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Investigations of soil solution during enhanced electrodialytic soil remediation

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Abstract

Electrodialytic soil remediation is a method to remove heavy metals from fine-grained polluted soil. The method has been developed at the Technical University of Denmark and has been used for over 10 years and is still being optimised. The removal of heavy metals during electrodialytic soil remediation is dependent on desorption of the heavy metals, as charged species, from the soil to the soil solution. Electromigration or electroosmosis will remove the heavy metals, when present in the soil solution. Previous investigations of soil solution sampling from electrodialytic experiments are limited.

Copper and chromium are strongly bound to the soil and desorption of these heavy metals to the soil solution in electrodialytic remediation, is dependent on the development of an acidic front. By adding desorbing agents to the soil e.g. base or acid, desorption can be accelerated and furthermore, the removal of copper and chromium from the soil should be faster.

Different soil solution sampling techniques are known from field sampling. The most common are zero – tension sampling (lysimeters, wick sampling systems and other passive sampling systems), tension sampling (different suction cells) and others (extraction and centrifugation). The most widely used non-destructive sampling system is tension sampling with suction cups.

A Teflon/quartz suction cup, which will allow non-destructive sampling at the same point in the soil, is chosen as soil solution sampler for the experimental work of this thesis. The sampler exhibit properties that makes it ideal for soil solution sampling in electrodialytic soil remediation: it is small enough to fit into the experimental cell and it will not sorb heavy metals.

Characterisation of the polluted soil, extraction experiments with different desorbing agents and different liquid/solid ratios were made in addition to six electrodialytic experiments. The results from the soil characterisation and the preliminary extraction experiments showed that ammonium citrate pH 8 was a good desorbing agent, and would give high concentration of both copper and chromium in the soil solution. Copper and chromium will form both positively and negatively charged complexes with ammonium citrate. Furthermore, the high pH in the soil would keep the carbonate in the soil immobile and thus, current would not be used to remove Ca^{2+} - ions from the soil.

It was possible to collect soil solution samples from the experiments by making a small change in the experimental set-up. The anioexchange membrane in the set-up was replaced by a passive membrane, which allows continuous addition of electrolyte to the soil and thus, keep the soil saturated during the experiment. The soil solution sampler was placed in the middle of the soil compartment. Applying vacuum to the soil solution sampler, exerted by a 20 ml syringe, collected the soil solution sample. Sampling of 2-5 ml of soil solution took 10 – 120 minutes and the sampling was generally easiest in the beginning of the experiment.

Copper and chromium were behaving very differently in the soil solution. The copper concentration in the soil solution during the experiment did not vary much from the start concentration, indicating that copper was easily desorbed by ammonium citrate and the desorption equilibrium was fast. The chromium concentration in the soil solution during the experiment was on the other hand higher than the start concentration, indicating that the desorption equilibrium of chromium is slower than for copper.

Copper was removed from the soil as both anions and cations, but chromium was removed from the soil mainly as anions. The formed chromium – ammonia complexes are probably too large to penetrate the cation – exchange membrane, which is the reason why chromium is not being removed to the cathode side of the cell.

Neither of the experiments were remediated for copper nor chromium and the high concentrations in the soil solution also supports this. Predicted soil and soil solution profiles were made. These profiles showed that when the soil is almost remediated, a sudden drop in the soil solution concentration could be expected, because the available fraction of copper and chromium will decrease. This concentration drop was not observed in any of the six experiments, indicating that the remediation period for the experiments was too short. The concentration profiles in the soil showed that copper would first be removed from a slice in the middle of the soil, and chromium would first be removed from the soil closest to the cathode.

If soil solution sampling is used to determine when the soil is remediated in electro-dialytic soil remediation, it is important to let the remediation continue, even if the drop in the concentrations in the soil solution is seen, because it will mean that only parts of the soil is remediated.

Resumé

Elektrodialytisk rensning er en metode til at rense tungmetaller fra finkornet jord. Metoden er udviklet ved Danmarks Tekniske Universitet. Den er blevet brugt i over 10 år og bliver stadig forbedret. Fjernelsen af tungmetaller under elektrodialytisk jordrensning er afhængig af, at tungmetallerne desorberer fra jorden til jordvæsken som ioner. Elektromigration og elektroosmose vil derefter fjerne tungmetallerne fra jordvæsken. Tidligere forsøg på at udtage jordvæske prøver fra elektrodialytiske jordrensningsforsøg er begrænsede.

Kobber og krom er hårdt bundet til jord og desorption af disse tungmetaller til jordvæsken i elektrodialytiske forsøg er afhængig af udbredelsen af syrefronten. Ved tilsætning af kemikalier, som f.eks. syre eller base, kan desorptionen accelereres og fjernelsen af kobber og krom vil være hurtigere.

Forskellige metoder for at udtage jordvæske er kendt fra felt prøveudtagning. De mest almindelige metoder for at udtage jordvæske, er gravitationsprøvetagere (lysimetre, væge-prøvetagere og andre passive prøvetagere), vacuumprøvetagere (forskellige sugeceller) og andre prøvetagningsmetoder (ekstraktion og centrifugering). Den mest brugte ikke-destruktive prøveudtagningsmetode er vakuump prøveudtagning med sugekopper.

