive side reaction (Eq. 33) can be:

Eq. 33: $OH° + OH° \rightarrow O_2 + 2\ H^+ + 2\ e$

It was also discovered that lower temperatures foster good performance. At 60 ℃ the efficiency drops down to 27 %. This might be due to thermal activation of the peroxodisulfate ions, see Eq. 34 and Eq. 35, [69, p. 488]:

Eq. 34: $S_2O_8^{2-} + \text{heat} \rightarrow 2\ SO_4^{-°}$

Eq. 35: $SO_4^{-°} + H_2O \rightarrow OH° + HSO_4^-$

Comninellis et al. [68] opine that peroxodisulfate ions decompose the following way, see Eq. 36 till Eq. 38:

Eq. 36: $S_2O_8^{2-} + H_2O \rightarrow 2\ HSO_4^- + 0.5\ O_2$

Eq. 37: $S_2O_8^{2-} + H_2O \rightarrow SO_5^{2-} + SO_4^{2-} + 2\ H^+$

Eq. 38: $SO_5^{2-} + H_2O \rightarrow H_2O_2 + SO_4^{2-}$

In order to measure the current efficiency, Faraday’s law is applied (see Eq. 39). The theoretical amount of generated oxidant in moles ($mol_{th}$) is:

Eq. 39:
$$mol_{th} = \frac{1}{z*F} * I * t * \eta$$

where z is the number of electrons transfered, F is the Faraday constant in As/mol, I the current in A, t is the time in s and η the current efficiency in percent. Measuring the amount of peroxodisulfate generated (in mol) the efficiency can be calculated.

According to [72, p. 528], peroxodisulfate can be produced over a wide range of pH. The optimum for a CVD BDD electrode is found in an electrolyte of $H_2SO_4$ and $Na_2SO_4$, each of the chemicals providing 0.5 mol of sulfate ions per liter (see Figure 16).

Thus, the most important parameters for efficient peroxodisulfate production are the concentration of sulfate in the electrolyte, the current density, pH-value and temperature.

Based on above cited literature peroxodisulfate production (sodium, potassium and ammonium peroxodisulfate) has been patented (EP 1148155A2). The process applies current densities between 400 and 900 mA/cm², anolyte concentrations of 300 up to 700 g $NaHSO_4$/l, catholyte concentrations of 300 till 400 g $H_2SO_4$/l or 300 till 500 g $Na_2SO_4$/l. Additionally, anode and cathode (distance of 2.2 cm) are separated by an ion exchange membrane. Operation temperature is at 45 ℃.

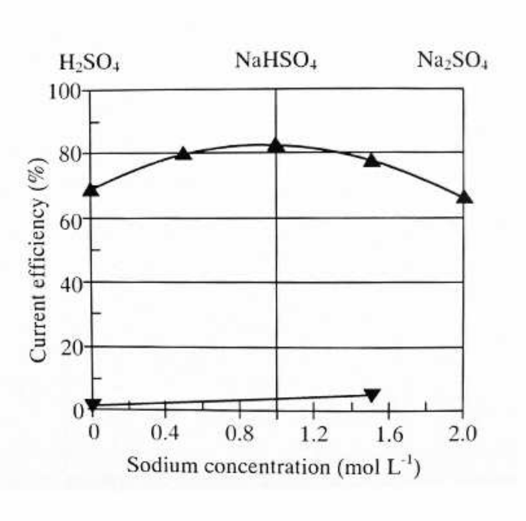

Figure 16: Current efficiency for peroxodisulfate production with varying pH-value at 25℃ and 23 mA/cm² (upper curve BDD electrode, bottom curve Pt electrode) [72, p. 528]

## 8.3 Practical Approach to Laboratory Scale Experimental Details

As mentioned in the introduction, the diamond electrode is operated as a separate subsystem producing oxidizing agents with the aim of delivering them to the electric field generated in the contaminated soil. Thus, the operation of the electrode was tested and optimized separately. Learning from the literature studied above, it turns out that a number of variables have to be considered carefully. Even though electro synthesis and waste water treatment are two different fields of diamond electrode application, it is assumed that the crucial reactions on the electrode surface are the same; namely the generation of hydroxyl radicals as presented in Eq. 21 on page 50. Following this, the hydroxyl radical can either oxidize organic substances or, with respect to peroxodisulfate synthesis, sulfate ions. So both modes of application are considered for a first determination of operation parameters. However, as all research referred to above has been conducted with monopolar CVD electrodes, there might be differences with regard to operating a bipolar MI electrode, meaning that for example higher current densities are necessary for MI than for CVD electrodes. In the following, the most important variables are presented and discussed in descending order:

- **Current Density:** For waste water treatment values range between 5 and 150 mA/cm², with 20 to 50 mA/cm² being the most common ones. Experiences from electro synthesis offer either around 20 mA/cm² or 200 mA/cm². Thus, with values differing one order of magnitude, the same range will have to be tested for the generation of peroxodisulfate with the MI electrodes.

- **Concentration of Sulfate:** Sulfate should not be the limiting factor for peroxodisulfate production. Authors speak of concentrations of < 2 M for current efficiencies below 90 % and of concentrations > 2 M till 7.5 M for higher current efficiencies. Thus, high solubility salts, sodium and ammonium sulfate, need to be applied aggregating sulfuric acid to reach high concentrations.

- **Acidity, pH-Value:** The matter of sulfate concentration leads directly to the question of the electrolyte's acidity. The limiting factor of the use of acid, is the resistance of the diamond electrode and its cell compartments. Therefore, before deciding for a highly concentrated sulfate electrolyte the electrode's resistance to acid needs to be determined.

- **Temperature:** Generally, temperature should be controlled during operation in order to maintain stable conditions. It is most probable, that temperature will rise during peroxodisulfate production as part of the energy will be transformed into heat. Therefore, working with a thermostat it advisable. Experiences from electro synthesis show that lower temperatures, 10 °C up to 25 °C, ar e optimal. With an increase in temperature the current efficiency will fall [71].

- **Membranes:** None of the scientific studies mentioned above have used membranes in order to establish separated anode and cathode compartments. However, as oxidation takes place at the anode, immediate reduction at the cathode could be an adverse effect. Sulfur is oxidized from $S^{6+}$ to $S^{7+}$ from sulfate to peroxodisulfate, so it can equally be reduced from $S^{7+}$ to $S^{6+}$ at the cathode. The industrial production of peroxodisulfate mentioned above uses separators between the electrodes.

- **Distance between Electrodes:** The distance between the electrodes is a main factor for the cell's resistance. Experiences in waste water treatment suggest using a maximum distance of 1 cm. Depending on the operation mode, batch reactor or flow cell, the distance could even be minimized. Finally, the energy consume, i.e. the resistance of the system, will determine the optimal arrangement.

Other factors to be determined are the area of the electrode, the volume and flow rate of the electrolyte and the cell arrangement. The final assessment of operation can be conducted with the Faraday equation, see Eq. 39. However, it has to be kept in mind, that it does include neither the electrode area nor the electrolyte volume, which both, however, might have an impact on the cell's performance.

# 9 Development of a New Remediation Process

The three major fields of investigation, i.e. the subsystems of the remediation method, are presented in this chapter. Chemical oxidation of diesel and phenol in soil, production of peroxodisulfate with diamond electrodes, and oxidant transport in soil have been tested parallel and independently from each other. Spiking tests have been undertaken extra before proceeding to contaminant elimination in soil matrix. All data for chemicals, analytical methods and laboratory equipment is presented in detail in Appendix 6 – Devices, Chemicals and Soil Material. Therefore, no extra specification is given in this chapter. All HC-index, phenol-index and COD analysis has been conducted in the laboratory of the Institute for Sustainable Waste Management and Technology, University of Leoben. TOC has been determined in the laboratory of Echem, Wiener Neustadt, if not stated otherwise.

## 9.1 Spiking of Test Soil

As mentioned in Chapter 5, a successful spiking methodology is the basis for a reliable interpretation of spike concentrations in soil for any kind of experiment. The initial coefficient of variance (CV) should not exceed 20 % in order to count with a homogeneity of at least 80 % of artificial contamination. In this study, spiking experiments had to be conducted previously to decomposition experiments of organic pollutants in order to assure precise contamination. The method was developed in co-operation with Böhm [86].

### 9.1.1 Materials and Methods

Spiking assays were conducted for two types of pollutants, namely diesel oil and sodium phenolate. Diesel oil was obtained as extra light heating fuel marked with red color from the A1 gas station in Leoben, Austria, and was stored in a glass bottle at room temperature. Sodium phenolate was stored in a plastic test tube at room temperature in the dark.

#### ***Spiking with Diesel Oil***

In order to spike the soil material with diesel oil, various soil components were mixed previously by hand. Generally, the synthetic soil was composed of sand, silt and zeolite (for specifications please see Appendix 6 – Devices, Chemicals and Soil Material) and had been dried beforehand. Then diesel oil was filled into a laboratory spray bottle made of glass with a capacity of 150 ml. According to previous tests, an amount of about 7 g diesel had to be applied to 1 kg of soil to obtain a concentration of ca. 5 g/kg, thus counting with a spiking efficiency of approximately 70 % due to evaporation and loss of diesel while spraying. The actual spiking was realized in an aluminum baking dish under a laboratory bell. A thin layer of soil was placed into the tray. The soil layer was subsequently sprayed with diesel so that the entire surface was wetted, then another layer of soil was added. This procedure was repeated until having used all soil material, while the spray bottle with diesel was weighed several times in order to spike the soil with the appropriate amount of contaminant. Afterwards, the spiked soil layers were mixed by using a stainless steel spoon which was moved in a zigzag line in both directions of the tray. Then, the material was filled into a plastic container in which two rectangular shaped steel bars were fixed. The receptacle was placed onto a mixer and agitated by rolling for 15 minutes. The steel bars fostered the mixing of the material. Afterwards, distilled water was added to the soil and it was mixed with a stainless steel spoon. The homogenized material was placed again into the cleaned baking dish from where five samples, one from each corner and one from the center, were withdrawn. Appendix 11 – Photos shows pictures of the procedure. The contaminated samples were analyzed according to the hydrocarbon index method EN ISO 9377 (for detailed information see Appendix 7 – Chemical Analytical Methods) as required by the Austrian Standard ÖNORM S 2088-1. TOC and COD were determined additionally in order to assure the reliability of the HC-index.

***Spiking with Sodium Phenolate***

As described above, the synthetic soil material was prepared prior to adding the contaminant. Na-Phenolate, was diluted in the respective amount of distilled water (500 mg phenol per kg of soil with a water content of 20 %) with a magnetic stirring bar at room temperature and then aggregated under constant mixing to the soil with a stainless steel spoon in a glass bowl. After having added the entire spike the material was mixed for five more minutes. Out of the entire material three samples were taken randomly. The samples were analyzed according to the phenol-index method DIN 38409-16 (for details see Appendix 7 – Chemical Analytical Methods) which is required according to the Austrian Standard of site evaluation. In order to counter check the method, TOC was measured as well. Pre-assays in order to verify the success of this spiking method have not been conducted as it was assumed that the water soluble contaminant would spread homogeneously in the wet soil.

### 9.1.2 Results and Discussion

The principal result of the spiking tests is the obtained homogeneity. Where possible, spiking efficiency is also presented, however, this parameter is not as important as the previous one as long as the exact initial concentration of a spiked specimen is determined before running an experiment. Homogeneity was calculated by equation Eq. 40:

Eq. 40: $$H = \left(1 - \frac{\sigma}{\mu}\right) * 100\%$$

where H is homogeneity, σ is the standard deviation of analysis results and μ is the mean value of the analyses' results from the samples taken.

***Diesel Oil***

Table 10 presents two spiking test series, which were the basis for choosing the above described methodology for preparing the contaminant decomposition experiments. The analysis is based on the HC-index method.

Table 10: Spiking tests analyzed for HC-index

| **Experiment** | | **1** | **2** |
|---|---|---|---|
| **Parameter** | **Unit** | | |
| **Soil** | % sand | 70 | 60 |
| | % loam | 30 | 20 |
| | % zeolite | 0 | 20 |
| | total mass kg | 3 | 3 |
| **Contamination** | g/kg DS | 7.0 | 7.8 |
| **Water Content** | % | 18.0 | 20.0 |
| **Samples** | # | 5 | 5 |
| | mass g | 20 | 20 |
| **Homogeneity** | % | **95.0** | **96.6** |
| **Efficiency** | % | 82.5 | 80.4 |

The mass of each analyzed sample equals 0.7 %, and the total of five samples 3.33 % of the entire material. The obtained homogeneity for different soil compositions and water contents, 95.0 and 96.6 %, is satisfying as the recommended homogeneity of 80 % is met. This means, that all values obtained in the decomposition experiments are subjected to a maximum coefficient of variance (CV) of 5 % due to spiking influence. Other tests have been conducted in order to verify the outcome of this analytical method. Therefore, samples were analyzed for TOC and COD as shown in Table 11.

Table 11: Spiking tests tnalyzed for TOC and COD

| **Experiment** | | **TOC** | | **COD** | |
|---|---|---|---|---|---|
| **Parameter** | **Unit** | **1** | **2** | **1** | **2** |
| **Soil** | % sand | 60 | 60 | 60 | 60 |
| | % loam | 20 | 20 | 20 | 20 |
| | % zeolite | 20 | 20 | 20 | 20 |
| | total mass kg | 1.5 | 1.0 | 1.5 | 1.0 |
| **Contamination** | g/kg DS | 7.3 | 7.8 | 7.3 | 7.8 |
| **Water Content** | % | 20 | 20 | 20 | 20 |
| **Samples** | # | 3 | 3; (2) | 3 | 3 |
| | mass g | 20 | 20 | 75 | 70 |
| **Homogeneity** | % | **95.6** | **85.6; (95.8)** | **94.6** | **98.4** |

The two alternative analysis methods show equally satisfying results compared to the HC-index method. Only the second spiking assay analyzed for TOC presents lower homogeneity. Taking into account the values obtained for each sample of the spiking experiment the third one seems to be an outlier. Calculating homogeneity from the first two values 95.8 % can be achieved. On this basis, an acceptable spiking precision of around 95 % for all analytical methods (HC-index, TOC and COD) is given. Therefore, it was decided to apply the HC-index method for analysis for the decomposition experiments as this is required by the Austrian Standard for site evaluation.

***Sodium Phenolate***

Table 12 shows the results of homogeneity for the actual treatment of soil with peroxodisulfate. Both analysis methods, TOC and phenol-index, were applied.

Table 12: Spiking tests analyzed for TOC and phenol-index

| **Experiment** | | **TOC** | | **Phenol-index** | |
|---|---|---|---|---|---|
| **Parameter** | **Unit** | **1** | **2** | **1** | **2** |
| **Soil** | % sand | 70 | 70 | 70 | 70 |
| | % loam | 30 | 30 | 30 | 30 |
| | % zeolite | 0 | 0 | 0 | 0 |
| | total mass kg | 5.0 | 5.5 | 5.0 | 5.5 |
| **Contamination** | g/kg DS | 0.5 | 0.5 | 0.5 | 0.5 |
| **Water Content** | % | 20 | 20 | 20 | 20 |
| **Samples** | # | 3; (2) | 3 | 3 | 3 |
| | mass g | 20 | 20 | 150 | 150 |
| **Homogeneity** | % | **76.4; (98.2)** | **98.4** | **82.6** | **82.9** |

The values obtained from the phenol-index method are within the acceptable range of homogeneity for the initial experimental material, i.e. superior to 82 %. However, it has to be considered that all results produced in the course of the decomposition assays will vary more than 17 %. Taking into account the TOC results for the same experiment, the presented values deviate strongly. While the TOC 2 result is close to an ideal homogeneity, TOC 1 is not situated within the acceptable range. However, leaving out the analysis of the third TOC sample in the experimental series TOC 1, homogeneity of 98.2 % is achieved. So assuming that this sample's analysis can be taken for an outlier, the TOC values show an excellent result for phenol spiking. Comparing the presented homogeneities by TOC and phenol-index analysis it strikes that the values differ by 16 percentage points. A possible explanation for this deviation is that phenol concentration was very high for the phenol-index analysis and samples had to be diluted up to 1000 times. This implies a source of error. Therefore, it can be concluded, that the chosen spiking method represents a good basis for chemical oxidation experiments of phenol.

### 9.1.3 Conclusion

Altogether, both spiking methodologies offer acceptable results on the basis of the presented data. A spiking homogeneity of > 95 % according to the HC-index for diesel oil and > 98 % according to TOC for phenol can be achieved. However, considering the two outliers, it has to be recommended to conduct further series of experiments in order to assure the good performance of the spiking procedure. Comparing the results with those cited from literature in Chapter 5, Doick et al. [20, p. 402] obtained a CV of 6.0 for spiking with 1 % of transformer oil, whereas above mentioned data implies average CVs of 4.2 for HC-index, 4.2 for TOC and 3.4 for COD for diesel spiking. Thus, an appropriate methodology for LNAPL spiking without solvent has been developed successfully.

## 9.2 Treatment of Soil with Peroxodisulfate

The purpose of the in the following described experiments was to test if the chosen oxidant, ammonium peroxodisulfate, is apt to decompose diesel oil and phenol in soil matrix. As mentioned in Chapter 7, there is almost no scientific data available on peroxodisulfate performance in soil on diesel oil, as most experiments have been conducted in aqueous media above 20 ℃ and with chlorinated compounds. T herefore, the following assays aim to simulate a more realistic situation in terms of reaction matrix and temperature conditions and to provide first data on diesel oil decomposition together with phenol oxidation in soil.

### 9.2.1 Materials and Methods

Chemical oxidation with peroxodisulfate has been conducted with sodium phenolate and diesel oil in synthetically spiked soil. The detailed spiking procedures have been described in the previous chapter. The soil material was composed of 70 % sand and 30 % loam, thus, providing coarse and fine grained particles for different adsorption and desorption mechanisms (see Chapter 3).

***Diesel Oil***

Ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) was added in its solid form in different quantities (+/- 0.1 g) to the spiked soil by mixing with a stainless steel spoon for approximately three minutes. Then, to half of the samples, iron sulfate heptahydrate ($FeSO_4$*7 $H_2O$) has been aggregated as catalyst by mixing the chemical powder (+/- 0.01 g) with the dry soil material. Finally, the respective amount of distilled water (+/- 5 ml) was added under stirring in order to obtain 20 % humidity. A concentration of around 9 g diesel per kg of soil with the mentioned humidity guarantees that diesel is present as NAPL as only 0.01 g solve in one liter of water. All samples had a mass of 250 to 350 g and were prepared individually. The difference in weight is due to distinct amounts of the oxidizing agent and catalyst. Three parameters were varied, namely oxidant quantity, reaction time and catalyst quantity as can be seen in Table 13. The samples, placed in 250 ml glasses with a plastic screw tap, were stored in the dark at a temperature ranging between 15 and 17℃.

Table 13: Variation of parameters in long-term diesel oil decomposition experiments

| Parameter | Unit | Value |
|---|---|---|
| time | weeks | 0; 1; 2; 4; 12 |
| oxidant amount | mol $(NH_4)_2S_2O_8$ per mol diesel | 0; 28.5; 142.3; 284.6 |
| catalyst | mg $FeSO_4$*7 $H_2O$ per g soil | 0; 0.7 |

The amounts of oxidant correspond to 0; 2.5; 12.5 and 25 mol ammonium peroxodisulfate per mol carbon in the spiked soil sample.

After the designated time of experiment, the sample was stirred by hand with a laboratory spatula for homogenization. Then 20 to 30 g were withdrawn in order to determine the dry substance. Previous experiments have shown that a determination with 20 g of material results in a standard deviation below 2 %. Another 20 g were handed in for HC-index analysis and stored in a refrigerator for subsequent processing or in a freezer for later analysis.

***Sodium Phenolate***

The dry synthetic soil was mixed with the respective amounts of ammonium peroxodisulfate (+/- 0.1 g) and iron sulfate (+/- 0.01 g) by stirring with a stainless steel spoon for three minutes. A certain amount of sodium phenolate (+/- 0.01 g) was diluted in distilled water in order to obtain a humidity of 20 % and a concentration of 0.50 g pollutant per kg of soil. The solution was added to each soil sample under constant stirring. All specimens weighed between 250 and 400 g due to the different amounts of added chemicals. The specimens were stored in 250 ml glasses with a plastic screw tap in the dark between 15 and 17℃. Table 14 presents the varied parameters and relative quantities of substances added.

Table 14: Variation of parameters in long-term phenol decomposition experiments

| Parameter | Unit | Value |
|---|---|---|
| time | weeks | 0; 2; 4; 8 |
| oxidant amount | mol $(NH_4)_2S_2O_8$ per mol phenol | 0; 10.7; 54.0; 107.5 |
| catalyst | mg $FeSO_4$*7 $H_2O$ per g soil | 0; 3.7 |

The quantities of oxidant correspond to 0; 1.8; 9.0; 18.0 mol of ammonium peroxodisulfate per mol of carbon in the spiked soil.

After having finished the experiments, the samples were homogenized during several minutes by mixing with a laboratory spatula. About 30 g were taken for dry substance determination and 150 g were handed in for phenol-index analysis. If the samples could not be processed immediately they were stored in glass bottles with plastic screw taps in freezers. After eight weeks of chemical oxidation with peroxodisulfate, the pH-value was measured in order to determine the reaction’s influence on soil acidity.

## 9.2.2 Results and Discussion

### *Diesel Oil*

As can be seen in Figure 17, it is possible to oxidize diesel oil with ammonium peroxodisulfate in soil at 15 ℃. The figure shows the relative extent of diesel oil decomposition in relation to time and amount of oxidizing agent. As expected, the more oxidant is used the more organic material is decomposed. 28.5 mol peroxodisulfate per mol diesel yield a decomposition of over 56 % in twelve weeks, whereas the five and tenfold amounts achieve 74 and 76 %, respectively. However, it has to be mentioned that the final results for 142.3 and 284.6 mol of peroxodisulfate barely show any difference, especially taking into account that the coefficient of variance is 13.6 %[1]. This means that higher amounts of oxidants than 142.3 mol are inefficient. Considering the curve of the control experiment under the same conditions but without peroxodisulfate, it can be observed that around 25 % of diesel oil is lost in the process. This might be due to evaporation of fugitive diesel components. The same result is obtained in the oxidation experiments with iron sulfate heptahydrate as catalyst (see Figure 18).

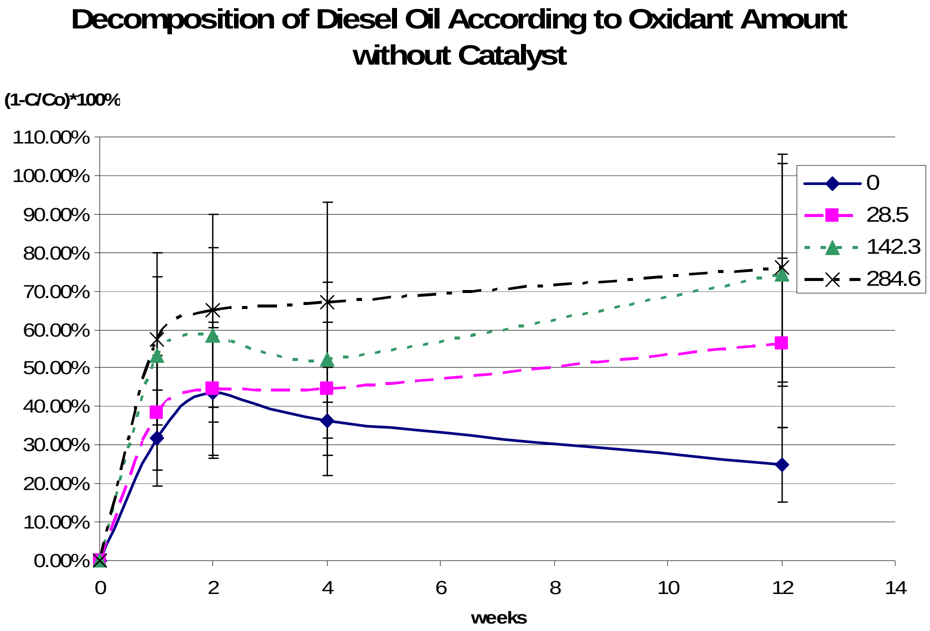

Figure 17: Decomposition of diesel with different amounts of peroxodisulfate analyzed with HC-index

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[1] The HC-index coefficient of variance for 1, 2 and 4 weeks is 38.8 %, for 12 week 13.6. However, the TOC CV is only 4.7 % for week 1, 2 and 4 detected from the same samples. This great difference might be due to the fact that the HC-index method has recently been developed in the respective laboratory for application in this analysis. Therefore, the high CV may not only be ascribed to heterogenic soil contamination but also to the analysis.

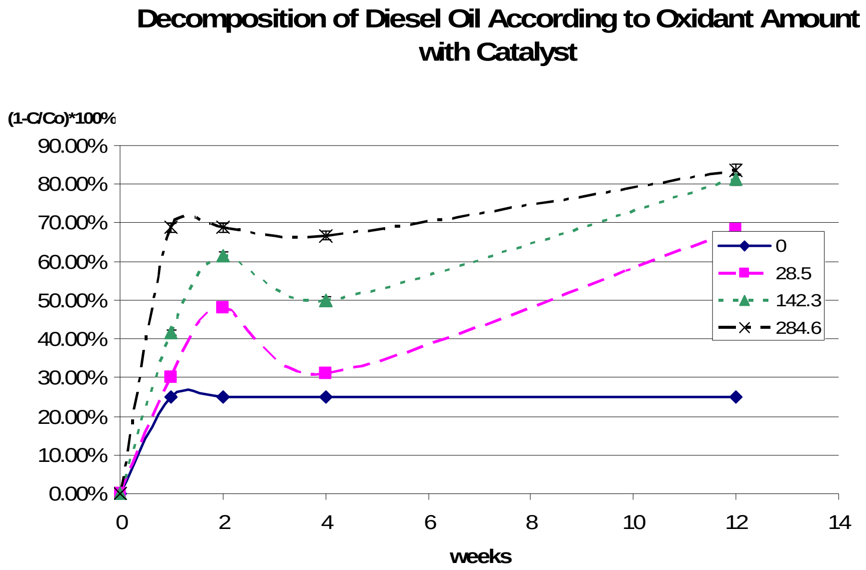


Figure 18: Decomposition of diesel with different amounts of peroxodisulfate and catalyst analyzed with HC-index

The overall elimination of diesel oil increases when applying a catalyst. In twelve weeks 28.5 mol of peroxodisulfate reduce the initial concentration by 68 %, 142.3 mol by 81 % and 284.6 mol by 84 %. Thus, it can be concluded that $Fe^{2+}$ serves as catalyst and can improve ammonium peroxodisulfate's performance, most probably by the formation of sulfate free radicals. Nevertheless, it has to be taken into account that the ratio between oxidizing agent and catalyst has not been constant in this case. For 28.5 mol peroxodisulfate the molar ratio of oxidant to catalyst is 341 : 1, for 142.3 and 284.6 it is 1704 : 1 and 3407 : 1, respectively. Therefore, it is recommendable to run further series of experiments in order to determine the most efficient amount of catalyst.

Appendix 8 – Chromatograms shows two selected chromatograms for diesel degradation with 142.3 mol oxidant and iron catalyst after one and twelve weeks.

Having a closer look at the curves presented in Figure 17 and Figure 18, it strikes that negative elimination occurs between weeks two and four. This would mean that a greater number of carbon chains with a length between $C_{10}$ and $C_{40}$ are detected. In Figure 18, up to 20 % more of diesel oil seems to be detected in the case of 28.5 mol peroxodisulfate addition. There are two theoretical explanations. First, carbon chains longer than $C_{40}$ might be degraded into shorter chains falling into the range of the HC-index analysis. Second, compounds with less than ten carbon atoms might polymerize. However, both possibilities are very improbable. Diesel oil is composed mainly of $C_{10}$ to $C_{21}$. Thus the fraction of chains greater than $C_{40}$ cannot have such great impact as the graphs suggest. Also, polymerization under the given circumstances is questionable. However, similar graphs were obtained in the Interland Project [31] with the same analytical methods suggesting that above presented data is no exception. So this leads to the necessity of understanding the mechanism of diesel degradation with peroxodisulfate more thoroughly. As neither the obtained results can offer sufficient information nor conclusions drawn by Watts et al. [42], i.e. aromatic compounds such as BTX are oxidized up to 95 % while less than 1 % dodecane is eliminated, further experiments have to be conducted. Aliphatic model substances within, below and above the range of 10 to 40 carbon atoms should be treated individually and analyzed by gas chromatography with a mass spectrometry detector. Thus, oxidation products can be clearly identified.

### *Phenol*

Figure 19 and Figure 20 present the results of phenol elimination with peroxodisulfate with and without catalyst analyzed for phenol-index. Both graphs show that it is possible to degrade phenol almost completely. Figure 19 shows that 10.7 mol oxidant per mol contaminant yield a decomposition of 93 % in eight weeks. The fivefold and tenfold amount of oxidizing agent yields in both cases > 99 %.

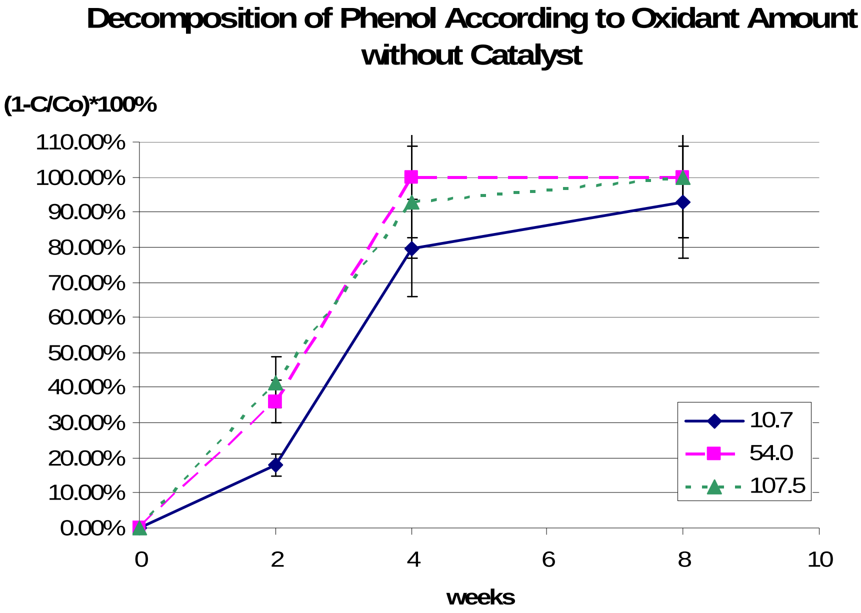


Figure 19: Decomposition of phenol with different amounts of peroxodisulfate analyzed according to phenol-index

Taking the coefficient of variance of 17.25 % into account, there is practically no difference between the performances of the three different oxidant concentrations after eight weeks. For weeks two and four the degree of phenol elimination is more distinct, i.e. about 15 percentage points between the 10.7 mol and the 54.0 mol values. It has to be noted that the highest concentration of peroxodisulfate does not improve the result of phenol eliminanation. This applies also to the degradation with iron(II) as catalyst as shown in Figure 20.

Comparing peroxodisulfate's performance with and without catalyst, results show that the application of iron sulfate heptahydrate yields faster degradation of the pollutant. After two weeks the amounts of 54.0 and 107.5 mol oxidant decompose 95 and > 99 % of phenol compared to 36 and 42 % without catalyst, respectively. As for 10.7 mol peroxodisulfate per mol phenol, there is only a difference in performance after two weeks, where it degrades 56 % instead of 18 % of phenol. The four and eight week values vary insignificantly.

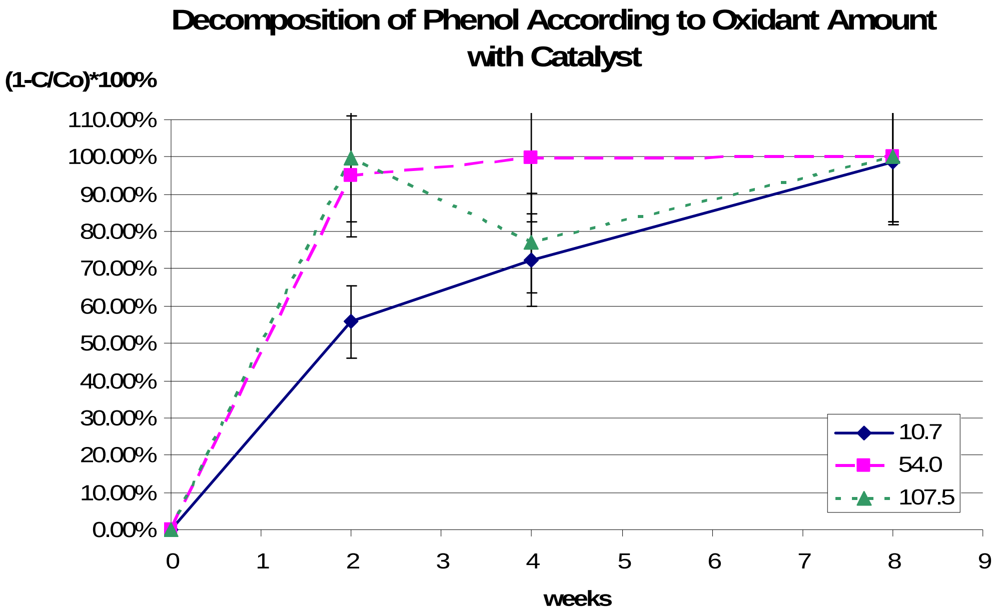


Figure 20: Decomposition of phenol with different amounts of peroxodisulfate with catalyst analyzed according to phenol-index

It can thus be concluded that an amount of 54.0 mol peroxodisulfate per mol phenol with an application of 3.7 mg $FeSO_4*7\ H_2O$ per g of soil can decompose > 95 % of the contaminant in two weeks and > 99 in four weeks. The double amount of oxidant cannot increase the performance significantly. Therefore, it is recommendable to investigate the performances of oxidant concentrations between 10.7 and 54.0 mol with an optimized amount of catalyst, as in this study the amount of catalyst has not been varied with the different concentrations of peroxodisulfate. Furthermore, analysis should be conducted after one week reaction time.

After eight weeks of reaction time, the influence on the soil's acidity was measured. Table 15 shows the impact of oxidant and catalyst on the material's pH-value.

Table 15: Soil pH alteration by peroxodisulfate and iron(II) application

| Specification | Amount Oxidant*) | pH-value | Specification | Amount Oxidant*) | pH-value |
|---|---|---|---|---|---|
| initial | 0 | > 8.0 | initial | 0 | > 8.0 |
| after 8 weeks | 0 | 7.8 | after 8 weeks with Fe(II) catalyst | 0 | 6.5 |
| | 10.7 | 5.5 | | 10.7 | 4.6 |
| | 54.0 | 3.9 | | 54.0 | 3.5 |
| | 107.5 | 3.4 | | 107.5 | 3.0 |

*) in mol per mol phenol

According to the obtained data, the pH-value in soil decreases with the amount of added peroxodisulfate. This conincides with the theoretic consideration of the formation of $HSO_4^-$ (see equations Eq. 11, Eq. 16 and Eq. 17 in Chapter 7). In case of catalyst application, the effect is even stronger. This is a possible disadvantage of peroxodisulfate application as ISCO chemical.

### 9.2.3 Conclusion

Due to different experimental conditions it is difficult to compare the obtained results for diesel oil elimination with other studies. In a thorough study of catalyst influence, Watts et al. [18] decomposed diesel oil in soil with hydrogen peroxide and iron(II) sulfate at a molar ratio of between 42 and 86 to 1 (oxidant to catalyst) and a molar ratio of between 237 and 340 to 1 of hydrogen peroxide to diesel. The 5 g soil samples were contaminated with a concentration of 1000 mg diesel per kilogram soil and mixed with 3.5 ml of oxidant and catalyst solution. After one hour hydrogen peroxide was consumed and yielded over 60 % of diesel elimination. Proper experiments resulted in the decomposition of 84 % diesel by 286.4 mol ammonium peroxodisulfate per mol contaminant with an iron(II) catalyst in a 300 g soil sample with 20 % humidity. However, depletion with peroxodisulfate took 12 weeks whereas Watts et al. [42] finished experiments after one hour. Nevertheless, the water content of the 5 g soil sample was above 40 % and the oxidant concentration was between 0.2 and 0.3 mol/g soil, whereas only 0.01 mol of peroxodisulfate accounted for 1 g soil in the proper experiments. Therefore, it can be assumed that the high elimination of 60 % diesel in one hour is due to an optimized contact between contaminant and oxidant, as well as between oxidant and catalyst, a factor which has not been sophisticated in the proper experiments in order not to detach too much from a realistic soil system under remediation conditions.

In order to meet the requirements of Austrian legislation, diesel contamination has to be reduced to below 500 mg/kg soil (intervention value) or even below 100 mg/kg soil (inspection value). Considering above presented results, oxidation with ammonium peroxodisulfate during twelve weeks does not meet the requirements. With an initial diesel contamination of more than 9.6 g/kg and a maximum elimination of 84 % still 1.56 g/kg remain. This implies that longer treatment times are required. It has to be considered as well, that the molar ratio between pollutant and oxidant, in this case 1 : 284.6, is very high. Additionally, the conditions for contaminant removal by peroxodisulfate oxidation at low concentrations around 500 mg/kg need to be investigated. Another subsequent treatment, for example bacterial remediation, might be necessary for the decomposition of low contaminant concentration, as in this case establishing contact between pollutant and oxidant may be very sumptuous.

Considering the facts that there has been detected a negative diesel oil elimination between weeks two and four according to the HC-index and that diesel is depleted up to 70 % during the first two weeks it is necessary to question these results and conduct further analysis.

Especially taking into account that Watts et al. [42] found that only 1 % dodecane can be eliminated under more favorable oxidation conditions. Thus, it is recommendable to analyze the oxidation products individually using single model substances and applying a mass spectrometry detector.

Applying the obtained results for phenol decomposition to the Netherlands' legislation on phenol contamination of soil (Austria's Standards only foresee intervention values for 30 µg/l groundwater contamination), the remaining phenol concentration with 54.0 and 107.5 mol oxidant after four weeks without catalyst are inferior to the intervention value of 40 mg/kg soil. After eight weeks all three concentrations meet the requirement. With catalyst application the two higher oxidant amounts degrade phenole sufficiently after two weeks, while 10.7 mol of oxidant decrease phenol to a concentration of 40 mg/kg after eight weeks. Considering the great amount of oxidants needed for fast degradation, an eight week period does not seem disadvantageous. However, considering the target value of 0.05 mg/kg, none of the oxidant concentrations can meet this limit. Soil has been contaminated with 500 mg/kg soil. Eliminating phenol down to a concentration of 0.05 mg/kg would require a performance of 99.99 %. Best yields of 99.97 % were achieved both with 54.0 and 107.5 mol with catalyst after eight weeks. Thus, it might be possible to meet the target value by in-situ oxidation with ammonium peroxodisulfate and iron(II) as catalyst.

As there are no similar experiments reported in Chapter 7 on in-situ oxidation of phenol in soil, it is difficult to position the obtained results. However, Huang et al. [45, p. 559] reported that peroxodisulfate activated at 40 °C preferably degrades carbon-carbon double bondings and benzene rings attached to functional groups instead of aliphatic saturated hydrocarbons. This observation can be confirmed by above obtained results as phenol is eliminated more quickly and thoroughly than diesel. After four weeks the best yield of diesel decomposition according to the HC-index is > 65 %, while phenol is eliminated more than 99 % according to the phenol-index.

Altogether, in-situ oxidation of diesel and phenol with ammonium peroxodisulfate seems a promising method for site decontamination. Above presented results show, that peroxodisulfate is able to eliminate > 99 % of phenol and 84 % of diesel with iron(II) sulfate heptahydrate at 15 °C and 20 % soil humidity. Nevertheless, the obtained results can only be considered a preliminary basis to a more thorough investigation for several reasons:

- assays for better understanding of diesel elimination need to be conducted in order to explain the behavior of the presented curves, e.g. decomposition of single constituents under the same conditions could be analyzed by gas chromatography with mass spectrometry,
- multiple experiments have to be run in order to confirm the obtained results,
- different concentrations of catalyst in accordance to the amount of oxidant have to be administered in order to foster an optimized performance,

- as the highest amounts of oxidant administered did not yield significantly better results than the medium concentrations, elimination performance of quantities between the intermediate and the lowest concentrations of peroxodisulfate should be investigated,
- temperature should be decreased to 10 °C in order to simulate better subsoil conditions,
- different soil types and water contents should be tested in order to be able to estimate the effects of sorption
- and pH conditions should be controlled.

A possible drawback of peroxodisulfate in-situ oxidation with $FeSO_4$*7 $H_2O$ could be the acidification of the site and the lixiviation of sulfate into the groundwater. According to the Austrian Standard S-2088-1, groundwater may not contain a concentration of sulfate superior to 150 mg/l. Effects of ammonium shall not be considered here, as it is assumed that only $S_2O_8^{2-}$ ions are administered via an electrical field in the remediation technology to be developed.

## 9.3 Generation of Peroxodisulfate with Diamond Electrodes

The principle idea of generating peroxodisulfate by anodic oxidation of sulfate on the surface of a diamond electrode is to prepare the oxidant solution on-site and to replace the usage of prepared chemicals such as sodium or ammonium peroxodisulfate avoiding the hazards caused by their transport and storage. Furthermore, fresh oxidant solution is continuously available. As mentioned in Chapter 8 the MI diamond electrode used in this study for peroxodisulfate production underwent several stages of development as the prototypes have been elaborated especially for this study. Here, only the most advanced experiments are presented, meaning that only assays with BDD electrodes on polymer basis are described leaving out experiments conducted with titanium based electrodes. Furthermore, the MI electrode models have been compared to a CVD electrode type in order to position performance of the newly developed MI diamond electrodes with an established model.

The purpose of the assays was to generate the greatest possible amount of peroxodisulfate ions from a sulfate solution neglecting considerations on efficiency. Therefore, major parameters of influence were changed individually in order to determine the optimal cell arrangement and mode of operation.

### 9.3.1 Materials and Methods

After a series of batch reactor experiments, where the BDD diamond anode and iron cathode were introduced into a beaker containing the electrolyte, a monopolar model of a flow cell was designed. Finally, the model was developed into a bipolar flow cell containing various sheets of polymer based diamond anodes and cathodes. Both cells are shown in Appendix

11 – Photos. The exact description of the diamond electrodes is presented in detail in Chapter 8, whereas the cells' set-ups are characterized in the following.

### *Monopolar Flow Cell*

The monopolar flow cell (see Figure 21) consisted of a plastic casing with one in- and outlet for electrolyte circulation, a stainless steel cathode and a diamond anode implanted in a polymer base contacted with a mixed oxide metal. The circular casing consisting of two halves had an inner diameter of 10 cm. In between the electrodes a glass fiber membrane was placed. The round steel cathode of an area of 79 cm² and the octagonal diamond anode of an area of 54 cm² were located at each side of the membrane at a total distance of about 1 cm. All experiments were conducted with one electrolyte circuit entering the anode compartment from the bottom and leaving at its top through silicon tubes circulated by a garden pump. This way produced gases can escape with the electrolyte from the electrolysis cell. As the glass fiber membrane did not seal the two electrode compartments completely, the electrolyte was able to enter the cathode room. The electrolyte was prepared from distilled water and sodium sulfate at a concentration of 0.85 M (+/- 0.01 M) and stored in a glass bowl. In case of temperature regulation, the electrolyte was circulated through a thermostat bath set at 10 ℃ in a plastic tube in order to obtain 15 ℃ (+/- 2℃) before entering the cell. The experiments were run galvanostatically at 14, 28 and 56 mA/cm².