En teflon/quartz sugekop, som tillader ikke-destruktiv prøveudtagning fra samme sted, vil blive brugt som jordvæske udtager i den eksperimentelle del af dette projekt. Prøveudtageren har egenskaber som gør den ideel for jordvæskeprøve udtagning i elektrodialytiske forsøg: den er lille nok til at passe ind i den eksperimentelle celle og den sorberer ikke tungmetaller.

Karakterisering af den forureneede jord, ekstraktionsforsøg med forskellige kemikalier og forskellig væske/jord forhold er udført, udover seks elektrodialytiske forsøg. Resultaterne fra jordkarakteriseringen og de indledende ekstraktionsforsøg viser, at ammonium citrat pH 8 er god til at desorbere både kobber og krom, og der vil opnås høje koncentrationer af begge disse metaller i jordvæsken. Kobber og krom vil danne både negativt og positivt ladede komplekser i ammonium citrat. Endvidere vil den høje pH gøre, at karbonat vil være immobiliseret i jorden, som betyder at strømmen ikke vil spildes ved at fjerne calcium -ioner fra jorden.

Det var muligt at udtage jordvæskeprøver fra forsøgene ved at lave en lille ændring i den eksperimentelle opstilling. Ændringen bestod i, at placere en passiv membran i kontakt med jorden i stedet for en anionbyttmembran. Den passive membran tillader nemlig transport af væske, som vil medføre, at jorden ikke udtørres og jordvæske prøver kan udtages gennem hele forsøget. Ved at påføre prøveudtageren vakuum med en 20 ml engangssprøjte, kunne jordvæsken udtages. Udtagning af 2-5 ml jordvæske tog mellem 10 – 120 minutter og prøveudtagningen var generelt nemmest i starten af forsøgene.

Kobber og krom opførte sig forskelligt i jordvæsken. Kobber koncentrationen i jordvæsken under forsøgene ændredes ikke nævneværdigt i forhold til start koncentrationen, hvilket indikerer, at kobber desorptions ligevægten til jordvæsken

indstilles hurtigt. Krom koncentrationen var meget højere under forsøget end start koncentrationen, hvilket tyder på, at desorptions ligevægten for krom indstilles langsommere end for kobber.

Kobber blev fjernet fra jorden både som anioner og kationer, mens krom hovedsageligt blev fjernet fra jorden som anioner. De dannede krom – ammoniak komplekser er sandsynligvis for store til at trænge igennem kationbyttermembranen, hvilket er grunden til at krom ikke genfindes i katode enden af cellen.

Ingen af forsøgene blev rensset for hverken kobber eller krom og de høje koncentrationer i jordvæsken underbygger dette. Mulige rensningsprofiler for jord og jordvæske blev lavet. Disse profiler viste, at når jorden er ved at være rensset, vil der ske et drastisk fald i jordvæske koncentrationen fordi den tilgængelige fraktion af kobber og krom i jorden vil mindske. Dette koncentrationsfald var ikke set i nogen af forsøgene, hvilket indikerer, at rensningstiden i forsøgene var for kort. Koncentrationsprofilerne for jord viste, at kobber først bliver fjernet et sted i midten af cellen og krom vil først blive fjernet fra jordskiven tættest på katoden.

Hvis jordvæske prøveudtagning skal bruges til at vurdere, hvornår jorden er rensset ved elektrodialytisk jordrensning, er det vigtigt at lade rensningen fortsætte, selv om det omtalte koncentrationsfald i jordvæsken observeres, fordi kun dele af jorden er færdig rensset, når dette koncentrationsfald observeres.

Preface

This rapport is the written part of my Master thesis, which is the final work in obtaining the Master of Science degree at the Technical University of Denmark, DTU. The thesis is credited 30 point in DTUs point system. The thesis has been made in the period from March 2001 to August 2001 at the Department of Civil Engineering.

I would like to thank my supervisor, associate professor Lisbeth M. Ottosen, for supervision during the project, and for being excellent in inspiring me to try new methods in the laboratory and always to have faith in my experiments.

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1 Introduction

Copper and chromium are essential nutrients for plants, animals and humans. However, copper and chromium can be toxic in high concentrations. In Denmark, copper and chromium have been used in e.g. wood preservation, and the soil at the wood preservation sites are highly polluted. Both copper and chromium are strongly bound to the soil and will not be mobile under natural conditions. Although the heavy metals will be immobile, the polluted soil cannot be used for any purposes and has to be remediated or disposed of. The remediation options for copper and chromium polluted soils are limited, but a method called electro-dialytic soil remediation can be used.

Electro-dialytic soil remediation has been used to remediate fine-grained heavy metal polluted soil for almost 10 years at the Technical University of Denmark. In electro-dialytic soil remediation, an electric field is used to decontaminate the soil and the electric current is the cleaning agent. When an electric field is applied to the soil, the electrochemical processes, electromigration and electroosmosis will occur, which transport the heavy metals out of the soil. Electro-dialytic soil remediation experiments can be performed in laboratory scale, bench scale or pilot scale. Glass or plastic cells are used in laboratory scale experiments, and in these experiments, the soil is encapsulated and cannot be influenced by other processes than electrochemical processes. Larger bench scale and pilot scale experiments are usually performed in open plastic vessels, where it is possible to collect soil samples, or add chemicals or liquid to the soil.

The electro-dialytic remediation method is still under development and improvement. Present research includes addition of different desorbing agents, both acids and bases, to the soil, to enhance the remediation of heavy metals.

The soil compartment of the laboratory experimental cell can be seen as a black box during the experiment. During an experiment it is possible to measure removed concentrations of heavy metals in the electrolytes, but knowledge of the processes and rates of releasing the heavy metals from the soil to the soil solutions are limited. Samples of the soil solution during the experiments would give valuable information of the behaviour of the heavy metals during the remediation, and ideas for optimising the method, since the electromigration of the heavy metals takes place in the soil solution.

Previous investigations concerning sampling of soil solution from electro-dialytic soil remediation experiments in laboratory scale are limited. Ribeiro (1998) found that direct extraction of soil solution from an electro-dialytic experiment by using vacuum extraction with a ceramic porous cup or a microporous sampler, which was placed in the middle of the soil, was almost impossible. The reason was that the soil becomes undersaturated during the electro-dialytic remediation and thus, there will not be enough solution to be sampled. Different methods to add water to the sampling point were tried in order to maintain the humidity in the soil, but none of them were found to be fruitful. Other experiments by Ribeiro (1998), showed that it was possible to collect soil solution samples from an electrokinetic remediation experiment (with passive membranes instead of ionexchange membranes). The most concerning problem with collecting soil solution from electrokinetic experiment is to collect sufficient amount of sample to be able to make all the desired analysis.

Nystrøm (2000) sampled soil solution from an electro-dialytic pilot plant experiment, called Megalab, using zero-tension sampling. The sampling system consisted of nylon filter wrapped around a plastic tube full of small holes and the tube was placed in the soil. The soil solution would enter into the tube and the sample could easily be taken. There were hardly any difficulties in collecting samples in this experiment, because liquid was frequently added to the soil and this could be done whenever the soil was getting dry.

2 Aim

The overall aim of this thesis is to investigate the soil solution during the enhanced electro-dialytic soil remediation. Since the knowledge on this field is limited, experiments in laboratory scale are conducted to answer the following questions:

- How is soil solution sampled from the electro-dialytic experiments?
- How do copper and chromium behave in the soil solution during the electro-dialytic experiments?
- How is the desorbing agent influencing the remediation?
- Can soil solution sampling be used to determine when the soil in electro-dialytic experiments is remediated?

2.1 Method

This thesis consists of a theoretical and a practical part. Since there does not exist theory about the soil solution in electro-dialytic remediation, the theory will be collected from the areas of the behaviour of heavy metals in soil, the different soil processes that determine the soil solution composition and the methods for sampling soil solution in the field. The theory of electro-dialytic remediation is presented, together with a prediction of the behaviour of the heavy metals in the soil solution and furthermore, the influence of the soil solution sampler in the electro-dialytic cell.

The practical part is based on different laboratory experiments. The whole project is based on pre-investigations made at Universidade Nova de Lisboa, Portugal, in the beginning of this year. The main results from the experiment are presented in Appendix 1.

The soil that is used for the experiments in this thesis will be characterised and a partly characterisation of the soil solution will be made. All the laboratory scale electro-dialytic experiments will include a soil solution sampler. Different electro-dialytic soil remediation experiments are made to compare, which changes varying current density and remediation period, have for the actual remediation of the soil and soil solution composition during the experiments. The influence of the soil solution sampler in the soil during the electro-dialytic experiments will also be tested.

In the experiments a soil containing the heavy metals arsenic, copper and chromium is being used, the origin of the pollution in the soil will be described in detail later. In this thesis only copper and chromium behaviour in the soil solution and the soil are investigated, because of insufficient measuring methods for arsenic at DTU.

In the field of soil solution and soil solution sampling, different terms are used. Soil solution is the term used for the water in the soil in this thesis. In many articles the terms soil water and pore water can be found. The term soil solution is chosen because in electro-dialytic soil remediation, chemicals are added to the soil and thus, changes the natural composition of the water in the soil.

Heavy metals in soil



In this chapter, the general behaviour of heavy metals in soil is presented and the processes that determine the occurrence of the heavy metals in the soil solution. The specific behaviour of copper and chromium in soil is also briefly described.

3 Heavy metals in soil

3.1 Sorption

3.1.1 Adsorption and absorption

In soils, heavy metals will bind to soil particles and thus be immobile. This process is called sorption and describes the distribution of the heavy metal between the solid and the soil solution. Sorption consists of adsorption and absorption. Adsorption is binding of the heavy metal to the soil surface and absorption is binding of the heavy metal in the soil's solid components. Adsorption is in general the most important sorption process for heavy metals. Sorption will always occur in soil even at low heavy metal concentrations. Clay minerals, organic matter, silica/aluminium/iron/manganese oxides, carbonates and phosphates are the predominant physical soil components that have the ability to sorb heavy metals (Kjeldsen and Christensen, 1996).