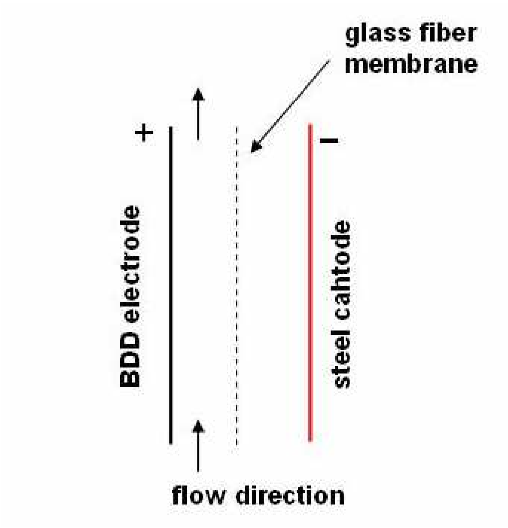


Figure 21: Schematic set-up of the monopolar MI BDD polymer electrode

The generated amount of oxidants, in this case peroxodisulfate, was measured by withdrawing approximately every 0.375 Ah a sample from the cell outlet. To an amount of 20 ml approximately 20 ml of 10 % $H_2SO_4$ and an excess amount of KI in solution were added. The samples were sealed by screw taps and kept in the dark over night before iodometric titration (iodometric titration is explained in Appendix 7 – Chemical Analytical Methods). Thus the total amount of produced peroxodisulfate was determined. The cells efficiency was calculated according to Faraday's law (see equation Eq. 39).

The mayor parameters changed were current density and number of glass fiber membranes. Table 16 shows a crucial series of experiments conducted with the monopolar flow cell.

Table 16: Resume of experiments conducted with the monopolar flow cell

| # | current density | temperature | sulfate concentration | # of membranes |
|---|---|---|---|---|
| | mA/cm² | ℃ | mol/l | |
| 1 | 14 | 15 | 0.85 | 1 |
| 2 | 28 | 15 | 0.85 | 1 |
| 3 | 56 | 15 | 0.85 | 1 |
| 4 | 14 | 15 | 0.85 | 5 |
| 5 | 28 | 15 | 0.85 | 5 |
| 6 | 56 | 15 | 0.85 | 5 |
| 7 | 28 | 15 | 0.85 | 10 |
| 8 | 56 | 15 | 0.85 | 10 |
| 9 | 28 | 15 | 0.85 | 30 |
| 10 | 28 | 15 | 0.85 | 47 |

### ***Bipolar Flow Cell***

Following the monopolar cell assays, a more elaborated bipolar flow cell was tested. This model consisted of two mixed oxide electrodes between which three diamond electrode foils on polymer basis were placed. The BDD electrodes were embedded in a polymer sheet. Between each electrode pair a total of four glass fiber membrane packages was located. The distance between the electrodes was 6 mm. Appendix 11 – Photos shows a picture of the cell, Figure 15 illustrated the basic scheme. The mixed oxide metal sheets were connected as anode and cathode, while the bipolar diamond electrodes functioned both as anode and cathode. The total area of the diamond anode surface was 45 cm². The cell disposed of two inlets and outlets, one pair for the cathodic and another for the anodic room. Thus, experiments were conducted with two electrolyte circuits. Both, anolyte and catholyte were administered by a garden pump at a maximum velocity of 25 l/h. The flow was regulated manually with laboratory valves. Therefore, the electrolytes did not always circulate with the same velocity. Consequently, a quasi stationary operation mode was simulated. The electrolytes were composed of a 0.85 mol/l sodium sulfate solution and sulfuric acid in different concentrations (0.17, 0.43 and 0.85 mol/l (+/- 0.01 mol/l)) and stored in glass beakers. These were surrounded by plastic tubes fed with cooling water. The electrolyte administration tubes were also conducted via a thermostat in order to temperate anolyte and catholyte. Operation was galvanostatic at different current densities. Table 17 presents the final series of conducted experiments, in which the parameters current density, temperature, electrolyte's sulfate concentration and number of membranes were varied.

Table 17: Resume of experiments conducted with the bipolar flow cell

| # | current density | temperature | sulfate concentration | # of membranes |
|---|---|---|---|---|
| | mA/cm² | °C | mol/l $Na_2SO_4$; mol/l $H_2SO_4$ | |
| 1 | 133 | n. c. | 0.85; 0 | 3 |
| 2 | 167 | n. c. | 0.85; 0 | 3 |
| 3 | 200 | n. c. | 0.85; 0 | 3 |
| 4 | 200 | 20 | 0.85; 0 | 3 |
| 5 | 200 | 30 | 0.85; 0 | 3 |
| 6 | 200 | 40 | 0.85; 0 | 3 |
| 7 | 200 | 45 | 0.85; 0 | 3 |
| 8 | 200 | 20 | 0.85; 0 | 3 |
| 9 | 200 | 20 | 0.85; 0.17 | 3 |
| 10 | 200 | 25 | 0.85; 0.43 | 3 |
| 11 | 200 | 25 | 0.85; 0.85 | 3 |
| 12 | 200 | 20 | 0.85; 0 | 0 |
| 13 | 200 | 20 | 0.85; 0 | 1 |
| 14 | 200 | 20 | 0.85; 0 | 3 |
| 15 | 200 | 20 | 0.85; 0 | 5 |
| 16 | 200 | 20 | 0.85; 0 | 3 |

with n.c. = not controlled

Parameters were altered subsequently, using always the most successful experiment, whose result was confirmed by repetition (not indicated in the table above), for the following experiments. Thus, after determining the optimal current efficiency, the best operation temperature was tested at the respective current density. Subsequently, sulfate concentration in the electrolyte was augmented by adding sulfuric acid and finally an adequate number of membranes was determined. The overall best result was confirmed in an experiment of eight hours (assay number 16 in Table 17), while all other runs lasted two hours.

Analysis was conducted as described for the monopolar flow cell, the only difference being that samples were taken from both anolyte and catholyte. The amounts of oxidants in both electrolytes were added afterwards.

### *Performance According to Stage of Cell Development*

Direct comparative experiments with different models of diamond electrode cells have not been conducted. However, similar operation conditions allow comparing the following electrode types as shown in Table 18. All experiments have been conducted with a 0.85 mol/l sodium sulfate electrolyte. Electrodes models 1, 2 and 4 have been tested in the set-up described for the monopolar flow cell. Model 3 corresponds to the description given for the bipolar flow cell. The chemical vapor deposition diamond electrode on titanium basis, model 4, was provided by the company DiaCCon GmbH, while all mechanically implanted models were obtained from the company pro aqua Diamantelektroden Produktion GmbH.

Table 18: Comparison of different electrode types

| # | electrode model | current density | temperature | # of membranes |
|---|---|---|---|---|
| | | mA/cm² | ℃ | |
| 1 | Ti-BDD | 45 | 15 | 5 |
| 2 | MPP-BDD | 56 | 15 | 5 |
| 3 | BPP-BDD | 67 | 20 | 3 |
| 4 | CVD-BDD | 62 | 15 | 5 |

with Ti-BDD = titanium based MI diamond electrode, MPP-BDD = monopolar metal oxide based MI diamond electrode, BPP-BDD = bipolar polymer based MI diamond electrode and CVD-BDD = chemical vapor deposition titanium based diamond electrode

## 9.3.2 Results and Discussion

### *Monopolar Flow Cell*

The principle idea of varying the current density is to find an optimum current application for major oxidant production. Theoretically, generation of oxidants increases with higher current density according to Faraday's law. The reason for changing the amount of membranes separating the anodic and cathodic room is to lower the reduction effect of the oxidized species at the cathode. Eq. 41 shows the possible reduction from $S^{7+}$ to $S^{6+}$.

Eq. 41: $0.5\ (S_2^{7+}O_8)^{2-} \rightarrow (S^{6+}O_4)^{2-}$

Figure 22 shows the results of experiments with different current densities and numbers of membranes presenting the produced amount of peroxodisulfate per liter as a function of Ah/l. Linearization of the curves as for the bipolar cell production has not been applied, because various coefficients of correlation were below 0.01. The graph implies that for current densities of 28 mA/cm² the production of peroxodisulfate is not influenced significantly by the number of membranes. All values range between 0.1 and 0.2 mmol/l peroxodisulfate production, while the titration error corresponds to 0.01 mmol/l. Doubling the current density, a significant change can be observed when applying 10 glass fiber membranes, as production rises to above 0.4 mmol/l total. For 5 membranes, production with a higher current density augments only after 3 Ah/l.

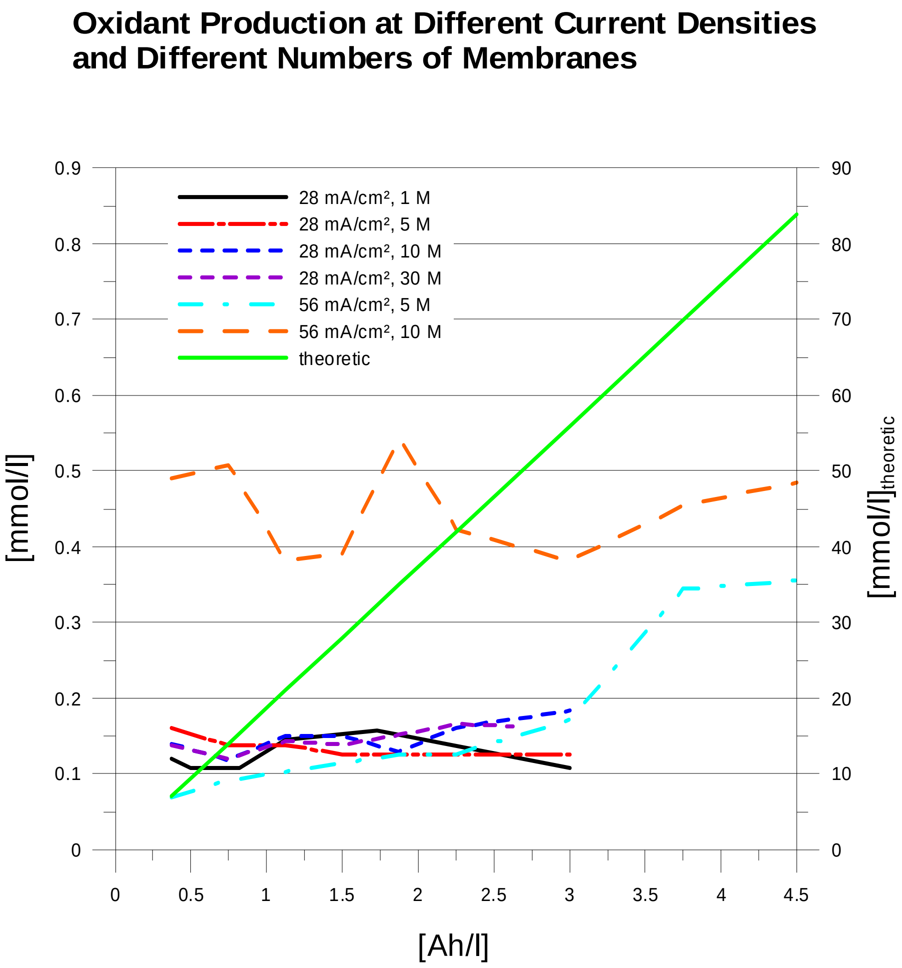


Figure 22: Oxidant production with a monopolar polymer based diamond electrode at different current densities and with different numbers of membranes (M)

Comparing the curves of the actual oxidant production (left y-axis) with the theoretically generated amount of peroxodisulfate (right y-axis), it strikes that the experimental data accounts only for one hundredth of the theoretic generation and does not show any increase in production over time. Oxidant generation should increase linearly according to Faraday's law. Thus, it can be deduced from the graph that adverse reactions take place. Considering the order of magnitude between theoretic and actual production, i.e. the poor efficiency below 0.5 % after 3 Ah/l, the application of membranes does not improve the process significantly. Therefore, reduction at the cathode does not seem to be the crucial factor. As the cyclic voltammogram presented in Chapter 8 confirms that the MI electrode is able to produce peroxodisulfate, the flat curves suggest that an oxidant species is formed and destroyed at the same time. Thus, elimination can only take place at the cathodic backside of the diamond foil [73]. The polymer basis was pressed onto the metallic oxide with a plastic sheet and cable binders. Therefore, the established contact did not eliminate completely empty space between the diamond foil and metal oxide leading to a cathodic charge at the backside of the diamond spiked polymer. It is assumed that this was the reason for the oxidant species' reduction.

### *Bipolar Flow Cell*

In order to overcome the above described reduction effect a bipolar flow cell with separated anolyte and catholyte circuits was developed. Systematically, four different parameters of influence have been varied. All curves presented in this section have been rectified by linear regression if not stated otherwise. Linear regression was chosen because the curves are linear according to Faraday's law. Theoretically, they should start at the origin (0, 0). However, as the system needed a certain time to adapt, results were interpreted from 0.25 Ah/l on. Table 19 shows an exemplary calculation while Appendix 10 – Linear Regression Calculations presents calculations. First, the on x dependent variable y was linearized based on the least squares method. Then slope and axis intercept were calculated from the linearized variables to establish the curve's equation. Finally, the coefficient of correlation was determined from the originally obtained experimental values.

Table 19: Exemplary calculation for linear regression

| **Parameter** | **Ah/l** | **mmol** | **mmol** | **coefficient of** | **slope** | **axis intercept** | **formula** |
|---|---|---|---|---|---|---|---|
| **mA/cm²** | **x** | **y** | **y_linear** | **correlation R²** | **k** | **b** | **y = kx+b** |
| **133.33** | 0.26 | 2.46 | 2.47 | 0.95 | 1.54 | 2.07 | **y=1.54x+2.07** |
| | 0.52 | 2.41 | 2.87 | | | | |
| | 0.80 | 3.42 | 3.30 | | | | |
| | 1.09 | 4.16 | 3.74 | | | | |
| | 1.39 | 4.41 | 4.21 | | | | |
| | 1.70 | 4.65 | 4.69 | | | | |
| | 2.03 | 5.09 | 5.20 | | | | |
| | 2.38 | 5.60 | 5.73 | | | | |

Figure 23 presents assays with different current densities. As could be expected, the production of peroxodisulfate increases with higher current densities. At 9 Ah/l, the bipolar diamond electrode cell generates 12 mmol oxidants for a current density of 200 mA/cm², 11 mmol for 167 mA/cm² and 8.5 mmol for 133 mA/cm². Thus, it was decided to realize all following experiments with 200 mA/cm². However, for 200 mA/cm² efficiency starts off at about 20 % and decreases to 6 % after 10 Ah/l (right y-axis). The presented efficiency curve was derived by regression ($y = 0.1292x^{-0.3187}$ with $R^2 = 0.98$). As it was the objective to produce the greatest amount of oxidants possible, the factor of efficiency was not included into considerations at this stage.

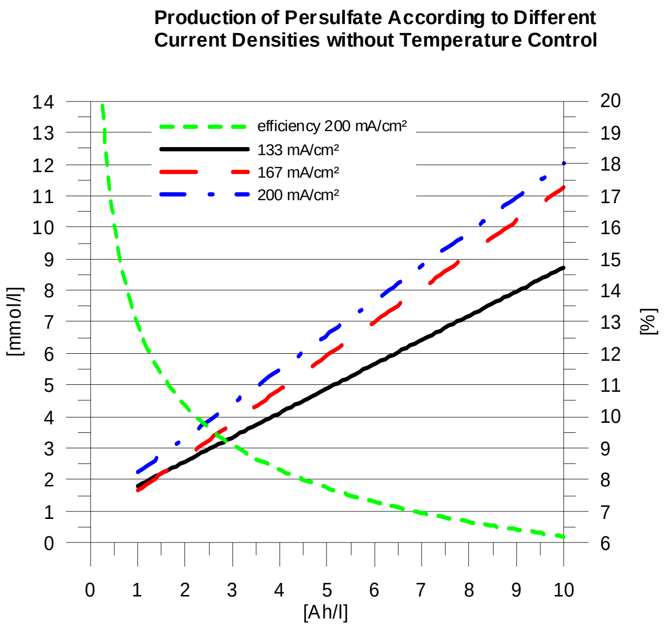


Figure 23: Dependence of peroxodisulfate production on current density with an electrolyte of 0.85 M $Na_2SO_4$

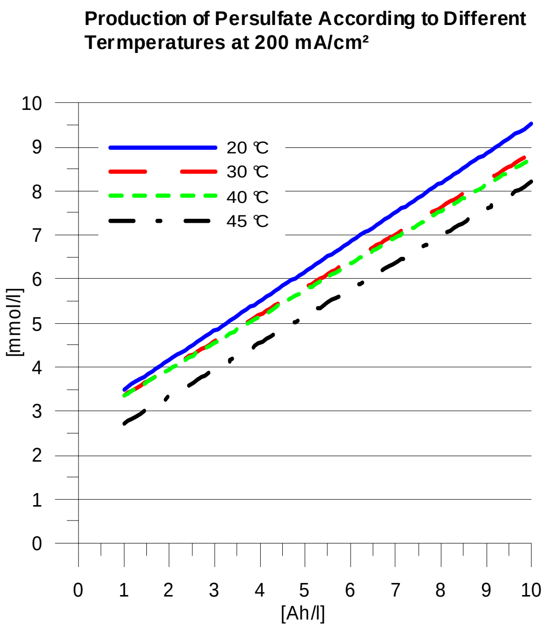
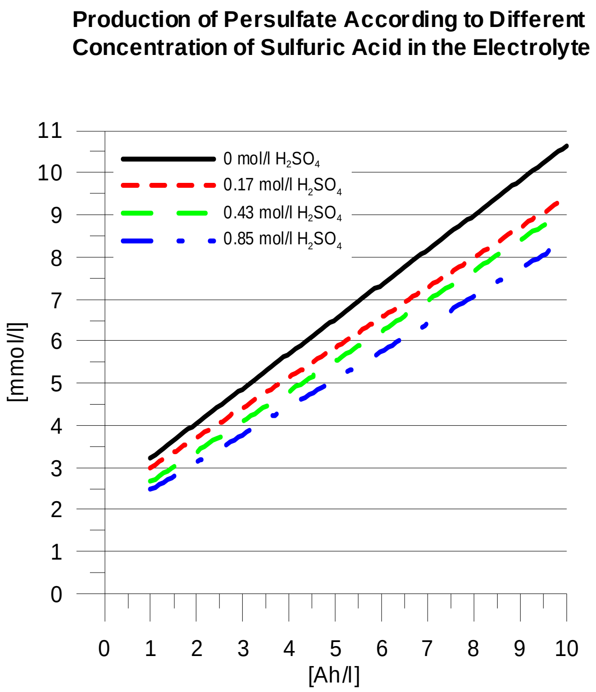


Figure 24: Dependence on temperature with an electrolyte of 0.85 M $Na_2SO_4$

Next, the influence of temperature on the cell's performance was tested (see Figure 24). Equally, as predicted by Serrano et al. [71], production decreases with higher temperatures. While operation at 20 °C yielded about 9 mmol at 9 Ah/l, operation at 30 and 40 °C resulted in 8.5 mmol and at 45°C below 8 mmol. There is no clear difference in production at 30 and 40 °C. Furthermore, considering the scale of 1/1000 mol, temperature's impact does not seem to be relevant. However, in order to prevent overheating and damage to the flow cell all further experiments were run at 20 °C.

Figure 25 illustrates the impact of sulfuric acid addition to the electrolyte. As for acid aggregation, the graph shows that a higher concentration of acid diminishes the cell's performance. This is an opposite result to findings of Serrano et al. [71], and Vatistas et al. [69] whose experiments resulted in efficiencies over 90 % for a sulfuric acid concentration of > 2 M at 23 mA/cm² and in over 75 % with a 7.5 M sulfuric acid electrolyte at 200 mA/cm², respectively, without compartment separation. Whereas proper assays did not exceed the initial 18 % mark. Thus, the cell needs to be operated without acid aggregation. Taking a closer look at the electrolytes' pH-values the following was observed: for assays without acid aggregation the pH-value oscillated below 3.5 for the anolyte and above 11 for the catholyte. When adding 0.17 mol/l of sulfuric acid both electrolytes had a pH-value of above 1, with 0.43 mol/l acid of 1 and with 0.85 mol/l below 0.5.



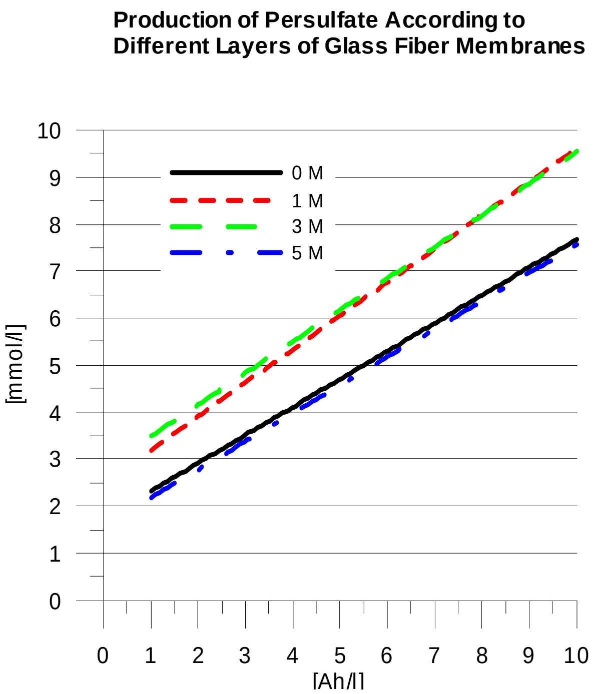


Figure 25: Dependence of peroxodisulfate production on the electrolyte’s acidity at 20℃ and 200 mA/cm²

Figure 26: Dependence of peroxodisulfate production on the number of applied membranes at 20℃ and 200 mA/cm²

Considering the influences of membrane application shown in Figure 26, it was found that one and three membranes yielded better results than none or five. Thus, the usage of a separator seems to be necessary for the operation of a bipolar flow cell. No utilization of membranes seems to lead to cathodic reduction of the produced oxidants. It was also observed that after an initial drop of the pH-value in the anolyte the system turned entirely alkaline with both electrolytes of a pH-value above 11. In the case of five membranes the resistance of the cell increased expressed by higher voltages. There is almost no difference in the use of one or three membranes. However, application of only one separator will decrease the cell’s electrical resistance, while the effect of separating anodic and cathodic reactions seems sufficient.

It can be concluded that operation performs best at 20 ℃ with no acid aggregation applying 200 mA/cm² and using between one and three membranes. The most significant influence in the range of variation of the tested parameters seems to have the current density. It marks a difference of 7 mmol in production at 9 Ah/l between 133 and 200 mA/cm², whereas all other parameters provoke changes of a maximum of 2 mmol.

***Performance According to Stage of Cell Development***

Figure 27 shows the operation performance at similar conditions of three different MI diamond electrode cells and one CVD diamond electrode cell. The curves represent linear regression functions obtained the same way as described above for the bipolar flow cell. Due to different diamond coverages of the electrodes' surfaces (Ti-based ca. 25 % [64], polymer based ca. 40 % [67] and CVD 100 %) regression results were divided by the diamond covered area. Calculations are included in Appendix 10 – Linear Regression Calculations.

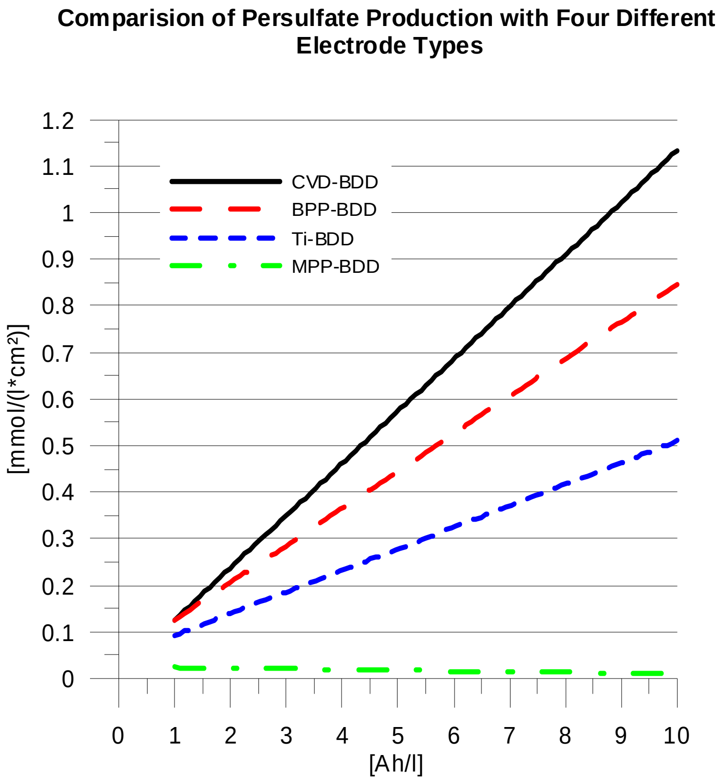


Figure 27: Performance of different diamond electrode types at 15 °C (20 °C for BPP-BDD) and 45 mA/cm² (Ti-BDD), 56 mA/cm² (MPP-BDD), 50 mA/cm² (CVD-BDD) and 67 mA/cm² (BPP-BDD)

The CVD electrode model (CVD-BDD) yields the best results under above described conditions. After 9 Ah/l it produces more than 1 mmol/(l*cm²), whereas the monopolar cell's production on polymer basis (MPP-BDD) remains below 0.05 mmol/(l*cm²). The titanium based electrode (Ti-BDD) yields close to 0.5 mmol/(l*cm²), thus, ten times more than the MPP electrode. The latest MI electrode model, the bipolar cell, improves performance producing nearly 0.8 mmol/(l*cm²). The low performance of the MPP-BDD cell has been explained above within the result section for the monopolar flow cell. Considering the difference between the CVD electrode and the bipolar MI electrode in peroxodisulfate production it has to be mentioned that latter model has been developed especially for the experiments in this soil remediation study. Thus, these first results are promising. They show that peroxodisulfate production with MI diamond electrodes is possible and that the production rate can still be improved. Furthermore, the company pro aqua Diamantelektroden GmbH disposes only of four years of experience while the CVD electrode providing company DiaCCon GmbH has been active for over ten years in the field of diamond chemistry.

### 9.3.3 Conclusion

The above presented results display that it is possible to produce oxidizing agents, in this case peroxodisulfate, with mechanically implanted diamond electrodes from sulfate containing electrolytes. Best confirmed yields are obtained with the bipolar model of 12 mmol/l after 9 Ah/l at 200 mA/cm$^2$. Combining results from the necessity of peroxodisulfate for the decomposition of phenol and the production of the oxidant at laboratory scale the following theoretical calculation can be conducted. 54 mmol peroxodisulfate are needed to degrade 1 mmol phenol to an extent > 99 % in four weeks. At 200 mA/cm$^2$ the production of peroxodisulfate obeys the linear equation $y = 1.09\,x + 1.14$. Thus, 48.5 Ah/l are needed to produce the necessary amount of oxidizing agent. This results in an operation of 16 hours and 10 minutes, assuming that one liter electrolyte is used. Counting with a voltage of around 45 V as observed in the experiments and a cost of 7.42 cents per kWh[2], the production would cost 16.36 cents. Thus, theoretical chemical production cost for the elimination of 1 mmol phenol are 32.72 cents counting that 50 % of the oxidant in solution reach the contaminant in the soil. Expenses for the application of 54 mmol ammonium persulfate as purchasable chemical would be about 25.61[3] cents or 51.22 cents if only 50 % of the oxidant reach the pollutant.

Comparing the results from the graph in Figure 23 with results obtained by Serrano et al. [71], with a CVD electrode, it turns out that this flow cell's performance accounts for less than one eights of the cell's capacity Serrano et al. used. At 5 Ah/l with an application of 200 mA/cm$^2$ and a concentration of 7.5 mol/l sulfuric acid > 60 mmol/l of peroxodisulfate were measured, whereas in this study only 7 mmol/l are registered. However, considering the ratio of the supplied sulfate amount and the produced peroxodisulfate both assays with 200 mA/cm$^2$ convert 0.8 % of the sulfate into peroxodisulfate. Therefore, efficiency of conversion is the same. In order to prove the great difference of peroxodisulfate production between mechanically implanted electrodes and CVD electrodes based on literature, a CVD electrode model has been tested, as well. For an experiment with 62 mA/cm$^2$ 1.1 mmol/(l*cm$^2$) oxidant after 9 Ah/l were obtained obeying a linear regression equation with a slope of 3.36 (see Appendix 10 – Linear Regression Calculations). At the same time the bipolar MI electrode cell yielded 0.8 mmol/(l*cm$^2$). Nevertheless, as mentioned beforehand, it has to be taken into account that the MI electrode prototypes counted with far less time of elaboration. Thus, there is potential for improvement.

## 9.4 Kinetics of Ion Transport in Soil by Electromigration

In order to be able to eliminate soil contamination by chemical oxidation it is necessary to establish contact between the oxidant and the pollutant. This project has considered the

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[2] Cost for small and medium scale enterprises by WienEnergie [74]

[3] Cost for 1 kg ammonium persulfate (puriss. p.a. ACS ≥ 98.0 %) is about € 20.80 according to [75]

option of distributing the oxidizing agent by means of electrokinetic migration. Therefore, a series of experiments has been conducted in order to investigate peroxodisulfate ion velocity (cm/h) in several types of soil subjected to different electric field gradients. The principle method for measuring the distance the peroxodisulfate ions traveled was optical determination by color distinction based on a chemical reaction of starch and iodine. Furthermore, changes in the soil's pH-values due to electrolysis near the electrodes and temperature alteration were measured.

### 9.4.1 Materials and Methods

Several approaches had to be taken in order to simulate ion transport in soil due to a variety of parameters that interfered with this purpose. First assays were conducted in a horizontal system, where the soil was infiltrated by pressure difference rather than by electrokinetic transport. This problem led to a second approach using a vertical arrangement. In order to exclude variables diminishing the performance of the chemical color reaction for travel distance determination the system was adapted again and another series of horizontal experiments was lanced. In the following the development and manner of operation of the transport systems are presented. The expressions sand, silt and clay correspond to the particle size definitions given in Chapter 3. The material used (sand, sialin and kaoline) together with other chemicals and accessories are described in more detail in Appendix 6 – Devices, Chemicals and Soil Material.

***First Horizontal Arrangement***

Figure 28 shows a horizontal transport system consisting of an acrylic glass cylinder, especially fabricated for this purpose (a more detailed description is given in Appendix 6 – Devices, Chemicals and Soil Material), filled with soil material. The length of the tube measures 40 cm, whereas only 30 cm were filled with soil. The inner diameter of the cylinder counted 10 cm. Both ends were closed by round stainless steel electrodes. Next to the cathode an electrolyte compartment was established by separating a section of the tube with glass fiber membranes in order to inhibit soil from entering this space. Also, the cathode was covered with glass fiber membranes to prevent peroxodisulfate reduction at the cathode. The electrolyte of 24.6 g/l ammonium peroxodisulfate was circulated by a garden pump at a maximum of 25 l/h. The soil material consisted always of 100 % sand with 16 % humidity except for one experiment where 60 % sand, 20 % loam and 20 % zeolite with 20 % water content were used. The specific water content was derived from experimental determination of field capacity for different soil types. Loam, in this case, refers to a material containing grain sizes of silt and clay (for specification see Appendix 6 – Devices, Chemicals and Soil Material). The soil was wetted with distilled water in which 5 g of KI were dissolved. Before adding water, 30 g of corn starch per kilogram soil were mixed into the material. The steel anode was also covered with two glass fiber membranes in order to diminish $Fe^{3+}$ transport into soil, as this would oxidize present iodide ions causing a color change which only should be provoked by peroxodisulfate ion presence.

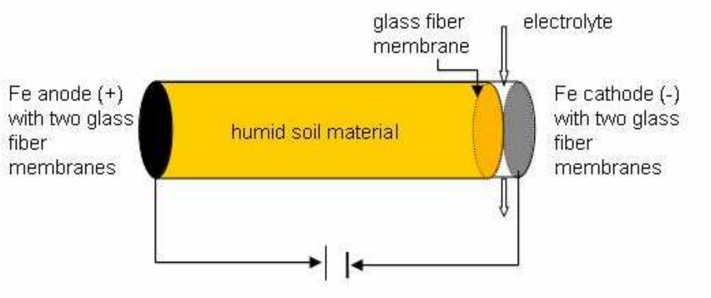

Figure 28: Horizontal transport system with electrolyte solution

The electrolyte was circulated through the respective compartment and an electric gradient of 1 V/cm was generated forcing the peroxodisulfate ions to migrate towards the anode. On their way, they oxidized iodide ions from KI to iodine ($I^0$), which then in the presence of starch and leftover iodide forms a dark blue or violet color complex. For optical analysis, the soil was pushed out of the tube maintaining its cylindrical shape and was sliced in 1 cm thick pieces. Dark violet colored soil indicated the distance traveled by the oxidizing ions.

***Vertical Arrangement***

Subsequent to the experiments in horizontal direction, assays were run in a vertical arrangement, an innovative approach to electromigration in soil. The principle of this arrangement was, that the oxidizing ions needed to travel upwards in order to reach the anode, thus overcoming gravity force. Therefore, a minimum value of migration velocity was measured. In the first series, two glass fiber tubes were placed upside down into a receptacle filled with 1 l of ammonium peroxodisulfate solution of 24.6 g/l. The cylinders were filled with various quantities of soil material, i.e. to different heights between 10 and 40 cm. At the bottom of the tubes, a glass fiber membrane was attached, protected by a permeable kitchen cloth from the soil material. The membranes simulated the barrier the peroxodisulfate ions would have to overcome in order to enter the soil system from the solution in a real case application. On top of the soil column stainless steel electrodes were placed and connected as anode and cathode. Figure 29 shows the schematic set-up of the experiments. After terminating the first series of experiments a second one was lanced in order to scale up the system obtaining a total length of soil column of at least 50 cm by using longer tubes and more soil material. Appendix 11 – Photos shows one picture of a vertical experimental arrangement. As described above, the soil was wetted and spiked with KI and starch for optical determination of peroxodisulfate ion migration. For analysis, the soil was pushed out of the cylinder and sliced in 1 cm thick pieces. Furthermore, the conductivity of soil material and pH-values after finishing the experiments were measured. Therefore, 50 g soil was mixed with 50 ml of distilled water in order to measure the pH-value and conductivity from the liquid phase. The osmotic flow was measured after experiments by filling the migrated water, which was collected on top of the cathode, into a measuring cylinder. Before starting and after terminating the experiments, soil temperature was measured directly at the electrodes with a laboratory thermometer.

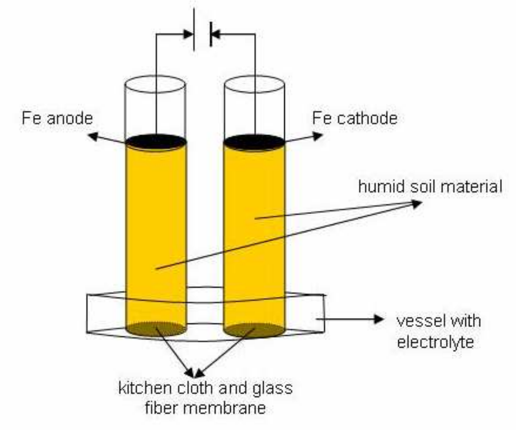

Figure 29: Vertical transport system

Table 20 gives an overview on the conducted experiments. First, assays were run with sand only testing ion migration velocity at different field strengths. Afterwards a high electrical gradient (in order to speed up the assays) was applied to different soil compositions. Thus, migration behavior dependent on soil particle distribution could be examined.

Table 20: Vertical transport experiments

| # | Soil Material *) | Humidity | Total Lengths +) | Field Strength | Current | Conductivity |
|---|---|---|---|---|---|---|
| | % s/% si/% c | % | cm | V/cm | A | µS/cm |
| 1 | 100/0/0 | 16 | 40 | 1 | 0.03 | 30 |
| 2 | 100/0/0 | 16 | 40 | 1.5 | 0.09 | 30 |
| 3 | 100/0/0 | 16 | 73 | 1.25 | 0.05 | 30 |
| 4 | 100/0/0 | 16 | 40 | 1.5 | 0.07 | 30 |
| 5 | 100/0/0 | 16 | 57 | 1.75 | 0.07 | 30 |
| 6 | 100/0/0 | 16 | 41 | 1.5 | 0.05 | 30 |
| 7 | 100/0/0 | 16 | 40 | 2.0 | 0.06 | 30 |
| 8 | 100/0/0 | 16 | 44 | 4.0 | 0.18 | 30 |
| 9 | 100/0/0 | 16 | 53 | 4.0 | 0.16 | 30 |
| 10 | 0/0/100 | 40 | 45 | 4.0 | 0.00 | 132 |
| 11 | 50/50/0 | 22 | 53 | 4.0 | 0.20 | 512 |
| 12 | 0/50/50 | 24 | 50 | 4.0 | 0.35 | 415 |
| 13 | 50/0/50 | 28 | 53 | 4.0 | 0.27 | 550 |
| 14 | 20/60/20 | 26 | 42 **) | 4.0 | 0.16 | 442 |
| 15 | 0/50/50 | 34 | 60 **) | 4.0 | 0.30 | 730 |
| 16 | 50/0/50 | 30 | 50 **) | 4.0 | 0.29 | 970 |
| 17 | 33/33/33 | 26 | 42 **) | 4.0 | 0.20 | 368 |
| 18 | 60/20/20 | 26 | 43 **) | 4.0 | 0.23 | 595 |

*) s = sand; si = silt, c = clay; +) lengths of the anodic and cathodic soil columns; **) tap water

A graphical illustration of the textural triangle is provided in Appendix 9 – Soil Textural Triangle. The water content was adapted roughly to the soil mixture’s field capacity.

### *Second Horizontal Arrangement*

As negative influences on the peroxodisulfate migration detection by the behavior of KI and starch in the electric field could not be excluded in above described experiments the second series of horizontal transport assays aimed to eliminate those. Two adverse effects of KI behavior were suspected to undermine peroxodisulfate detection. For one, $I^-$ ions also migrate towards the anode and are likely faster than the oxidant due to their smaller size. For another, the osmotic flow towards the cathode might flush the iodide ions into the electrolyte vessel. This could be observed by the change of electrolyte color from transparent to purple. Furthermore, if KI and starch are washed out of the soil, peroxodisulfate can equally be inhibited from traveling towards the anode due to the flushing effect. Therefore, a different kind of experimental set-up was chosen. A polypropylene tube of 15 cm length and 4 cm diameter was filled with 2 cm of wetted soil material, then with 2 cm of wetted soil material spiked with ammonium peroxodisulfate and the left over 11 cm were filled again with wetted soil material. On each side, a fleece soaked in NaCl solution was located between the soil and electrode for better electrical contact. A titanium based diamond electrode functioned as anode in order not to release any oxidative ions, which could provoke a color reaction with iodine and starch. A stainless steel electrode served as cathode. The soil material was wetted with tap water to its field capacity. The two centimeters of spiked material consisted of 35 g of soil, 3.5 g (+/- 0.1 g) of ammonium peroxodisulfate and the respective amount of water. After having installed the tube and electrodes, the peroxodisulfate ions were subjected to an electric field. For analysis, the soil was pushed out of the tube centimeter by centimeter and sliced. The slices were located in a white ceramic dish. Then solutions of starch and 0.05 M KI were added in drops. In presence of peroxodisulfate ions the purple iodine starch color complex formed and the travel distance could be determined. Figure 30 illustrates the color change during analysis. Appendix 11 – Photos presents the procedure of soil sample slicing.

Figure 30: Analysis of horizontal transport experiments with peroxodisulfate spiked soil

In addition to the above described qualitative analysis, also quantitative determination of peroxodisulfate presence according to the traveled distance was conducted. Therefore, slices of exactly 1 cm were shacked for 30 min in 60 ml of distilled water in a horizontal shaker at 200 mov/min. Then the mixture was centrifuged for 2.5 min at 5000 rpm. From the clear solution 20 ml were extracted and mixed with an excess amount of KI and 20 ml of 10 % sulfuric acid. The solution reacted in the dark over night before iodometric titration. Thus, the amount of peroxodisulfate ions could be determined. Table 21 presents the kinds of experiments conducted.

Table 21: Horizontal transport experiments with 1 V/cm

| # | Quantitative | Soil Type | Humidity | Current | Conductivity |
|---|---|---|---|---|---|
| | | % s/ % si/ % c | % | A | µS/cm |
| 1 | no | 100/0/0 | 19 | 0.08 | 30 |
| 2 | no | 100/0/0 | 20 | 0.05 | 30 |
| 3 | no | 70/20/10 | 18 | 0.01 | 133 |
| 4 | no | 70/20/10 | 18 | 0.01 | 133 |
| 5 | no | 70/20/10 | 18 | 0.01 | 133 |
| 6 | no | 60/20/20 | 18 | 0.01 | 103 |
| 7 | no | 60/20/20 | 18 | 0.01 | 103 |
| 8 | no | 50/30/20 | 18 | 0.01 | 201 |
| 9 | no | 50/30/20 | 18 | 0.01 | 201 |
| 10 | no | 80/10/10 | 18 | 0.01 | 66 |
| 11 | no | 80/10/10 | 18 | 0.01 | 66 |
| 12 | yes | 70/20/10 | 18 | 0.01 | 133 |
| 13 | yes | 60/20/20 | 18 | 0.01 | 103 |
| 14 | yes | 50/30/20 | 18 | 0.01 | 201 |
| 15 | yes | 80/10/10 | 18 | 0.01 | 66 |
| 16 | yes | 100/0/0 | 18 | 0.05 | 30 |

with s = sand, si = silt, c = clay

Appendix 9 – Soil Textural Triangle locates the experimental runs on the textural triangle. For each type of soil one control run has been realized with a field strength of 0 V/cm and 0.00 A.

### 9.4.2 Results and Discussion

**_First Horizontal Arrangement_**

This series of experiments did not provide any useful results as the oxidant solution infiltrated the cylinder filled with soil. This was caused by the pressure from pumping with which the electroyte entered the compartment between cathode and soil column. Thus, the color change in the soil material was caused by water flow rather than by electromigration.

**_Vertical Arrangement_**

The first assays were conducted only in sand varying the applied field voltage between 1 and 4 V/cm. Figure 31 presents the peroxodisulfate ion velocity towards the anode. The data points at 1.50 and 4.00 V/cm represent average values (see Table 20). As can be seen, the velocity increases with higher field strengths. It has to be noted that the data points 1.00, 1.50, 2.00 and 4.00 V/cm picture almost a linear curve while velocities at 1.25 and 1.75 V/cm do not fit exactly into this tendency. However, generating a linear graph from the first four mentioned values a coefficient of correlation > 99 % results. Thus, oxidant administration in sandy soil could be predicted quite precisely. However, further experiments should be conducted in order to confirm the linear migration behavior, especially for 1.25, 1.75 V/cm.

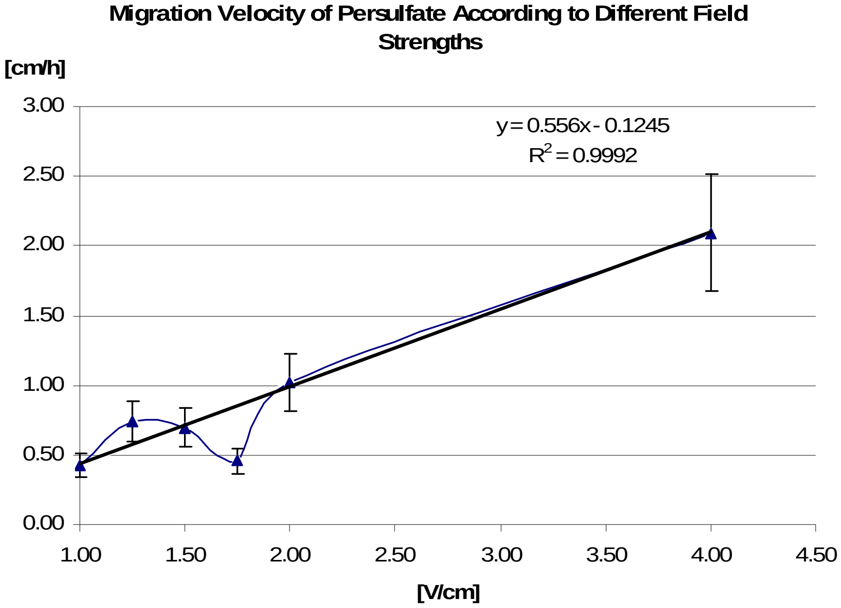

Figure 31: Migration velocity of peroxodisulfate ions in sand depending on different field strengths

Even though, a velocity of > 2 cm/h of migration can be achieved, it has to be considered that 4 V/cm imply high voltages at e. g. one meter electrode distance, i.e. 400 V. Thus, velocities below 1 V/cm should be investigated as field applications are run at gradients inferior or equal to 1 V/cm.