3.1.2 Specific / non-specific sorption

Soil particles are generally negatively charged. The negatively charged sites in the soil can be permanent due to isomorphous substitution, or pH – dependent on the edges on clay minerals, on humus polymers and oxides (Alloway, 1995). Heavy metals can be sorbed specifically or non-specifically. Non-specific sorption is characterised by a general attraction of the heavy metal to the soil and is governed by electrostatic forces and is seen in Figure 1 as “Outer-sphere complex” and “diffuse ion”. Specific sorption is characterised by a stronger form of binding than for the non-specific sorption, which causes formation of an “inner-sphere complex”, as seen in Figure 1 (Kjeldsen and Christensen, 1996).

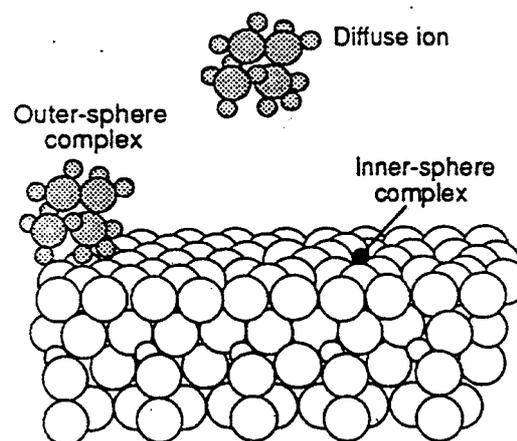


Figure 1: Illustration of types of bonds involved in the sorption of heavy metals to particle surfaces (from Kjeldsen and Christensen, 1996)

All heavy metals can sorb non-specifically and the magnitude of this type of sorption depends on the charge of the heavy metal ion, the size of the metal ion and coordination water. Not all heavy metals will sorb specifically, and this type of sorption depends on the electro configuration of the metal ion (Kjeldsen and Christensen, 1996).

3.1.3 Sorption isotherms

To describe the equilibrium between the amount of sorbed heavy metal and the concentration of the heavy metal in the soil solution, empirical sorption isotherms are used. The sorption isotherms are classified by the shape of the curve and are categorised as S/H/L and C-curves, see Figure 2.

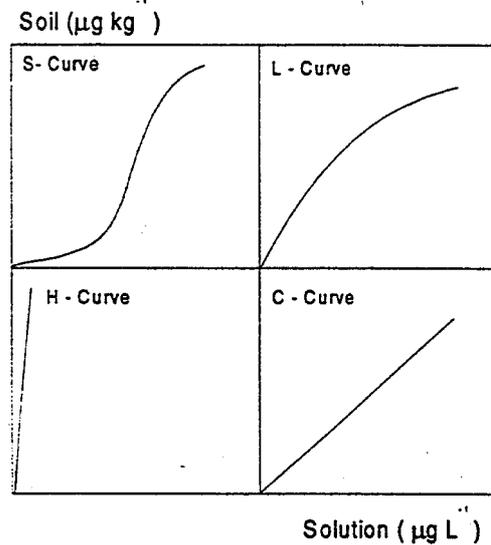


Figure 2: Classifications of sorption isotherms (from Kjeldsen and Christensen, 1996)

The S-curve shows sorption at low heavy metal concentrations in the soil, the H-curve is describing an extreme sorption situation, the L-curve shows sorption as linear at low heavy metal concentrations, where the sorption decreases at higher concentrations and finally and finally, the C-curve shows a linear sorption. The L-curve can be described by either a Langmuir-isotherm or a Freundlich-isotherm and the C-curve can be described by a linear isotherm. In common for all empirical sorption isotherms are that the distribution coefficient (K_d) is the wanted estimated parameter. The distribution coefficient gives an estimate of the degree of sorption in a given soil and for a given heavy metal (Kjeldsen and Christensen, 1996). For example is the linear sorption isotherm described as (Kjeldsen and Christensen, 1996):

$$K_d = \frac{C_s}{Me^{2+}}$$

Where C_s is the concentration of the metal in the soil and Me^{2+} is the concentration of a divalent metal cation in the soil solution.

The most important factor for sorption is pH. In acidic soils, the H^+ -ions will compete for the sorption sites and thus, at alkaline pH-values the sorption will be higher. In alkaline soils, monohydroxy-complexes will also sorb to the soil and gives an even higher sorption, than at neutral pH in the soil (Kjeldsen and Christensen, 1996).

3.2 Desorption

Kjeldsen and Christensen (1996) presumes that sorption in soil is reversible and that desorption can happen to the same extent as sorption. This is based on the following arguments:

- Sorption is primarily associated with the particle surfaces and the metal bonds are readily exposed to changes in the aqueous phase
- Cadmium sorption has been investigated for two Danish sub soils and sorption was found to be practically reversible
- When the documentation is so limited it is more cautious to make a conservative assumption, that of full reversibility rather than to assume an undocumented irreversibility

3.3 Precipitation

Many heavy metals will form insoluble precipitates, which can play a role in controlling their solubility in the aqueous phase. At neutral and alkaline pH, many heavy metals will form e.g. non-soluble hydroxycomplexes (Kjeldsen and Christensen, 1996), like malachite (Ottosen et al., 2000a). Heavy metals can also co-precipitate, where more than one heavy metal can precipitate with e.g. secondary soil minerals (Kjeldsen and Christensen, 1996). The precipitation equilibrium can be written as follows:

$$K_{so} = IP = [Me^{2+}]^a [B]^b$$

Where K_{so} is the solubility product, Me^{2+} is the metal ion and B is the anion the metal ion precipitates with. When the ionproduct (IP) is higher than the solubility product, precipitation will occur.

3.4 Metal complexation

Formation of dissolved complexes with heavy metals increases the solubility and the mobility of the metal. The possible complexes a heavy metal ion can form, depends on the heavy metal ions coordination number, i.e. the number of ligands that can be attached to the metal ion. A ligand that forms one bond to a metal ion is called a unidentate ligand. Other ligands that form more than one bond are called chelates. Chelates can form two bonds to a heavy metal ion (bidentate) or more than two bonds (polydentate). The most known polydentate ligand is EDTA, which effectively surrounds the heavy metal ion, making this a very stable complex. Other ligands for heavy metal complexation can be both organic and inorganic substances (Zumdahl, 1992).

The formation of a complex can be written as follows (Christensen, 1999):



The left side of the reaction represents the central metal ion (M) and the ligand (L), and the right side represents the complex ion (ML). The ligand can also be protonated (HL),

or the ligand can have ionised a proton that would not be ionised in the absence of the metal ion (H_{-1}).

The equilibrium between the precipitated, sorbed, complexated and dissolved heavy metal in the soil is seen in Figure 3.

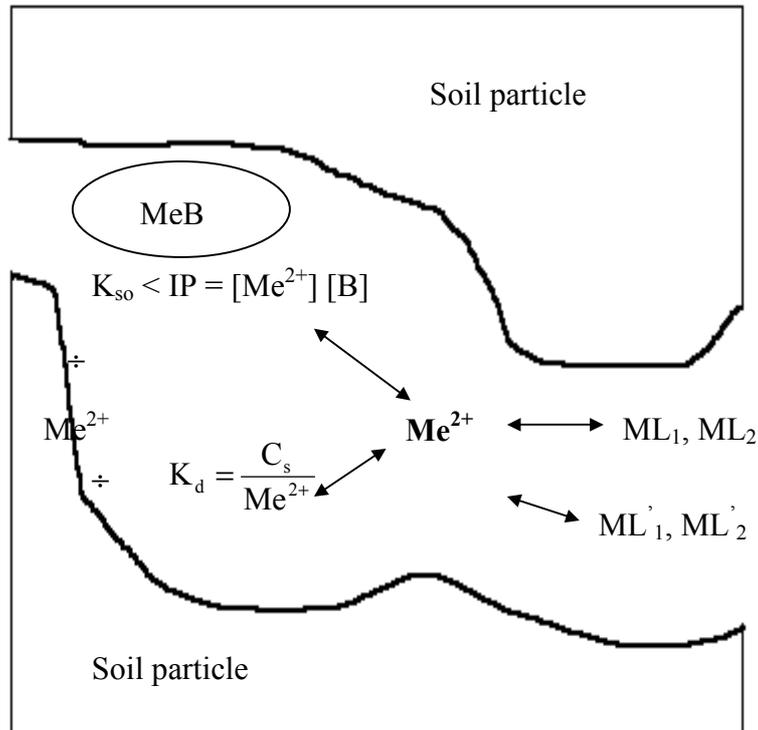


Figure 3: The distribution of the free metal ion between sorption, complexation, precipitation and the dissolved ion in soil and soil solution (modified from Christensen, 1999)

The solubility of the heavy metal will increase with complexation because the presence of complexation will shift sorption towards the aqueous phase, increasing the aqueous concentration of the free metal ion and thus, the mobility of the heavy metal, as illustrated in Figure 3.

Solid phase humic substances, such as humic and fulvic acids can form chelate complexes with heavy metals. The stability constants of chelates with heavy metals are usually in the decreasing order (Alloway, 1995):



The number of carboxyl groups in humic and fulvic acids are determining the maximum amount of a given metal that can form these organic complexes (Alloway, 1995).

3.5 Cation exchange

The negative charged surfaces in the soil is balanced by cations to maintain electroneutrality. The cations on the surface can be exchanged with other cations in the soil solution, and this is called cation exchange. This process is reversible, diffusion controlled, stoichiometric and normally, there is a selectivity of a cation over another by

the charged surface, determined by the valency and degree of hydration. The higher the valence of the ion, the greater is the ions ability to replace another ion. Adsorption due to cation exchange can also be described as outer-sphere complexes, see Figure 1. The cation exchange capacity (CEC) is defined as the soils capacity to absorb and exchange cations. The CEC for mineral soils can be from a few to 60 meq/100 g DM (Alloway, 1995).

3.6 Copper in soil

Copper is an essential nutrient for both plants and animals. The natural concentration of copper in terrestrial soil is about 30 mg/kg and is only toxic in high concentrations. Contaminated soil has typically a copper concentration between 50 – 22000 mg/kg (Kjeldsen og Christensen, 1996). Copper contamination of soil originates mainly from wood preservation, metal foundry and manufacturing industries.

Table 1 shows how copper contaminated soil is classified at different pollution levels by Frederiksberg kommune et al. (2001).