Besides testing ion migration in sand, several different soil types have been applied. Figure 32 shows results for peroxodisulfate ion migration towards the anode (negative direction) and towards the cathode (always positive direction). Also results of $Fe^{3+}$ mobilization from the anode towards the cathode and the osmotic flow are presented. It strikes, that there is no transport for 100 % clay soil. The soil right under the anode dryed out completely so that no electric contact could be maintained. As for anion migration towards the anode, it is registered only with 0 % clay in the soil mixture. This suggests that interaction between clay particles and peroxodisulfate ions inhibits displacement measurable under the given conditions. Ion movement in a 50/50/0 soil, namely 2.2 cm/h, is faster than in sand only. Comparing these two soil compositions, faster ion migration might be due to a higher water content in the finer grained soil (22 % vs 16 %), fostering current conduction (0.20 vs 0.16 A). Transport towards the cathode is facilitated when 50 % or more of the soil consists of silt.

This can be due to diffusion or dragging by osmotic flow. Latter seems a sounder explication as stronger osmotic flow of > 15 ml/h occurs in all three cases.

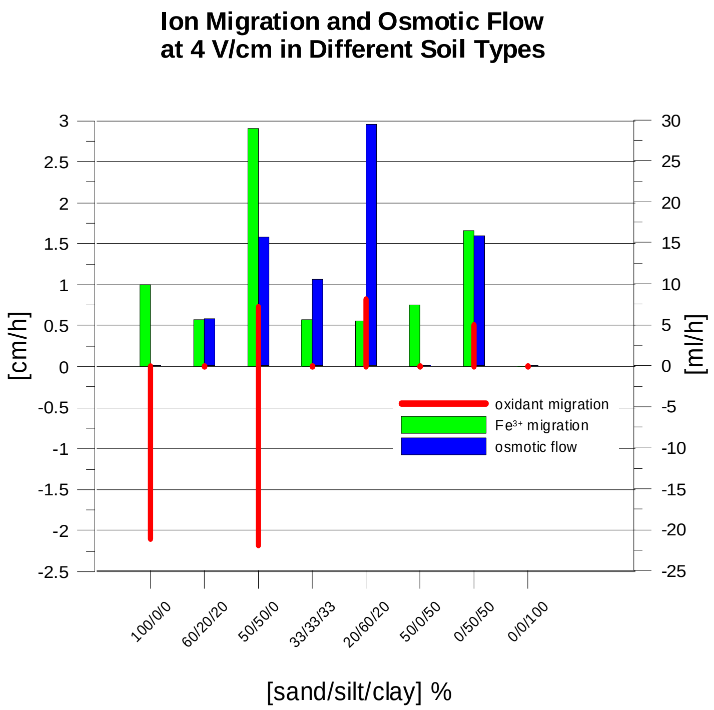

Figure 32: Migration velocity of peroxodisulfate and iron ions in different types of soil under an electric gradient of 4 V/cm

Figure 32 describes also $Fe^{3+}$ movement, originating from the stainless steel anode, in cathode direction. For a composition of 50/50/0 iron migration is fastest, just as peroxodisulfate displacement. This suggests that an application of this oxidant distribution method is best apt for this type of soil aiming to initiate a Fenton like reaction to create sulfate free radicals from peroxodisulfate ions.

Generally, osmotic flow is measured only when silt is present. Figure 33 shows the correlation between the amount of migrated water and the ratio of silt in the soil mixture. The more silt the soil contains the higher the displacement of water.

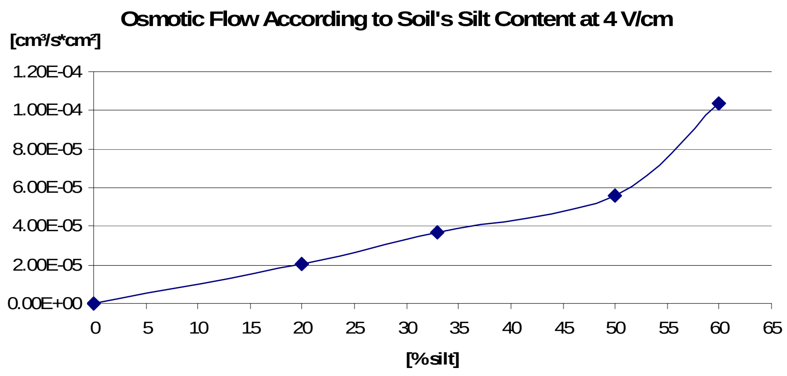

Figure 33: Osmotic flow in dependence to the soil's silt content

Furthermore, two additional parameters have been measured, namely pH-value and temperature. Temperatures rose during an average of five hours from 15 ℃ soil temperature to a maximum of 50 ℃ and averagely to above 40 ℃, meaning that energy is lost in heating the soil near the electrodes. This might result in volatilization of organic composites of high vapor pressure. The soil's pH-value was also altered while applying an electric gradient to the soil column. As described in Chapter 6, electrolysis will occur near the electrodes resulting in an acidic environment near the anode and an alkaline near the cathode. Figure 34 illustrates the change in pH. The extremes of the bars represent the pH-value measured at the anode (low values) and cathode (augmented values) after running the experiment. The black marks on the bars indicate the initial soil pH.

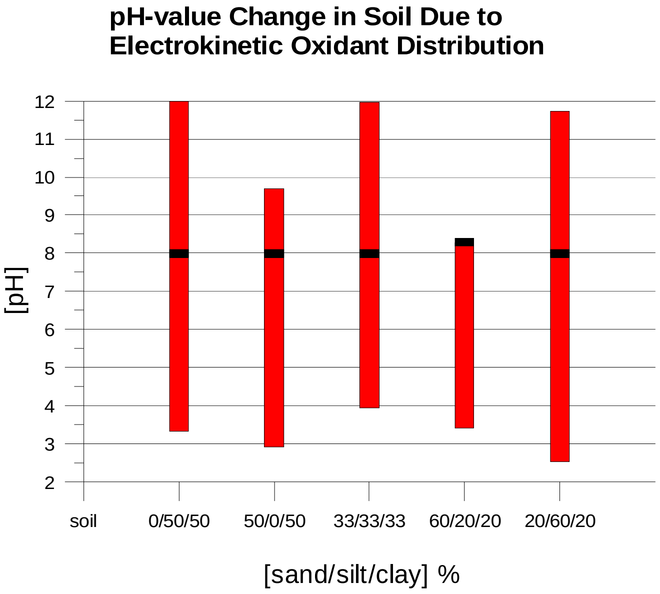

Figure 34: pH-value alteration caused by application of electric gradient to soil

As mentioned above, it was suspected that iodide was mobilized either by migration towards the anode or by a flushing effect caused by the electro osmotic flow. Therefore, after terminating and analyzing the experiments the slices of the soil column were spiked with an ammonium peroxodisulfate solution. If the soil turned dark iodide was present, meaning that the peroxodisulfate ions from the electrolyte did not migrate to this point. However, if the soil did not change color no iodide was available, indicating that it had been displaced. This test was applied for the last three conducted experiments (33/33/33, 60/20/20, 20/60/20), where no iodide was found at the bottom of the column from where the peroxodisulfate ions enter the soil. Additionally, the electrolyte changed color from transparent to purple, suggesting that part of the iodide was washed out. Thus, another series of experiments was run in horizontal direction without adding KI to the soil as follows.

### *Second Horizontal Arrangement*

First experiments were analyzed qualitatively, meaning that each centimeter slice reacted with KI and starch solution while the color change was determined optically by eyesight

(Appendix 11 – Photos shows a respective picture). Figure 35 presents the net velocity of persulfate ions meaning that detected movement of the control run was substracted.

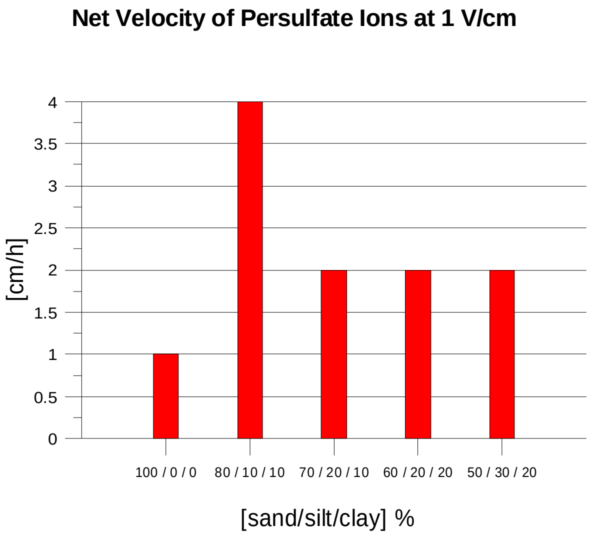

Figure 35: Qualitative net migration velocity of peroxodisulfate ions in different types of soil under an electric gradient of 1 V/cm

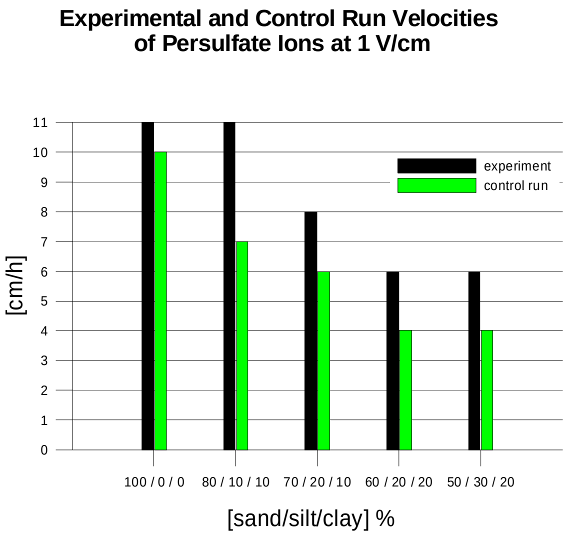

Figure 36: Qualitative migration velocity of peroxodisulfate ions in different soil types at 1 V/cm

A soil mixture of 80/10/10 yields the best result of 4 cm/h for 1 V/cm during 60 minutes. Tests in mixtures of more fine grained soils result in 2 cm/h migration velocity. Only sand yields the lowest result of 1 cm/h which is contrary to above obtained values in a vertical system. But the tendency coincides with the theoretic prediction. Finer grained soils are able to retain more water in their pores fostering current conduction [7, p. 160]. The higher migration velocities in comparison to the vertical experiments can be explained by a deficiency of this horizontal experimental set-up observed in the control runs. The soil's humidity begins to move driven by gravity. As the tube remains still during the experiment, water accommodates at the bottom. Thus, peroxodisulfate ions begin to migrate with the water and a certain traveling velocity can be detected without application of an electric field.

Considering the retention capacity for water of coarse and fine grained soils, water in pure sand will accommodate more quickly. Thus, less difference between a control run and the actual experiment under can be detected, what results in low net migration velocities. So, it is difficult to interpret above presented results, as the influence of water accommodation seems too crucial (see Figure 36).

Quantitatively analyzed assays support this observation. Figure 37 shows the amounts of peroxodisulfate detected depending on the distance the ions have traveled. A negative quantity of peroxodisulfate means that more ions were detected in the control run at this distance than in the transport experiment. This occurred especially for sand only. This was due to a longer waiting time until sample preparation for analysis. The actual experiments were prepared first for analysis and subsequently the control runs, where water thus could accommodate during longer time. The 80 % sand sample, having yielded the best qualitative analysis, presents electromigration for four centimeters in one hour. Then, no difference between control and actual experimental run can be detected. This reflects the qualitative observations where also 4 cm/h were determined. For the soil mixture of 70 % sand, electromigration can be detected from centimeter six on. Rising curves near centimeter eleven might be due to anodic influences rather than electromigration. It has to be taken into account that the generated current does not exceed 0.01 A in all experiments, except for only sand assays, where 0.05 A were measured. This explains as well the little difference between control and actual runs. Therefore, it is recommendable to enhance contact between electrodes and soil for better current conduction.

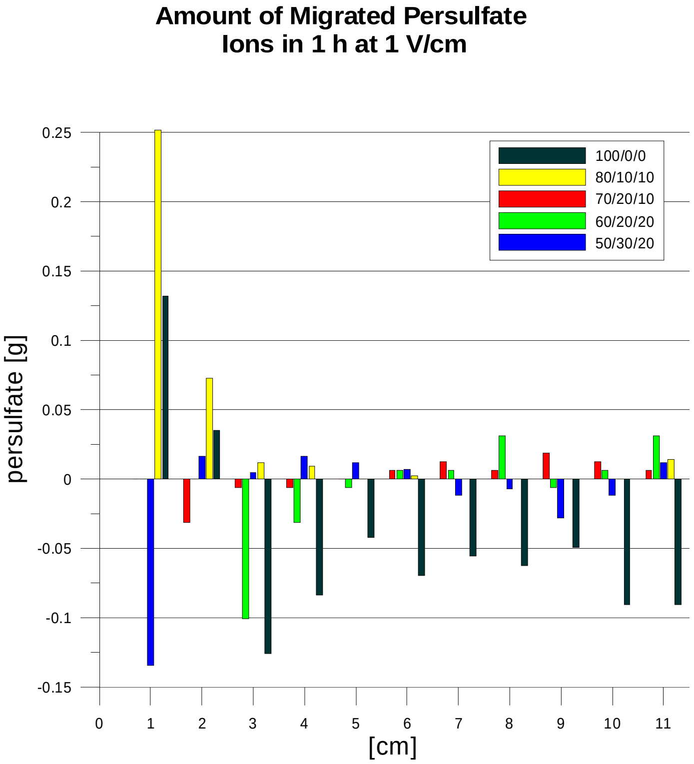

Figure 37: Quantitative analysis of the amount of peroxodisulfate migrating in different types of soil under an electrical gradient of 1 V/cm

### 9.4.3 Conclusion

Drawing conclusions from the obtained results in the vertical and horizontal arrangement, the most crucial parameter for peroxodisulfate ion transport is the composition of soil. Figure 32 shows clearly that the direction and velocity of oxidant migration, as well as, the movement of iron (III) and the extent of the osmotic flow depend strongly on the type of soil. However, above presented results are not able to lead to a clear cut conclusion in which soil type distribution of peroxodisulfate ions functions best. Vertical experiments suggest a 100/0/0 (sand/silt/clay %) or 50/50/0 composition, whereas horizontal experiments indicate best results for 80/10/10 qualitatively and 70/20/10 quantitatively. So in this study, the highest ion migration velocities were obtained in soils with low clay content. This does not coincide with reviewed literature which states that rather fine grained soils with high clay content are apt for electrokinetic ion movement [7, p. 160], [8, p. 160].

Thus, a set-up eliminating drawbacks of both arrangements should be elaborated and final experiments be conducted in order to determine soil compositions to which the technique can be applied best. An ideal outcome would be a complete velocity profile for the textual triangle. Knowing ion migration velocities in different soil types next to other factors (pollutant concentration, oxidation kinetics etc.) makes it possible to predict the amount of time needed for site remediation. Figure 38 pictures a recommended design for further assays. The horizontal arrangement imitates the actual direction of migration while the administration of peroxodisulfate ions functions via a perforated tube surrounded by a glass fiber membrane, through which the oxidant solution is circulated. The ions will be mobilized by the applied electric field. This mode of administration is closer to a possible real site application then spiking the soil with the oxidant. The flow can be stopped at any time, eliminating the crucial problem of the horizontal experiments. Analysis will be conducted by slicing and spiking with KI solution and starch. Preferably, a soil compartment of a diameter of 5 cm and a length of 30 cm should be chosen and experiments run for several hours.

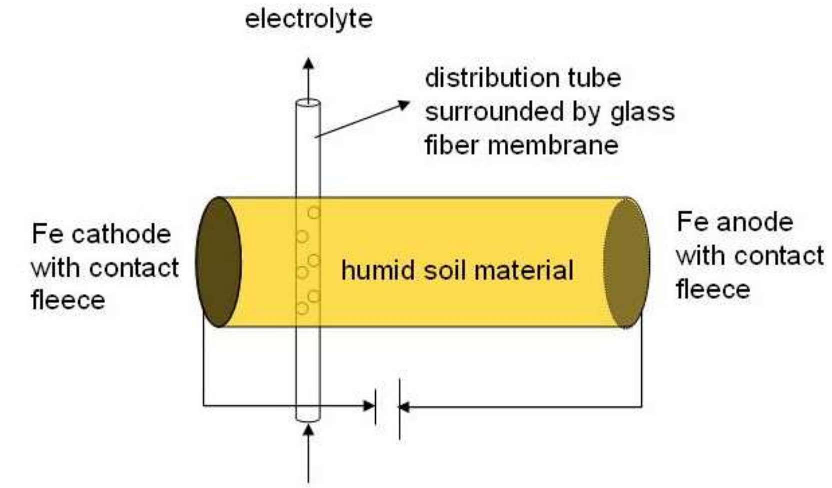

Figure 38: Recommended design for additional transport experiments

Besides the soil type, humidity is an important factor. A specific ratio of water content and soil particle distribution will finally determine the remediation conditions. As for the electric gradient, Figure 31 suggests a linear behavior between migration velocity and applied voltage. However, experiments should be conducted at a lower gradient near 1 V/cm in order to simulate real site application. Furthermore, two adverse effects have been detected. For one the changes in pH near the electrodes. Acidification and alkalinization can be mitigated by enhanced electrokinetic distribution using electrode casings with buffer solutions. For another, temperature rises significantly in short periods of time. Therefore, it is recommendable to apply lower voltages and enhance electrical contact between soil and electrodes.

# 10 Recommendations and Outlook

In order to provide a reliable laboratory scale foundation for pilot experiments on the electrokinetic remediation method involving electro synthesis of peroxodisulfate and in-situ contaminant oxidation the following recommendations are given:

- As for soil spiking, few assays have been conducted. Thus, in order to support 98 % homogeneity for phenol spiking according to TOC and 95 % for diesel spiking according to the HC-index more analysis should be conducted to establish a statistically sound basis. Especially in one case of diesel spiking for decomposition experiments, the coefficient of variance was nearly 39 %. Considering phenol, a coefficient of variance of 17 % for several conducted oxidation experiments can still be improved.

- As far as contaminant decomposition is concerned, the amounts of catalyst and oxidant (the molar ratio of pollutant to oxidant was very high, 1 : 284.6 for diesel and 1 : 107.5 for phenol) should be defined more clearly in additional experiments at lower temperatures (e.g. 10 ℃). Furthermore, mechanisms of diesel oil elimination have to be investigated more thoroughly in order to design an analytical method providing more reliable results. Between weeks two and four the HC-index suggests that diesel oil is formed. Therefore, several constituents of diesel oil could be oxidized with peroxodisulfate under the same conditions as for the already conducted experiments. The outcome should be analyzed by gas chromatography with a mass spectrometer. Thus, the mechanism of diesel oil degradation can be clarified and the already obtained elimination curves can be explained or the analysis method be adapted. Additionally, the intermediate species formed in the process should be characterized. Metabolites might be more toxic than the actual contaminant to the environment. Also, the amount of sulfate which may possibly enter groundwater resources as leachate should also be determined. Finally, the influence of soil organic matter should also be investigated.

- Considering the results of oxidant production with diamond electrodes, two issues should be discussed. For one, the bipolar MI electrode model needs to be enhanced in order to be able to compete with the tested CVD electrode. For another, an estimation of investment and electrochemical peroxodisulfate production cost (for both electrode types) should be elaborated and compared to the cost of purchasing peroxodisulfate as a chemical, a viable alternative for in-situ soil remediation involving electrokinetic oxidant distribution.

- With reference to the transport experiments, a recommendation on how to improve the experimental arrangement has already been given in Chapter 9. The system should be arranged horizontally in order to avoid adverse effects against the oxidant's migration by osmotic flow and gravitiy. Furthermore, the administration of peroxodisulfate needs to be controllable. Additionally, behavior in real soil should be investigated.

Giving an outlook on how to simulate the complete remediation technique at laboratory scale, an oxidant solution administration facility should be designed, optionally as recommended in Chapter 9. Subsequently, ion transport with coupling oxidant production and electrokinetic distribution needs to be tested determining the relative amount of peroxodisulfate entering the soil system from the administration solution. Finally, all three subsystems need to be unified and coordinated in order to complete the laboratory phase of the project before continuing at pilot scale.

# 11 Resume

In Austria, 93 % of the contaminated sites are affected by organic compounds. Out of these sites 40 % are polluted by mineral oil and phenol which cause a potential threat to ground and drinking water resources [2]. Therefore they have been chosen as model contaminants in this study. Up to the present day, there is no adequate in-situ remediation method for diesel or phenol contaminated land in Austria. Thus, the Institute of Sustainable Waste Management and Technology is developing a new in-situ electrokinetic remediation method. The technology is composed of three subsystems, which are electro synthesis of peroxodisulfate with diamond electrodes, electrokinetic distribution of the oxidant in soil and in-situ oxidation of diesel and phenol.

The goals of this master thesis were to present the methodological approach taken in this project, elaborating and naming crucial parameters of influence on the subsystems and giving further recommendations for the method's enhancement. The strategy for creating the new electrokinetic remediation method consisted of establishing each subsystem individually before unifying them (which was not part of this thesis). As a basis for the laboratory work, literature experiences from electrokinetic soil remediation (EK), in-situ chemical oxidation (ISCO) and electro synthesis (ES) with diamond electrodes have been utilized. In the following, the results of each field of investigation are summarized.

### *Spiking of Test Soil*

Before starting assays on contaminant decomposition in soil, the material has to be spiked homogeneously with the pollutant. An acceptable coefficient of variation should be inferior to 20 % [20, p. 401]. This means that any result referring to the contaminants concentration in the sample obtained after spiking is subjected to the coefficient of variance. Therefore, spiking tests were conducted prior to realizing soil decontamination by chemical oxidation. Diesel oil concentration in the spiked soil was determined by HC-index, TOC and COD. All methods yielded satisfying results with coefficients of variance of 4.2, 4.2 and 1.6, respectively, not counting outliers. For phenol analysis TOC and phenol-index were applied yielding coefficients of 1.6 and 17.3, respectively.

### *Decomposition of Contaminants in Soil*

The actual remediation work of the technology is conducted by chemical in-situ oxidation. The selected oxidant, peroxodisulfate, of an oxidation potential of 2.0 V is known to be able to degrade various types of organic compounds, amongst those phenols and petroleum hydrocarbons. Oxidation's performance can be enhanced by a Fenton like reaction, i.e. administering $Fe^{2+}$ as catalyst for sulfate free radical formation. Those are even more powerful oxidants with a potential of 2.6 V. Even though successful application of activated peroxodisulfate has been reported for aqueous media, tests on the oxidant's performance in soil are rare [9, pp. 20], [10, pp. 13]. So experiments were run with sandy loam soil with 20 % water content at 15 to 17 °C in the dark. The diesel spike concentration was 9.6 g/kg, phenol's concentration 0.5 mg/kg. Results revealed that phenol can be eliminated up to 99 % within four weeks with 54.0 mol peroxodisulfate per mol phenol in presence of iron(II) as catalyst, while diesel could be eliminated up to 84 % in twelve weeks also in presence of the catalyst with 284.6 mol peroxodisulfate per mol diesel. Referring to the outcome of phenol degradation, a higher amount of peroxodisulfate than 54.0 mol is inefficient. However, for both pollutants the amount of needed oxidant is very high. Considering more carefully the elimination curve of diesel oil, HC-index analysis detected an increase in hydrocarbons after two weeks of oxidation. Thus, the contaminant's oxidation needs to be investigated more thoroughly in order to be able to interpret the behavior or adapt the analytical method. In order to be able to further evaluate the success of chemical oxidation with peroxodisulfate of diesel and phenol, intermediate species should be monitored as they could be more harmful to the environment than the original pollutant. Furthermore, the potential amount of sulfates leaching into the groundwater should be determined.

### *Electro Synthesis of Peroxodisulfate with Diamond Electrodes*

Boron doped diamond (BDD) electrodes are known to have a high overpotential for water decomposition which makes them able to produce highly oxidative species, amongst those peroxodisulfate. Various researchers have shown that production of peroxodisulfate with chemical vapor deposition BDD electrodes is possible [68], [69], [70], [71]. However, assays with mechanically implanted (MI) BDD electrodes have not been reported. Thus, experiments have been conducted with various types of MI electrodes which have been developed especially for this study. These were a monopolar titanium based electrode, a monopolar electrode on polymer basis and a bipolar flow cell on polymer basis. The amount of oxidant was determined by iodometric titration. The final model provided best results within the group of MI electrodes. A kind of sensitivity analysis was conducted varying several parameters subsequently. It turned out that current density is the most crucial parameter. The best operation mode resulted at 20 °C with 0.85 M sodium sulfate electrolyte, three membranes and at 200 mA/cm². After 5 Ah/l more than 6 mmol/l peroxodisulfate could be generated. Under these conditions elimination of one mmol phenol would cost 36.72 cents. Additionally, a CVD electrode has been tested at 50 mA/cm² with five membranes at 15 °C and an electrolyte of a 0.85 M sodium sulfate solution yielding 1.1 mmol/(l*cm²), while the MI electrode under similar condiditions produced 0.8 mmol/(l*cm²) referred to the diamond covered area of the electrodes surface. Even though these results suggest opting for a CVD electrode, it has to be considered that these experiments were the first ones conducted with the MI BDD electrode cell prototypes, whereas the CVD electrode had been sophisticated during several years. Thus, results are promising for the MI electrode. Furthermore, investment and operation cost of both electrode types should be compared to the cost of peroxodisulfate purchase.

### *Electrokinetic Transport*

Electrokinetic (EK) remediation is classically applied for contaminant transport in soil towards a designated area. However, it can also be used to distribute an oxidant species in soil for in-situ oxidation. EK techniques are applicable to saturated and unsaturated soils with low permeabilities down to $10^{-9}$ m/s. The electric gradient provided by two field electrodes is supposed to spread homogeneously through the soil. Ion species are thus moved by electromigration or dragged by electroosmotic flow. Adverse effects on ion transport may occur due to physiochemical interactions with the soil particles, thus depending strongly on the soil type and texture. Usually, electrical gradients of 1 V/cm are applied. A possible drawback of this manner of ion distribution in soil is electrolysis occurring at the field electrodes provoking an acid front movment from the anode towards the cathode. [6, pp. 192], [8, p. 39], [22, p. 2640], [23, p. 100] Experiments conducted in the course of this project investigated mainly transport behavior of peroxodisulfate ions under several electrical gradients and in different soil compositions. For analysis, the soil was spiked with KI and starch so that peroxodisulfate presence would provoke a color reaction. Out of a series of eight different soil compositions, it was found that peroxodisulfate ions only migrated towards the anode when no clay was present. The fastest velocity was achieved in a 50 % sand and silt soil with 2.2 cm/h. Osmotic flow occurred every time silt was present. Generally, the pH-value dropped below 4 near the anode and rose to above 11 near the cathode. Temperature rose to over 40 ℃ near the electrodes. Another series of experiments with sand only varying the electric gradient from 1 to 4 V/cm showed that peroxodisulfate velocity obeys a linear equation of a slope of 0.56. Subsequent horizontally arranged experiments yielded different results. The highest ion migration velocity was found in an 80 % sand and each 10 % silt and clay soil with 4 cm/h. This is contrary to the reviewed literature which claims that soils with high clay content yield the best results. Thus, it is recommendable to enhance the set-up in order to produce more reliable results. In any case, experiments revealed that the soil texture and water content play a crucial role in ion migration.

Table 22 and Table 23 give a final overview of the most important results.

Table 22: Most crucial parameters

| **Field of investigation** | **Parameter** |
|---|---|
| contaminant decomposition | presence of catalyst |
| production of oxidant | current density<br>type of electrode |
| electrokinetic transport | soil composition<br>water content |

Table 23: Overview of obtained results

| Field of Investigation | Issue | Result | Specification |
|---|---|---|---|
| **Soil spiking** | homogeneity of diesel contamination | > 95 % | analysis: HC-index |
| | homogeneity of phenol contamination | > 98 % | analysis: TOC |
| **Decomposition of Contaminants** | elimination of diesel | > 84 % | in twelve weeks with 285 mol $Na_2S_2O_8$ per mol diesel and 0.7 mg $FeSO_4*7H_2O$ per gram of soil at 15 to 17 °C |
| | elimination of phenol | > 99 % | in four weeks with 54 mol $Na_2S_2O_8$ per mol phenol and 3.7 mg $FeSO_4*7H_2O$ per gram of soil at 15 to 17 °C |
| **Electro synthesis of peroxodisulfate** | monopolar MI diamond electrode on polymer basis | < 0.05 mmol/(l*cm²) | after 5 Ah/l, at 15 °C, 1 liter 0.85 mol/l $Na_2SO_4$ electrolyte, 67 mA/cm², 5 glass fiber membranes |
| | bipolar MI diamond electrode on polymer basis | 0.8 mmol/(l*cm²) | after 5 Ah/l, at 20 °C, 1 liter 0.85 mol/l $Na_2SO_4$ electrolyte, 45 mA/cm², 3 glass fiber membranes |
| | CVD diamond electrode | 1.1 mmol/(l*cm²) | after 5 Ah/l, at 15 °C, 1 liter 0.85 mol/l $Na_2SO_4$ electrolyte, 50 mA/cm², 5 glass fiber membranes |
| **Electrokinetic transport of peroxodisulfate ions** | vertical arrangement | 2.2 cm/h | in 50 % sand and silt soil, 4 V/cm |
| | horizontal arrangement | 4 cm/h | in 80 % sand and 10 % silt and clay soil, 1 V/cm |

Although, each domain of investigation needs further testing as recommended in Chapter 10, the outcome of the first experiments suggests that the new electrokinetic remediation method will work. Peroxodisulfate can be synthesized electrochemically with MI diamond electrodes and can be transported in soil by means of an electric gradient. The oxidant is able to eliminate diesel and phenol in soil. Thus, the three subsystems need to be combined and tested at larger scale while possible shortcomings of this method (soil acidification and sulfate lixiviation into groundwater) need to be considered more carefully.

# 12 Indices

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## 12.2 Tables

## 12.3 Figures

## 12.4 Abbreviations

| Abbreviation | Explanation |
|---|---|
| AC | alternating current |
| BDD | boron doped diamond electrode |
| BPP-BDD | bipolar polymer based boron doped diamond electrode |
| BTEX | benzene, toluene, ethylbenzene, xylene |
| CHC | chlorinated hydrocarbon compounds |
| COD | chemical oxygen demand |
| CV | coefficient of variance |
| CVD | chemical vapour deposition |
| CVD-BDD | chemical vapor deposition boron doped diamond electrode |
| DC | direct current |
| DCE | dichloroethene |
| DNAPL | dense non-aqueous phase liquid |
| DS | dry substance |
| EDTA | ethylenediaminetetraacetate |
| EK | electrokinetic remediation or treatment |
| EPA | Environmental Protection Agency (US) |
| FEA | Federal Environment Agency (Austria) |
| GC-MS | gas chromatography mass spectrometer |
| HC | hydrocarbon |
| HFCVD | hot filament chemical vapour deposition |
| HOC | hydrophobic organic compounds |
| ISCO | in-situ chemical oxidation |
| LC | lethal concentration |
| LD | lethal dose |
| LNAPL | low-dense non-aqueous phase liquid |
| MI | mechanically implanted |
| MPP-BDD | monopolar polymer based boron doped diamond electrode |
| MTBE | methyl tert-butyl ether |
| NAPLs | non-aqueous phase liquids |
| OC | organic carbon |
| ÖNORM | Austrian Standard |
| PAH | polycyclic aromatic hydrocarbons |
| PCB | polychlorinated biphenyls |
| PCE | perchloroethene |
| PP | polypropylene |
| SCE | standard calomel electrode |
| SHE | standard hydrogen electrode |
| SOM | soil organic matter |
| TCA | Trichloroethane |
| TCE | trichloroethene |
| Ti-BDD | titanium based boron doped diamond electrode |
| TOC | total organic carbon |
| TPH | total petroleum hydrocarbons |
| VOC | volatile organic carbons |
| WHO | World Health Organization |

# Annexure

# Appendix 1 – Contaminated Sites in Austria

Table 24: Austrian Standards concerning contaminated sites

| Austrian Standard | Concern |
|---|---|
| ÖNORM S 2085 | Contaminated Sites – Course of Action for Treatment of Waste Deposits and Industrial Sites: This standard determines the course of action for standards of the series S 2086 until S 2089. |
| ÖNORM S 2086 | Contaminated Sites – Terms and Definitions: This standard defines terms, which describe the technical background for the investigation and assessment of contaminated sites, as well as measures for hazard reduction and elimination. |
| ÖNORM S 2087 | Contaminated Sites – Identification and Investigation of (potentially) Contaminated Sites: This standard provides a practical overview on common identification and investigation methods, gives advice for efficient acquisition of information and regulates the comparability of results, which serve as a basis for the planning of treatment measures. |
| ÖNORM S 2088-1 | Contaminated Sites – Risk Assessment Concerning the Pollution of Groundwater Which Is to Be Safeguarded: This standard applies to the assessment of sites with respect to endangerment of groundwater. It provides inspection and intervention values which serve as a basis for further action. |
| ÖNORM S 2088-2 | Contaminated Sites – Risk Assessment for Polluted Soil Concerning Impacts on Surface Environments: This standard describes the foundations for the evaluation of investigation results of potentially contaminated sites and determines the assessment of the resulting endangerment of soil environments. |
| ÖNORM S 2088-3 | Contaminated Sites – Risk Assessment for Public Asset Air Which Is to Be Safeguarded: This standard describes the foundations for the evaluation of investigation results of potentially contaminated sites and determines the assessment of the resulting endangerment to public air. Its goal is to determine the necessity of containment or remediation measures. |
| ÖNORM S 2089 | Contaminated Sites – Security Measures and Remediation: This standard describes the current applied containment and remediation technologies. |
| ÖNORM S 2091 | Contaminated Sites – Solid Sampling: Extraction of Solid Samples from Contaminated Sites: This standard determines the requirements of solid sampling. The results are the basis for the assessment of the site’s hazard to humans and the environment or the foundation for control measures during site remediation. |

Table 25: Number of localized contaminated sites in Austria at 1, January 2006 [1, p. 13]

| **Province** | **Abandoned Landfills** | **Old Industrial Sites** | **Sum** |
|---|---|---|---|
| Burgenland | 100 | 3,098 | 3,198 |
| Carinthia | 472 | 32 | 504 |
| Lower Austria | 946 | 2,341 | 3,287 |
| Upper Austria | 1,465 | 9,105 | 10,570 |
| Salzburg | 411 | 5,602 | 6,013 |
| Styria | 377 | 4,306 | 4,683 |
| Tyrol | 644 | 1,449 | 2,093 |
| Vorarlberg | 14 | 6 | 20 |
| Vienna | 340 | 14,499 | 14,839 |
| **Sum** | **4,769** | **40,438** | **45,207** |

Table 26: Number of registered potentially contaminated sites in Austria at 1, January 2006 [1, p. 18]

| **Province** | **Abandoned Landfills** | **Old Industrial Sites** | **Sum** |
|---|---|---|---|
| Burgenland | 38 | 2 | 40 |
| Carinthia | 35 | 12 | 47 |
| Lower Austria | 369 | 46 | 415 |
| Upper Austria | 850 | 123 | 973 |
| Salzburg | 124 | 15 | 139 |
| Styria | 223 | 14 | 237 |
| Tyrol | 104 | 5 | 109 |
| Vorarlberg | 12 | 3 | 15 |
| Vienna | 41 | 14 | 55 |
| **Sum** | **1,796** | **234** | **2,030** |

Table 27: Status quo of contaminated sites management actions by 1, January 2006 [1, p.30]

| | **Contaminated Sites** | | | **Potentially Contaminated Sites** | | | |
|---|---|---|---|---|---|---|---|
| **Action** | **A. L.** | **O. I. S.** | **Sum** | **A. L.** | **O. I. S.** | **Sum** | **Total** |
| Remediation started | 4 | 14 | 18 | 0 | 0 | 0 | 18 |
| Securing started | 20 | 5 | 25 | 0 | 0 | 0 | 25 |
| Subtotal | 24 | 19 | 43 | 0 | 0 | 0 | 43 |
| Remediated | 30 | 21 | 51 | 18 | 6 | 24 | 75 |
| Secured | 17 | 2 | 19 | 5 | 1 | 6 | 25 |
| Subtotal | 47 | 23 | 70 | 23 | 7 | 30 | 100 |
| **Total** | **71** | **42** | **113** | **23** | **7** | **30** | **143** |

with A. L. = abandoned landfill and O. I. S. = old industrial site

# Appendix 2 – Additional ISCO Chemicals

### Permanganate

Permanganate is the most tested ISCO chemical both on scientific and practical level. Therefore, a wide range of information is available. The substance is easy to handle, except for dust production, and does not produce heat or gas while reacting in the soil matrix. It can be applied for a wide range of pH-values. Its reaction mechanism is as follows (see Eq. 42 till Eq. 44):

Eq. 42: $MnO_4^- + 8\ H^+ + 5\ e \rightarrow Mn^{2+} + 4\ H_2O$ (for $pH < 3.5$)

Eq. 43: $MnO_4^- + 2\ H_2O + 3\ e \rightarrow MnO_2 + 4\ OH^-$ (for pH 3.5 – 12)

Eq. 44. $MnO_4^- + e \rightarrow MnO_4^{2-}$ (for $pH > 12$)

The main disadvantage of permanganate is the formation of manganese peroxide, which can reduce pore conductivity in certain soil types. Its main advantage is its stability. Therefore, it can remain up to months in the subsurface and diffuse into lower permeability zones. Permanganate reacts by direct electron transfer in contrast to the Fenton's reagent and peroxodisulfate free radical. Nevertheless, large amounts are necessary to mineralize e.g. phenol (15.7 g potassium permanganate per g phenol) as has been tested in waste water treatment. Another shortcoming of permanganate is that it shows poor efficiency in oxidation of DNAPLs, benzene and MTBE. High concentration of permanganate in the injection solution might also lead to inefficient remediation and long term release of manganese into groundwater. Therefore, the EPA has established a threshold value of 0.05 mg/l. [10], [34], [9]

### Ozone

Ozone is the only gaseous oxidant used in the context of in-situ soil remediation. It is administered as an air ozone mixture to the soil, where it is mainly applied in vadose zone treatment, but it can also be injected under the water table for groundwater treatment functioning as in waste water treatment. As it is short-lived, it needs to be produced on-site. However, its generation is sumptuous. Ozone can react by direct electron transfer mainly attacking carbon double bondings or by radical reactions (see Eq. 45 and Eq. 46 respectively):

Eq. 45: $O_3 + 2\ H^+ + 2\ e \rightarrow O_2 + 2\ H_2O$

Eq. 46: $O_3 + OH^- \rightarrow O_2 + OH^\circ$

The following reaction steps involving radicals are identical to Eq. 8 and Eq. 9. Oxygen will continuously be produced as reaction product, which can enhance aerobic microbial activity in soil and support the oxidation success. Special attention has to be paid to soils rich in carbonates as those function as scavengers just like iron, manganese and organic carbon (not being component of a pollutant). A further drawback is the volatilization of contaminants. An advantage over permanganate and peroxodisulfate is that it does not leave any residual products such as $MnO_2$ or $SO_4^{2-}$.

Alternatively, ozone and hydrogen peroxide can be applied together, thus offering the advantages of both chemicals. The two oxidants also produce hydroxyl radicals (see Eq. 47).

Eq. 47: $2\,O_3 + H_2O_2 \rightarrow 2\,OH° + 3\,O_2$

[10], [34], [9]

# Appendix 3 – Patents

Several patents exist concerning ISCO techniques with persulfate application. The following Table 28 lists a selection of patents and their claim of invention.

Table 28: Patents concerning ISCO treatment with persulfate

| **Patent Number** | **Invention** |
|---|---|
| WO 2004002902A1 | The patent claims to oxidize soils, groundwater and waste water contaminated with VOCs. The preferred chemical is sodium persulfate. For in-situ soil remediation the oxidant is catalyzed by chelated transition metals (preferred catalyst is iron and chelating agent EDTA). |
| CA 255484A1<br>WO 2005/081996A3 | The patent claims to remove organic contaminants from soil and groundwater systems and the like by combinations of soluble peroxygen compound, such as sodium persulfate, at a pH higher than 10 buffered with metal hydroxides. |
| US 6474908B1 | The patent claims to treat soil contaminated with volatile organic compounds with either one or both oxidants. The preferred oxidants are sodium persulfate and potassium permanganate. |
| US 2004/0197150A1 | The patent claims to treat soil, sludge, groundwater and waste water contaminated with organic or inorganic pollutants. An aqueous solution of persulfate anions is provided and activated by chelated catalysts producing free radicals which oxidize the contaminants. |
| US 006019548A | The inventions claims to treat soils contaminated with VOC injecting a combination or individually persulfate and permanganate. |

# Appendix 4 – Chemical Vapor Deposition Process

### Chemical Vapor Deposition

CVD is the more common method for BDD fabrication. Three techniques are available:

1. plasma-assisted CVD,
2. hot filament CVD and
3. combustion flame CVD.

Basically, a carbon containing species in gas-phase, mostly methane, is transformed under low pressure into a cubic crystalline form with controlled integration of boron in an enriched hydrogen atmosphere. In the plasma-assisted process, it is the task of the plasma to generate atomic hydrogen and produce appropriate carbon precursors for diamond growth, i.e. $sp^3$ carbon. $Sp^2$ carbon corresponds to graphite and would leave an impure diamond surface on the electrode, which diminishes its properties [76, pp.11 – 14]. As the hot filament CVD (HFCVD) process is the most common and succeeded in producing the largest area electrodes in CVD processes, up to 0.5 $m^2$, this method will be explained more in detail, leaving out explanations for the combustion flame method. The base materials for HFCVD are refractory metals, such as Ti, Nb, W and also silicon or ceramics. The most common substrate is titanium. The first step is to pretreat the base metal. This can be done by sand-blasting for cleaning and increasing the surface's roughness. Then the filament is heated up to 2200 till 2600 °C and placed at some 20 cm from the substrate, whose temperature is at about 700 till 925 °C. The pressure is leveled at 10 to 50 mbar. A gas mixture of hydrogen (96 – 99%), methane (0.5 – 2.5 %) and boron (10 – 200 ppm) is introduced. [55, pp. 1951] Hydrogen is decomposed to atomic hydrogen due to the high filament temperature. This reacts with methane to hydrogen and an $sp^3$ carbon, which is deposited on the substrate.

The net reaction can be described as follows [76, p. 17]:

Eq. 48: $CH_{4\,(g)} \rightarrow C_{diamond} + 2H_2$

The surplus of hydrogen etches away the formed graphite. Figure 39 illustrates the process.