Level 1 (clean soil)	Level 2 (slightly polluted soil)	Level 3 (polluted soil, should be disposed of)	Level 4 (very polluted soil, should be disposed of or treated)
<500 mg/kg	>500 mg/kg	750 mg/kg	> 750 mg/kg

Table 1: Classification of soils polluted with copper (modified from Frederiksberg kommune et al., 2001).

Copper in the terrestrial environment is mainly found as Cu (I) or Cu (II). Cu (I) is very unstable in water, so Cu (II) is the dominant ion species, as Cu^{2+} (Kjeldsen og Christensen, 1996).

3.6.1 Sorption of copper

Sorption is a significant process for distribution and retardation of Cu (II) in soil. Sorption of copper is pH-dependent and copper is mainly bound to organic matter, oxides and clay after decreasing strength (Baker and Senft, 1995):

Organic matter > iron/manganese – oxides >> clay particles

In soils with pH higher than 5.5, copper and copper complexes will be specific sorbed (Baker and Senft, 1995). Thus, the specific sorbed copper will not contribute to cation exchange processes or be released to the pore water by this process. According to Kjeldsen and Christensen (1996) and Atanassova and Okazaki (1997), the Freundlich or the Langmuir sorption isotherm can describe copper sorption.

3.6.2 Desorption

Artificial copper contaminated soils (spiked soils) have been used to study sorption and desorption of copper in acidic soils (Atanassova, 1994, Atanassova and Okazaki, 1997). The aim of these experiments was to determine how the copper was distributed between specific and non-specific sorption. Primarily, a sorption experiment was made, followed by a desorption experiment. The desorbed amount of copper corresponds to the non-

specific bound copper. The total desorbed amount of copper varied from soil to soil, but was in the range of 39 – 88%. This indicates that a significant amount of copper is specifically sorbed to the soil and will be difficult to mobilise. The same experiments made with the clay fraction of the soil gave a higher desorption rate, 50 – 95%. The highest desorption rate was found in clay with low organic matter content, which indicates that copper sorbs strongly to organic matter in the soil, which is in agreement with Baker and Senft (1995). These experiments also showed that desorption was increasing with decreasing pH values.

3.6.3 Precipitation

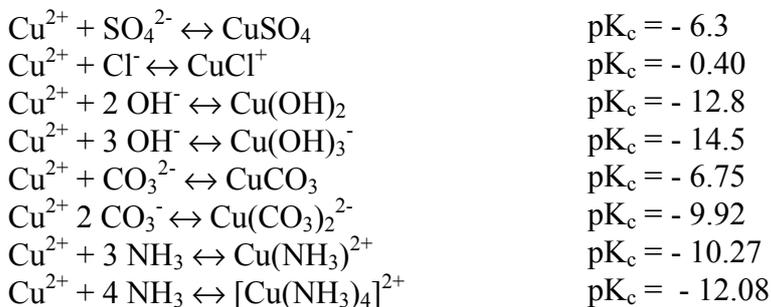
Cu (II) will precipitate with oxides, hydroxides and carbonates under aerobic conditions. The most important precipitation reactions and their solubility products (K_{so}) are (Kjeldsen and Christensen, 1996):



Clearly, at high pH – values, precipitation of Cu (II) will be important.

3.6.4 Complexation

Copper forms readily both organic and inorganic complexes with different ligands, especially sulfate, chloride, hydroxide and carbonate. The dominating complexes in natural soil and their stability constants (K_c) are (Kjeldsen and Christensen, 1996):



Furthermore, Cu (II) will form complexes with organic matter, and these complexes are characterised by inner-sphere bindings and thus, makes this kind of copper immobile. At high pH, complexation of copper will be important for the distribution in the soil (Kjeldsen and Christensen, 1996).

3.6.5 Copper in soil solution

The occurrence of copper in natural soil solution is typically between 0.5 – 100 µg/l, where contaminated soil solutions from landfills, will contain copper concentrations up till 10000 µg/l. The distribution of copper in soil solution will typically be 30 - 35% as dissolved Cu^{2+} -ions, 50 – 55% as carbonate complexes and a small fraction of other complexes for a calcareous soil. In contaminated soil solution from a landfill, copper will solely form complexes and hardly any dissolved Cu^{2+} - ions will be present (Kjeldsen and Christensen, 1996).

3.7 Chromium in soil

Chromium is, like copper, an essential nutrient for plants and animals, but will result in allergic reactions at high concentrations. Hexavalent chromium is classified as carcinogenic. The natural concentration of chromium in terrestrial soils is 1 – 100 mg/kg and 25 – 3400 mg/kg in polluted soil. Chromium contaminations of soils originate from combustion of fossil fuels, different metal industries and wood preservation (Kjeldsen and Christensen, 1996).

Table 2 shows how chromium contaminated soil is classified at different pollution levels by Frederiksberg kommune et al. (2001).

Level 1 (clean soil)	Level 2 (slightly polluted soil)	Level 3 (polluted soil, should be disposed of)	Level 4 (very polluted soil, should be disposed of or treated)
< 500 mg/kg	> 500 mg/kg	750 mg/kg	> 750 mg/kg

Table 2: Classification of soils polluted with chromium (modified from Frederiksberg kommune et al., 2001).

Chromium is found in different oxidation states, but the most stable in natural environment are trivalent chromium Cr(III) and hexavalent chromium Cr(VI). Cr(III) occurs as hydroxide complexes at pH > 4 and as Cr³⁺ at lower pH. Cr(VI) occurs as HCrO₄⁻ at pH 4-6 and as CrO₄²⁻ (chromate) at higher pH values. This makes Cr(VI) the most mobile of the two chromium oxidation states. Reduction of Cr(VI) to Cr(III) makes Cr(III) the most stable of the two species (Kjeldsen and Christensen, 1996).

3.7.1 Sorption

Sorption for Cr(VI) as chromate (CrO₄²⁻) is dependent on pH, type of clay minerals in the soil and the concentration of the competing anions. Chromate sorbs to hydroxy groups on iron - and aluminium oxides in the soil. Since chromate is a negatively charged species, the amount of chromate removed by sorption is low due to the very low number of positively charged sites on the soil particles (Kjeldsen and Christensen, 1996). Tzou et al. (1998) found that chromate sorption was greater in acidic soils than in alkaline soils.

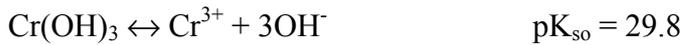
Sorption of trivalent chromium can take place, although its behaviour is predominantly controlled by precipitation, which is described later in this chapter.

3.7.2 Desorption

Tzou et al. (1998) investigated chromate desorption in both acidic and alkaline soils. Desorption of chromate was found to be greater for the acidic soil than for the alkaline soil. Desorption also increased with longer equilibrium times, but the desorption was not in the same order as the sorption, which indicates that most of the chromate will bind more strongly to the soil.

3.7.3 Precipitation

Cr(III) will precipitate with hydroxide in natural environment (Kjeldsen and Christensen, 1996):



Cr(VI) can also precipitate with cations, but precipitation of Cr(III) is most significant.

3.7.4 Complexation

Cr(VI) will not form complexes because of its presence as chromate.

Cr(III) will readily form complexes with both organic and inorganic ligands. In the environment, complexation with hydroxide is the most significant (Kjeldsen and Christensen, 1996).



3.7.5 Chromium in soil solution

The occurrence of chromium in soil solution is typically between 0.1 – 10 µg/l and in contaminated solution up to 1500 µg/l. In soil solution chromium will almost entirely occur as chromium – hydroxy complexes (Kjeldsen and Christensen, 1996).

Electrodialytic soil remediation



In this chapter the principles of electro-dialytic soil remediation is presented. The use of desorbing agents to enhance the remediation is also discussed.

4 Electrodialytic soil remediation

The cell used for electrodialytic soil remediation is seen in Figure 4.

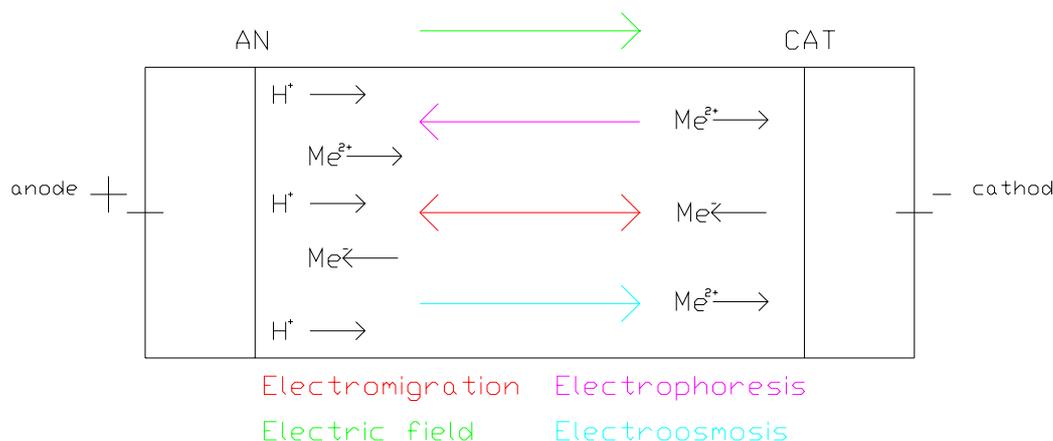


Figure 4: The electrodialytic remediation cell, where CAT is a cationexchange membrane and AN is an anionexchange membrane

The cell consists of three compartments, two electrolyte compartments and one compartment containing the contaminated soil. The contaminated media could also be e.g. fly ashes or impregnated wood. The contaminated soil is separated from the electrolytes by ionexchange membranes acting as physical and chemical barriers. Electrodialytic soil remediation is based on electrokinetic soil remediation. The difference is in the experimental set-up. In electrokinetic soil remediation, passive membranes are used to separate the soil from the electrolytes. The passive membranes act only as physical barriers, as opposed to ionexchange membranes. The pollutants in the contaminated media, which can be removed by the electrokinetic and the electrodialytic method, can be inorganic species, organic compounds and radionuclides. Amongst the inorganic species metals such as lead, cadmium, copper, chromium, arsenic, zinc and iron have been proved to be removable.