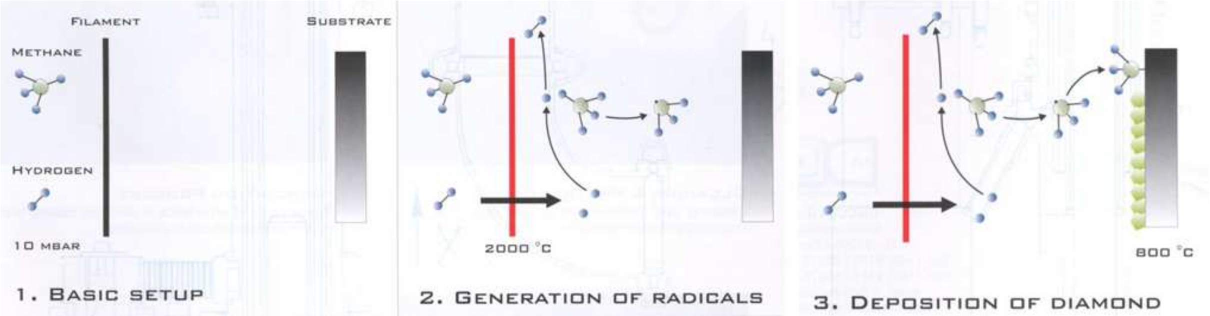


Figure 39: Hot filament CVD process [57]

The so generated BDD electrode works as a p-type conductor with semi metallic characteristics. It is characterized by a high electrical conductivity, a resistance of $10^4$ Ωcm at moderate doping levels of $10^8$ B atoms/$cm^3$, high chemical inertness and a wide potential window for water stability. The resistance is controlled by the concentration of boron in the diamond coating [58, p. 36], [59, p. 192]. The diamond film is about 1 to 5 µm thick and growth rates of about 0.2 to 1.0 µm/h are achieved [55, p.1952].

However, the titanium carbide layer which is generated during the process and located between the titanium substrate and the diamond film is responsible for poor adhesion of the diamond crystals on the metal. This is due to the different thermal expansion coefficients of the three materials. Because of the heat in the reactor the expansion leads to shearing stress in the BDD electrode [56, pp.1063]. Another disadvantage is that the titanium surface might be passivated by oxygen to titanium oxide. If the surface passivates the working area of the electrode becomes smaller and efficiency decreases.

# Appendix 5 - Waste Water Treatment with BDD Electrodes

This appendix reports briefly investigations on the degradation of organic compounds in water with diamond electrodes. Even though this project does not aim at waste water treatment, the reported literature has been studied in order to obtain a number of parameters that are crucial for successful BDD electrode operation. This is due to the fact, that BDD electrode performance has been studied best until now in the context of waste water treatment. Furthermore, a general application of the MI BDD used in this work for degradation of organic compounds in aqueous media has been tested in order to be able to compare the performance of the MI electrode with the CVD electrodes.

When treating waste water with BDD electrodes direct and indirect oxidation can occur. The first takes place at potentials below oxygen evolution, i.e. where water is stable. The latter option functions via electro generation of active species, normally OH°, in the potential region above water stability. These oxidative species have high potentials and can therefore oxidize organic compounds. The potential for phenol oxidation for example is 1.67 V. [59, pp. 192]. For the evaluation of the degradation performance, the current efficiency is measured. This generally depends on the initial concentration of the pollutant and the applied current density. At higher concentrations, the reaction is kinetically controlled, which means that there is no limitation in mass transport [59, p. 193].

The success of waste water treatment with BDD electrodes is very promising as various authors report current efficiencies of over 90 % and almost complete depletion of the pollutant (EDTA, malic acid and others [77]; EDTA, cooling lubricants and cyanides [62]; phenol [78]). Panizza et al. [59] give a complete overview on a number of studies in a critical review from 2005.

In Table 29 the main parameters, which have been considered in mentioned investigations shall be listed. They were taken as a basis for the proper experiments of the soil remediation project.

As degradation success is limited by mass transfer for low concentrations, Vatistas et al. [69] suggest using a two reactor set-up. Figure 40 shows such a system. Hydroxyl radicals are generated in the electrolysis cell and then pumped with the electrolyte into an oxidation chamber where, the waste water is treated. The oxidizing species are activated by heat or UV radiation. With turbulent mixing the mass transfer problem should not occur. This application is interesting for the soil remediation project as the soil's pollutant cannot be treated directly at the electrode. Therefore, oxidizing agents are produced in the electrochemical cell and are introduced into the soil, where they are activated by Fe(II) as catalyst. So in principle, these two procedures resemble each other.

Table 29: Parameters for degradation of organic compounds with BDD

| Parameter | Value | Application to | Reference |
|---|---:|---|---|
| **current density [mA / cm$^2$]** | 30 | 2,4-dinitrophenol | [79], [80] |
| | 30 - 50 | EDTA | [62] |
| | 30 | phenol | [61] |
| | 33,100,150 | paracetamol | [81] |
| | 4,16,36 | malic acid | [77] |
| | 10,20,40 | dyes | [82] |
| | 5,11,22,32 | benzoic acid | [83] |
| | 5, 60 | phenol | [84] |
| **temperature [℃]** | room | malic acid | [77] |
| | 25 | 2,4-dinitrophenol | [79], [80] |
| | 10,30,50 | dyes | [82] |
| | 25 | phenol | [84] |
| **electrode area [cm$^2$]** | 78 | 2,4-dinitrophenol | [79] |
| | 50 | phenol | [78] |
| | 50 | phenol | [84] |
| | 50 | benzoic acid | [83] |
| | 3 | paracetamol | [81] |
| **distance between electrodes [mm]** | 4 | malic acid | [77] |
| | 9 | 2,4-dinitrophenol | [79], [80] |
| | 10 | benzoic acid | [83] |
| **conductivity [mS/cm]** | 9,86 | EDTA | [77] |
| **electrolyte [g/l]** | 5 Na2SO4, H2SO4 | 2,4-dinitrophenol | [79] |
| | 2 Na2SO4 | dyes | [82] |
| | 0.5 M HClO4 | benzoic acid | [83] |
| | 1 M HClO4 | phenol | [84] |
| **flow rate [l/h]** | 150 | 2,4-dinitrophenol | [79] |
| **cathode material** | Ti | malic acid | [77] |
| | stainless steel | 2,4-dinitrophenol | [79] |
| | graphite | paracetamol | [81] |
| | stainless steel | dyes | [82] |
| | zirkonium | benzoic acid | [83] |

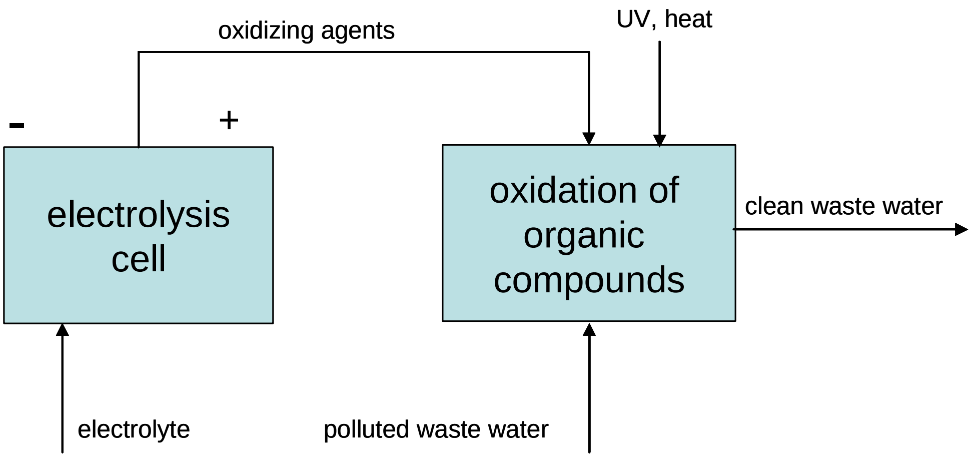


Figure 40: two step advanced oxidation process (compare [69, p. 484])

# Appendix 6 – Devices, Chemicals and Soil Material

Table 30: Devices used for laboratory experiments

| **Device** | **Application** | **Specification** |
|---|---|---|
| Analytical Balance | spiking, transport, decomposition of contaminants, persulfate production | Sartorius BP 221S (0 - 210g, 0.0001g) |
| Balance | spiking, transport, decomposition of contaminants, persulfate production spiking, | Sartorius GM 3101 (0 – 3000g, 0,1g) |
| Gas chromatograph | Hydrocarbon-index | Shimadzu GC-2010 mit AOC-20i Auto Injector, PTV |
| Conductivity Sensor | transport, persulfate production | WTW Multi 340i |
| Glasses | contaminant decomposition | 250 ml glasses with plastic screw taps |
| Glasses | sample keeping | 30 ml glasses with plastic screw taps |
| Horizontal Shaker | quantitative analysis of second horizontal transport experiments | IKA Labortechnik HS 501 digital |
| Overhead Shaker | pre-assays for decomposition of contaminants | Heidolph Reax 20 |
| pH meter | transport, decomposition of contaminants, persulfate production | WTW Multi 340i with WTW SenTix 41 |
| Power Supply | first horizontal and vertical transport, persulfate production | EA-HV 900-600-2000 (0 – 600 V; 0 – 3.33 A) |
| Power Supply (small) | second horizontal transport | Voltkraft PS 2403 D (0 – 40 V; 0 – 3.33 A) |
| Pumps | persulfate production | O.K. Zimmerbrunnenpumpe ZP 300, 300 l/h, 1m |
| Redox Sensor | persulfate production | WTW Multi 340i with WTW Sensolyt pt |
| Spectrometer | Phenol-index | UNICAM UV/VIS spectrometer UV 4 (measured at 460 nm) |
| Thermostat | persulfate production | Julabo F 34 - MD |
| Transport cylinder long | second series of vertical set-up | acrylic glass, length 1 m, inner diameter 10 cm |
| Transport cylinder small | first horizontal and vertical set-up | acrylic glass, spezial facturation, length 40 cm, inner diameter 10 cm, at 90° angles on the outer radius 4x3 sampling points, silicon tightening |
| Transport tubes | second horizontal set-up | PP sewage tubes, d = 4 cm, length 15 cm |
| Zentrifuge | quantitative analysis of second horizontal transport experiments | Sigma 3K18 |

Table 31: Chemicals

| Chemical Name | Purity | Molecular Weight | Brand |
|---|---|---|---|
| Ammonium persulfate | > 98 % | 228.2 | Roth |
| Ammonium sulfate | > 99 % | 132.1 | Roth |
| Hydrochloric acid | > 95 % | 36.4 | Roth |
| Iron(II) sulfate heptahydrate | > 99 % | 278.0 | Roth |
| Potassium iodate | > 99.7 % | 214.0 | Roth |
| Potassium iodide | > 99 % | 166.0 | Roth |
| Potassium sulfate | > 99 % | 174.3 | Roth |
| Sodium phenolate trihydrate | > 99 % | 154.0 | Aldrich |
| Sodium sulfate | > 99 % | 174.3 | Roth |
| Sodium thiosulfate | > 99 % | 248.2 | Roth |
| Starch | - | - | Maizena |
| Sulfuric acid | > 95 % | 98.1 | Roth |

Table 32: Soil material

| Material | Particle size | Density | Specification | Company |
|---|---|---|---|---|
| Sand | 0.06 – 2.00 mm | 1500 kg/m$^3$ | washed, $SiO_2$ > 90 % | Scherf |
| Sialin | 0.005 – 1.0 mm | 2600 kg/m$^3$ | bulk density 1200 kg/m$^3$, $SiO_2$ 76.2 %, $Al_2O_3$ 13.7 % | Kamig |
| Kaoline | 99.4 % < 20 µm | - | specific surface area 12.9 m$^2$/g, $SiO_2$ 47.6 %, $Al_2O_3$ 36.8 % | Kamig |
| Loam | - | - | - | pro Lehm |
| Zeolite | 3 – 60 µm | - | - | IPUS GmbH |

# Appendix 7 – Chemical Analytical Methods

## Hydrocarbon-Index

The hydrocarbon-index was determined according to ÖNORM EN ISO 9377-2:2001 by the laboratory of the Institute for Waste Management and Technology, University of Leoben, [85]. The following specifications have been applied:

1. sample mass: 5.0 g (+/- 0.1 g)
2. samples were mixed with 20 ml RTW standards
3. thermal program: 80 ℃ / 3 min, 20 ℃ / min auf 305 ℃ / 15 min, 20 ℃ / min auf 360 ℃ / 5 min (cleaning)
4. carrier gas: nitrogen, 48,6 cm / s
5. column: Retex XTI-5 (30m x 0,32 mm, 0,25µm)
6. Detector: flame ionization

## Phenol-Index

The phenol-index was determined according to DIN 38409-16 by the laboratory of the Institute for Waste Management and Technology, University of Leoben, [85]. The method is based on photometric determination of 4-aminoantipyrine without distillation with dye extraction. All standard chemicals were used and are not named in the chemical list. Samples were diluted mainly 1:400, several times 1:800 and one time 1:1000 with distilled water. The spectrometer was used at 460 nm.

## Iodometric Titration

Preparation of titration solution

One liter of distilled water was prepared by boiling for sterilization and down-cooling to room temperature. A respective amount of sodium thiosulfate was added in order to prepare a 0.1 M solution. For stabilization 1 g of amylalcohol was added.

Determination of the titration factor

$KIO_3$ was dried at 180℃ and cooled in an exsiccator. Then an amount of between 0.08 and 0.1 g were added to 200 ml distilled water in an Erlenmeyer flask. The exact amount of added $KIO_3$ has to be noted. Approximately 1 g of KI was aggregated together with 20 ml of hydrochloric acid (1:2 dilution). Finally, the prepared solution is titrated with the 0.1 M titration solution. As 1 ml of 0.1 M thiosulfate solution correspond to 3.567 mg of $KIO_3$ the following calculation leads to the theoretically needed amount of thiosulfate.

$$x = \frac{Y\,mg\,KIO_3^- * 1ml\ Na_2S_2O_3}{3{,}567\,mg\,KIO_3^-}$$ with Y = exact amount of $KIO_3$

The factor corresponds to the ratio of theoretical amount over actual amount of titration solution.

Determination of oxidants

The prepared samples (20 ml sample with 20 ml of 10 % sulfuric acid and an excess amount of KI) haven been titrated with the thiosulfate solution after a reaction time of at least three hours. The orange sample solution turns yellow and then transparent during titration. Before changing color to transparent a few drops of starch solution have been added in order to color the sample blue (due to the starch iodine complex) for better color distinction. The concentration of oxidant, i.e. persulfate, was calculated as follows:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Two moles of thiosulfate reduce one mol of iodine. Iodine has been formed by the oxidizing agents in the sample from the added KI. So the molar amount of iodine in the sample corresponds to the volume in ml of thiosulfate titrated multiplied with its concentration (0.1 M).

$$nI_2 = \frac{nS_2O_3^{2-}}{2} = \frac{cV\,S_2O_3^{2-}}{2}$$

As it was assumed that one mole persulfate oxidizes two moles of iodide into one mole of iodine, the determined amount of iodine ($nI_2$) is equal to the amount of persulfate having been present in the sample.

# Appendix 8 – Chromatograms

The following Figure 41 and Figure 42 show chromatograms for diesel degradation with 142.3 mol oxidant and iron catalyst after one and twelve weeks.

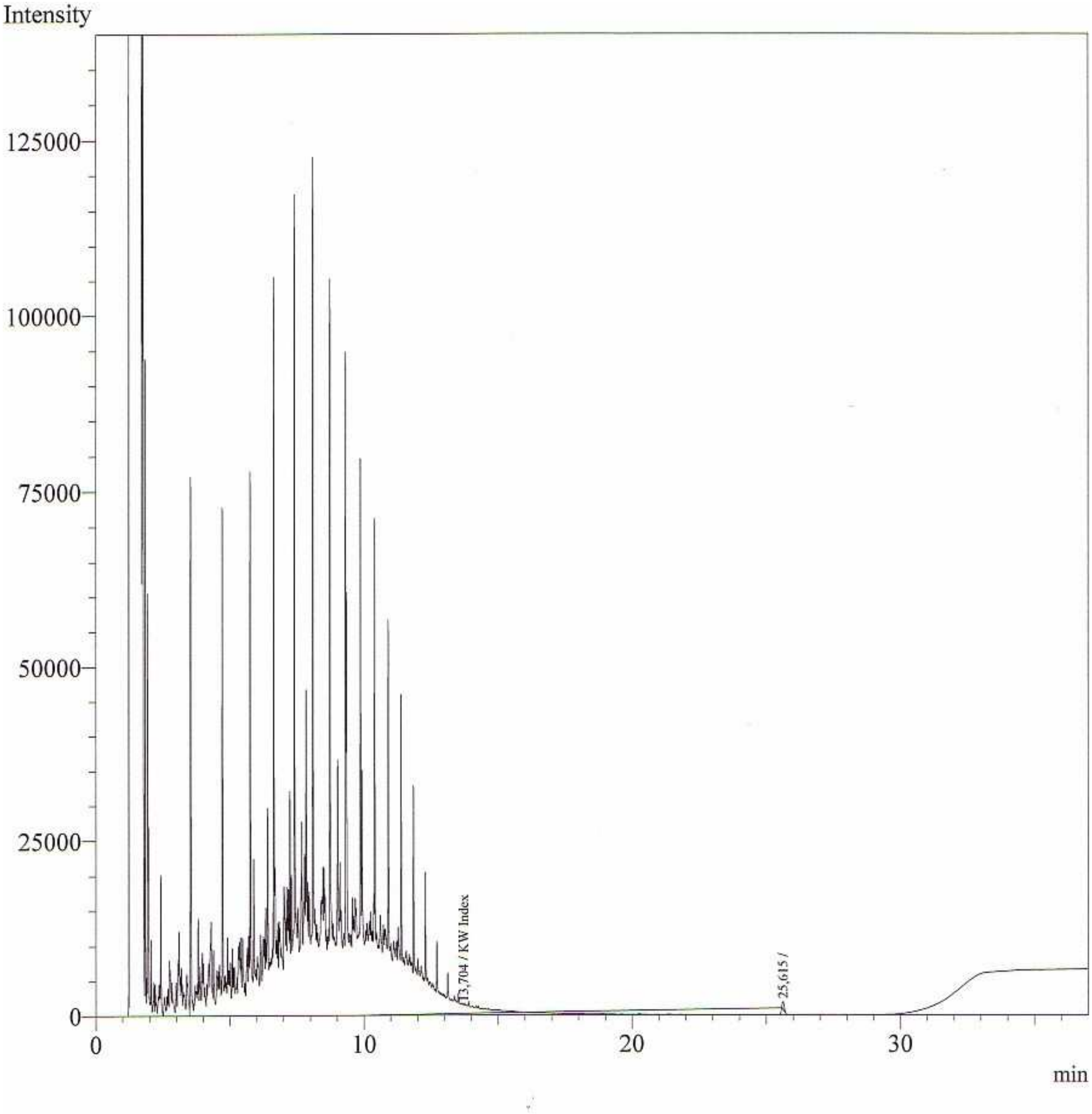


Figure 41: Chromatogram for diesel after one week of chemical reaction with 142.3 mol of persulfate and iron (II) catalyst [85]

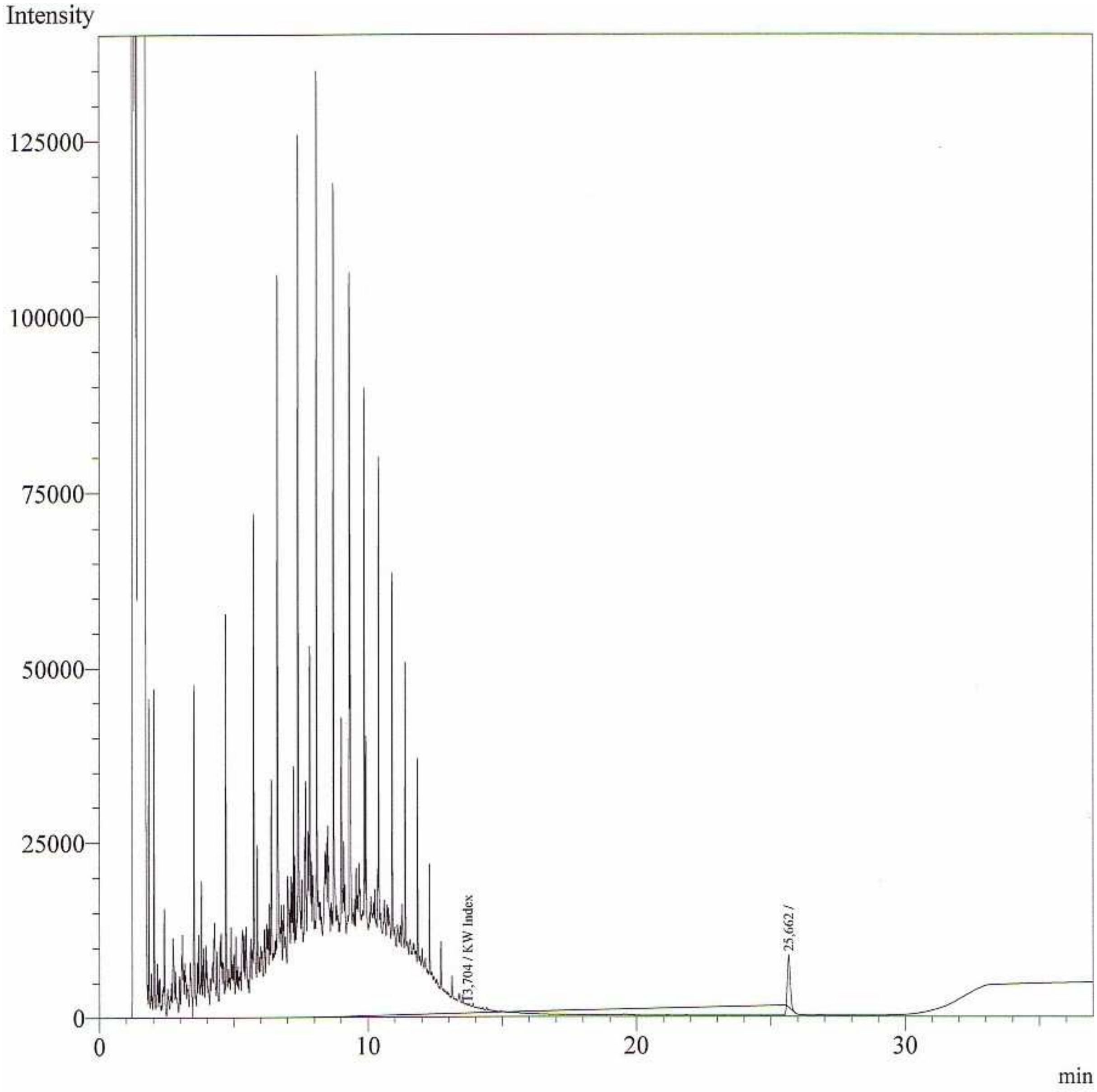


Figure 42: Chromatogram for diesel after twelve weeks of chemical reaction with 142.3 mol of persulfate and iron (II) catalyst [85]

Optically, the two chromatograms cannot be distinguished. Integration, however, reveals that after one week about 40 % and after twelve weeks about 80 % have been degraded.

# Appendix 9 – Soil Textural Triangle

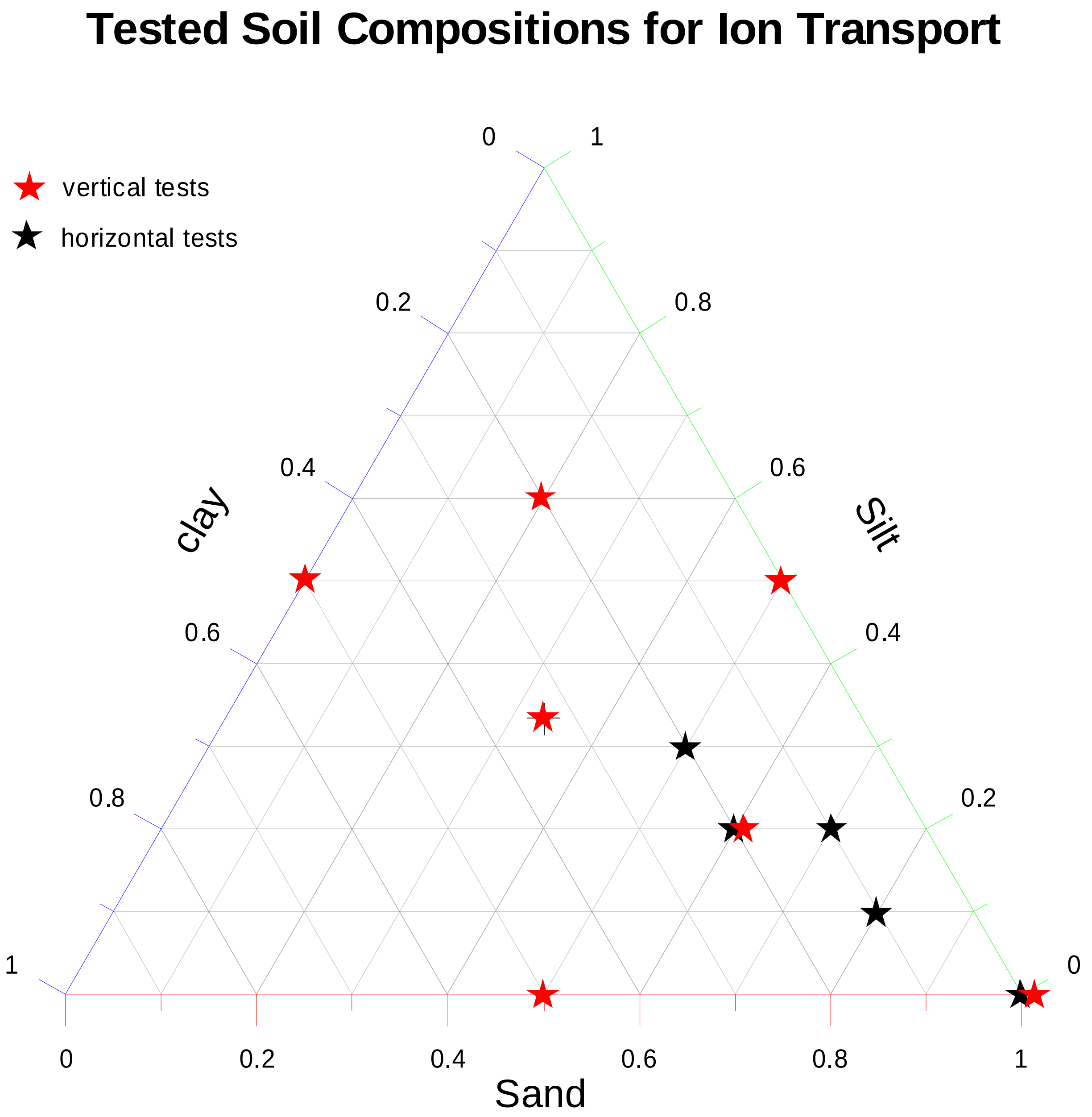


Figure 43: Tested soil compositions in vertical and horizontal arrangement for electrokinetic persulfate transport

# Appendix 10 – Linear Regression Calculations

Table 33: Linear regression calculation for oxidant production with the bipolar flow cell on polymer basis

| Parameter | Ah/l x | mmol/l y | mmol y_linear | coefficient of correlation R² | slope k | axis intercept x-axis b | formula y = kx+b |
|---|---|---|---|---|---|---|---|
| **mA/cm²** | | | | | | | |
| **133.33** | 0.26 | 1.23 | 1.23 | 0.95 | 0.77 | 1.04 | **y = 0.77x + 1.04** |
| | 0.52 | 1.21 | 1.44 | | | | |
| | 0.80 | 1.71 | 1.65 | | | | |
| | 1.09 | 2.08 | 1.87 | | | | |
| | 1.39 | 2.21 | 2.10 | | | | |
| | 1.70 | 2.32 | 2.35 | | | | |
| | 2.03 | 2.54 | 2.60 | | | | |
| | 2.38 | 2.80 | 2.86 | | | | |
| **166.67** | 0.32 | 0.80 | 0.92 | 0.92 | 1.07 | 0.58 | **y = 1.07x + 0.58** |
| | 0.65 | 1.39 | 1.27 | | | | |
| | 1.00 | 1.77 | 1.64 | | | | |
| | 1.36 | 1.97 | 2.03 | | | | |
| | 1.74 | 1.98 | 2.43 | | | | |
| | 2.13 | 3.21 | 2.85 | | | | |
| | 2.54 | 3.63 | 3.29 | | | | |
| | 2.98 | 3.44 | 3.75 | | | | |
| **200.00** | 0.38 | 1.26 | 1.56 | 0.95 | 1.09 | 1.14 | **y = 1.09x + 1.14** |
| | 0.78 | 1.82 | 1.99 | | | | |
| | 1.20 | 2.63 | 2.44 | | | | |
| | 1.63 | 2.96 | 2.91 | | | | |
| | 2.08 | 3.83 | 3.41 | | | | |
| | 2.56 | 4.17 | 3.92 | | | | |
| | 3.05 | 4.44 | 4.46 | | | | |
| | 3.57 | 4.61 | 5.03 | | | | |
| **°C** | | | | | | | |
| **20** | 0.78 | 2.85 | 3.34 | 0.97 | 0.67 | 2.81 | **y = 0.67x + 2.81** |
| | 1.63 | 3.81 | 3.91 | | | | |
| | 2.56 | 4.68 | 4.53 | | | | |
| | 3.57 | 5.46 | 5.21 | | | | |
| | 4.69 | 6.30 | 5.96 | | | | |
| | 5.92 | 7.15 | 6.79 | | | | |
| | 7.29 | 7.68 | 7.71 | | | | |
| | 8.82 | 8.26 | 8.74 | | | | |
| **30** | 0.78 | 2.75 | 3.22 | 0.95 | 0.61 | 2.75 | **y = 0.61x + 2.75** |
| | 1.63 | 3.54 | 3.74 | | | | |
| | 2.56 | 4.49 | 4.31 | | | | |
| | 3.57 | 5.12 | 4.93 | | | | |
| | 4.69 | 6.15 | 5.61 | | | | |
| | 5.92 | 6.66 | 6.36 | | | | |
| | 7.29 | 7.18 | 7.20 | | | | |
| | 8.82 | 7.61 | 8.14 | | | | |
| **40** | 0.78 | 2.85 | 3.22 | 0.97 | 0.60 | 2.75 | **y = 0.60x + 2.75** |
| | 1.63 | 3.63 | 3.73 | | | | |
| | 2.56 | 4.28 | 4.28 | | | | |
| | 3.57 | 5.19 | 4.89 | | | | |
| | 4.69 | 5.78 | 5.56 | | | | |
| | 5.92 | 6.75 | 6.30 | | | | |
| | 7.29 | 7.07 | 7.12 | | | | |
| | 8.82 | 7.59 | 8.04 | | | | |
| **45** | 0.78 | 2.12 | 2.59 | 0.95 | 0.61 | 2.11 | **y = 0.61x + 2.11** |
| | 1.63 | 2.83 | 3.10 | | | | |
| | 2.56 | 3.96 | 3.67 | | | | |
| | 3.57 | 5.03 | 4.29 | | | | |
| | 4.69 | 5.00 | 4.97 | | | | |
| | 5.92 | 5.80 | 5.72 | | | | |
| | 7.29 | 6.36 | 6.55 | | | | |
| | 8.82 | 7.29 | 7.49 | | | | |

Continuation of Table 33: Linear regression calculation for oxidant production with the bipolar flow cell on polymer basis

| mol acid / l | | | | | | | |
|---|---|---|---|---|---|---|---|
| **0.00** | 0.78 | 2.85 | 3.06 | 0.99 | 0.82 | 2.41 | **y = 0.82x + 2.41** |
| | 1.63 | 3.81 | 3.76 | | | | |
| | 2.56 | 4.68 | 4.52 | | | | |
| | 3.57 | 5.46 | 5.35 | | | | |
| | 4.69 | 6.30 | 6.27 | | | | |
| | 5.92 | 7.15 | 7.29 | | | | |
| **0.17** | 0.78 | 2.40 | 2.85 | 0.95 | 0.71 | 2.29 | **y = 0.71x + 2.29** |
| | 1.63 | 3.58 | 3.45 | | | | |
| | 2.56 | 4.47 | 4.11 | | | | |
| | 3.57 | 5.11 | 4.84 | | | | |
| | 4.69 | 5.57 | 5.63 | | | | |
| | 5.92 | 6.26 | 6.51 | | | | |
| **0.43** | 0.78 | 2.19 | 2.51 | 0.94 | 0.72 | 1.95 | **y = 0,72x + 1.95** |
| | 1.63 | 3.18 | 3.11 | | | | |
| | 2.56 | 3.74 | 3.78 | | | | |
| | 3.57 | 5.01 | 4.51 | | | | |
| | 4.69 | 5.52 | 5.31 | | | | |
| | 5.92 | 5.76 | 6.19 | | | | |
| **0.85** | 0.88 | 2.01 | 2.40 | 0.93 | 0.66 | 1.82 | **y = 0.66x + 1.82** |
| | 1.85 | 3.62 | 3.03 | | | | |
| | 2.85 | 3.65 | 3.69 | | | | |
| | 3.90 | 4.35 | 4.38 | | | | |
| | 5.00 | 4.82 | 5.10 | | | | |
| | 6.16 | 6.01 | 5.87 | | | | |
| **# membranes** | | | | | | | |
| **0** | 0.78 | 1.94 | 2.19 | 0.98 | 0.59 | 1.73 | **y = 0.59x + 1.73** |
| | 1.63 | 2.77 | 2.70 | | | | |
| | 2.56 | 3.31 | 3.25 | | | | |
| | 3.57 | 3.78 | 3.85 | | | | |
| | 4.69 | 4.75 | 4.52 | | | | |
| | 5.92 | 5.32 | 5.25 | | | | |
| | 7.29 | 6.29 | 6.06 | | | | |
| | 8.82 | 6.64 | 6.97 | | | | |
| **1** | 0.78 | 2.40 | 3.05 | 0.93 | 0.71 | 2.49 | **y = 0.71x + 2.49** |
| | 1.63 | 3.46 | 3.65 | | | | |
| | 2.56 | 4.59 | 4.31 | | | | |
| | 3.57 | 5.28 | 5.03 | | | | |
| | 4.69 | 6.15 | 5.83 | | | | |
| | 5.92 | 7.32 | 6.71 | | | | |
| | 7.29 | 7.97 | 7.68 | | | | |
| | 8.82 | 7.87 | 8.77 | | | | |
| **3** | 0.78 | 2.85 | 3.34 | 0.97 | 0.67 | 2.81 | **y = 0.67x + 2.81** |
| | 1.63 | 3.81 | 3.91 | | | | |
| | 2.56 | 4.68 | 4.53 | | | | |
| | 3.57 | 5.46 | 5.21 | | | | |
| | 4.69 | 6.30 | 5.96 | | | | |
| | 5.92 | 7.15 | 6.79 | | | | |
| | 7.29 | 7.68 | 7.71 | | | | |
| | 8.82 | 8.26 | 8.74 | | | | |
| **5** | 0.78 | 1.64 | 2.05 | 0.98 | 0.60 | 1.59 | **y = 0.60x + 1.59** |
| | 1.63 | 2.61 | 2.56 | | | | |
| | 2.56 | 3.43 | 3.11 | | | | |
| | 3.57 | 3.83 | 3.72 | | | | |
| | 4.69 | 4.24 | 4.39 | | | | |
| | 5.92 | 5.46 | 5.12 | | | | |
| | 7.29 | 5.95 | 5.94 | | | | |
| | 8.82 | 6.59 | 6.86 | | | | |

Table 34: Linear regression calculation of different diamond electrode flow cells at similar conditions referred to diamond covered surface

| Cell | Ah/l<br>x | mmol/l<br>y | mmol<br>y_linear | coefficient of<br>correlation R$^2$ | slope<br>k | axis intercept<br>x-axis b | formula<br>y = kx+b |
|---|---|---|---|---|---|---|---|
| **67 mA/cm$^2$, 20 °C, 3 membranes** | | | | | | | |
| **bipolar flow cell** | 0.13 | 0.88 | 1.00 | 0.98 | 1.44 | 0.82 | **y = 1.44x + 0.82** |
| | 0.26 | 1.18 | 1.19 | | | | |
| | 0.40 | 1.45 | 1.39 | | | | |
| | 0.54 | 1.66 | 1.60 | | | | |
| | 0.69 | 1.92 | 1.82 | | | | **y = 0.08x + 0.04 *)** |
| | 0.85 | 2.05 | 2.04 | | | | |
| | 1.02 | 2.28 | 2.28 | | | | |
| | 1.19 | 2.44 | 2.53 | | | | |
| **56 mA/cm$^2$, 15 °C, 5 membranes** | | | | | | | |
| **monopolar flow cell** | 0.38 | 0.57 | 0.54 | 0.85 | -0.03 | 0.55 | **y = -0.03x + 0.55** |
| | 0.75 | 0.50 | 0.53 | | | | |
| | 1.13 | 0.50 | 0.51 | | | | |
| | 1.50 | 0.50 | 0.50 | | | | |
| | 1.88 | 0.48 | 0.49 | | | | **y = -0.001x + 0.02 *)** |
| | 2.25 | 0.46 | 0.47 | | | | |
| | 3.00 | 0.46 | 0.45 | | | | |
| | 3.75 | 0.43 | 0.42 | | | | |
| **45 mA/cm$^2$, 15 °C, 5 membranes** | | | | | | | |
| **Ti flow cell** | 0.38 | 0.96 | 1.06 | 0.98 | 0.76 | 0.78 | **y = 0.76x + 0.78** |
| | 0.75 | 1.35 | 1.35 | | | | |
| | 1.13 | 1.73 | 1.63 | | | | |
| | 1.50 | 2.06 | 1.92 | | | | |
| | 1.88 | 2.22 | 2.21 | | | | **y = 0.05x + 0.05 *)** |
| | 2.25 | 2.40 | 2.49 | | | | |
| | 2.63 | 2.63 | 2.78 | | | | |
| | 3.00 | 3.17 | 3.07 | | | | |
| **50 mA/cm$^2$, 20 °C, 5 membranes** | | | | | | | |
| **CVD flow cell** | 0.38 | 1.51 | 1.67 | 0.99 | 3.36 | 0.41 | **y = 3.36x + 0.41** |
| | 0.75 | 2.66 | 2.93 | | | | |
| | 1.13 | 4.47 | 4.19 | | | | |
| | 1.50 | 5.42 | 5.45 | | | | |
| | 1.88 | 6.87 | 6.70 | | | | **y = 0.11x + 0.01 *)** |
| | 2.25 | 8.59 | 7.96 | | | | |
| | 3.00 | 9.68 | 10.48 | | | | |
| | 3.75 | 13.18 | 13.00 | | | | |

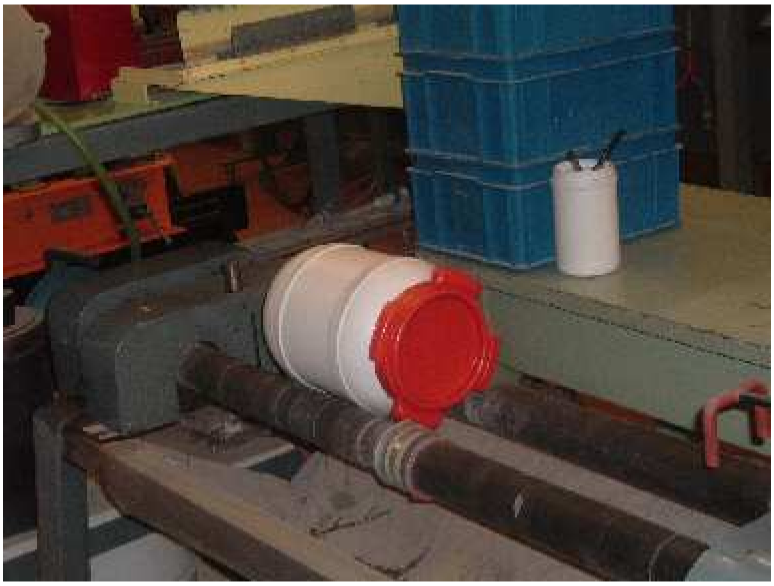
***) referred to diamond covered surface**

Table 35: Net diamond covered surface of different diamond electrode types

| Cell | Electrode surface<br>cm$^2$ | Diamond coverage<br>% | Diamond covered surface<br>cm$^2$ |
|---|---|---|---|
| bipolar flow cell | 45 | 40 | 18 |
| monopolar flow cell | 54 | 40 | 21.6 |
| Ti flow cell | 66 | 25 | 16.5 |
| CVD flow cell | 30 | 100 | 30 |

# Appendix 11 – Photos

Picture 1: Soil spiking with diesel oil



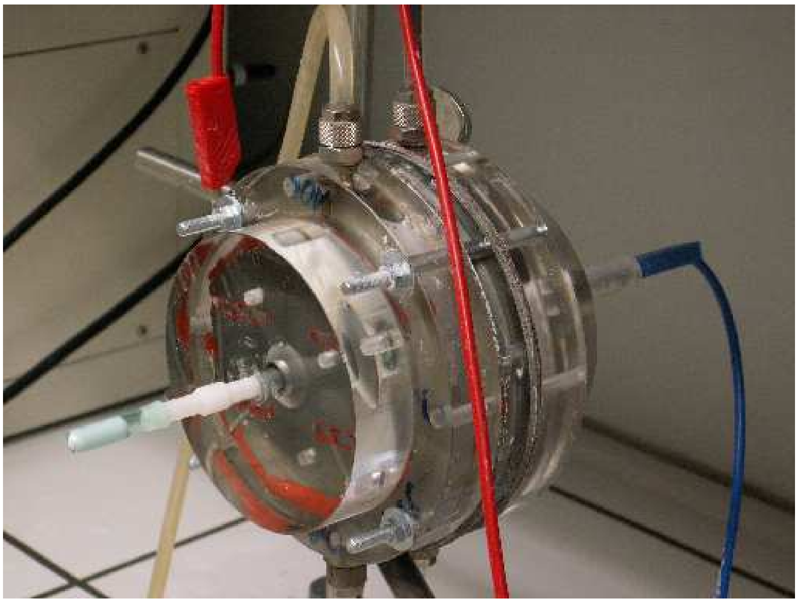
Picture 2: Mixing of spiked soil

Picture 3: First horizontal transport system with integrated oxidant solution circulation

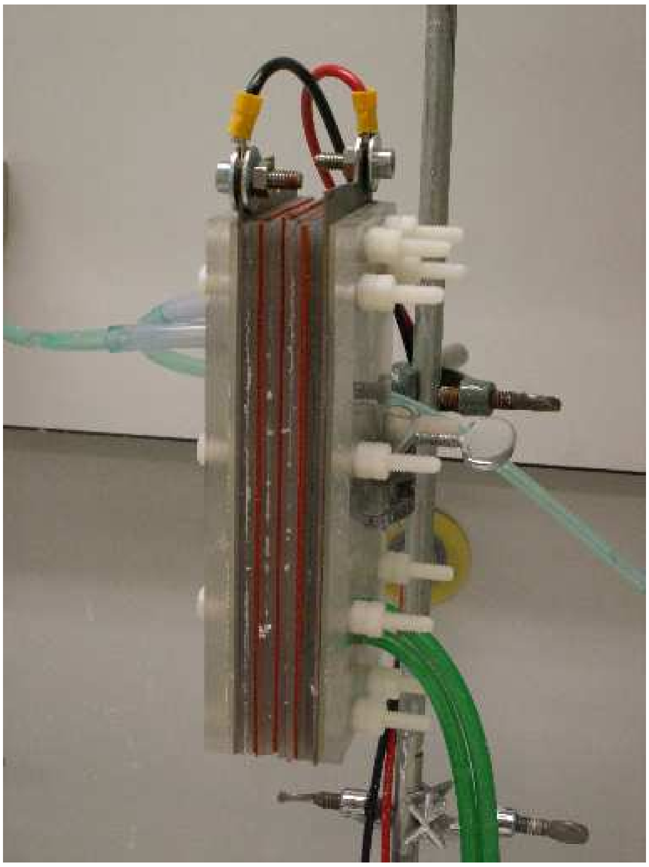
Picture 4: Vertical transport assay

The anode is located on the left side. Both cylinders are placed into the oxidant solution.

Picture 5: Pushing out the soil column in order to produce slices for analysis



Picture 6: Monopolar flow cell on polymer basis



Picture 7: Bipolar flow cell on polymer basis