4.1 Physical processes

Applying an electric field to a solid media by the use of a direct current between electrodes will transport charged species in the media towards the one of the electrodes, according to the charge. The theory for electrical transport mechanisms in soil are far more complicated for soil than for liquid, and the net transport of ions depends on complex interactions. Generally, there are three main physical transport processes are responsible for movements in the soil and these are also seen in Figure 4:

- Electromigration
- Electroosmosis
- Electrophoresis

Electromigration is the most important process for transporting charged species out of the soil. The cations and the anions in the soil solution will be transported towards the cathode and anode, respectively. Electric current will pass through the media, where the

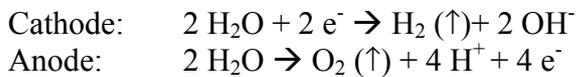
electrical resistance is lowest. This is in the electrical double layer close to the soil particles, where ions are accumulated and non – specifically sorbed (Ottosen, 1995). The electrical double layer is described later in this chapter.

Electroosmosis occurs in the soil because the soil consists of a solid and a liquid phase. When an electric field is applied and the ions are transported through the solid, they exert a viscous drag on the water around them. The soil water will move in the direction where the greatest part of the electromigration takes place. Normally this is towards the cathode since there are more cations than anions in the negatively charged soil. The size of electroosmosis depends on k_e , the coefficient of electroosmotic hydraulic conductivity and the voltage gradient (Mitchell, 1993). The migration velocity of the ions in the soil solution is dependent on the mobility of the ion, the applied electric field, the porosity of the soil and the electroosmotic coefficient (Baraud et al., 1997), when electromigration and electroosmosis are the dominant transport mechanisms.

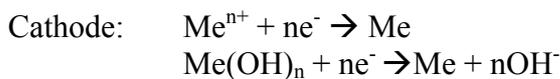
Electrophoresis occurs because the charged particles in the soil will move towards one of the electrodes usually the anode, because the soil particles are negatively charged (Mitchell, 1993). In extreme cases of electrophoresis, the particle composition of the soil matrix can change.

4.2 Electrode reactions

Inert electrodes made by carbon, platinum or titanium are used in electrodialytic soil remediation because inert electrodes do not take part in the electrode reactions. The applied current leads to electrolysis of water at the electrodes:



Thus, acid is produced at the anode and base is produced at the cathode. When the metal concentration in the electrolytes increase, precipitation of metal at the electrode surface can occur:



4.3 Ionexchange membranes

Ionexchange membranes are membranes made of polymers with charged surfaces. The surface will attract dissolved ions, with the opposite charge (counter-ions) from the pore water of the membranes. The counter-ions will be transported through the membrane due to the electrical current and the co-ions (with the same charge as the surface of the membrane) will be rejected. Figure 5 shows a general sketch of an ionexchange membrane.

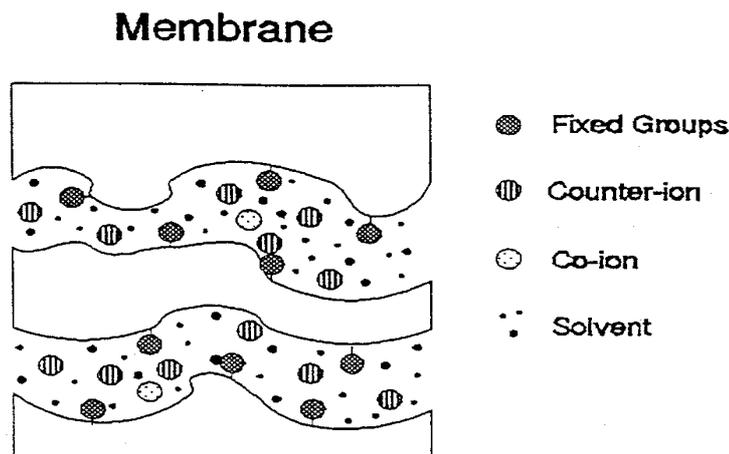


Figure 5: Sketch of an ionexchange membrane (from Hansen, 1995)

The ionexchange membranes will not be 100% effective, which means that some co-ions can pass the membrane together with the counter-ion (Hansen, 1995). The ionexchange membranes furthermore prevent the produced acid and base at the anode and the cathode, respectively, to enter into the soil and be transported through the soil (Hansen et al., 1997a).

4.4 Limiting current and acidic front

Since there are less anions in the soil than cations, the limiting current for the anionexchange membrane will be exceeded. This means that the flux of anions moving towards the anode is too low to carry the current. To compensate for the low flux, dissociation of water will take place at the anionexchange membrane and the OH^- ions can be transported through the membrane. The rate of water splitting is dependent on the current density (Ottosen et al., 2000a) and the anionexchange membrane catalyses the water splitting. The H^+ - ions will be transported towards the cathode and produce an acidic front through the soil (Ottosen et al., 1997). This is the key to removal of heavy metals from the soil in unenhanced electro-dialytic soil remediation, because a decrease in pH in the soil will lead to desorption of the heavy metals, which then can be dissolved in the soil solution and transported out of the soil.

The limiting current for the cationexchange membrane is higher than for the anionexchange membrane and therefore an alkaline front seldom develops in the soil matrix (Ottosen et al., 1997). Development of an alkaline front is not desirable because an increase in the soil pH will lead to metal precipitation.

4.5 Double-layer theory

Since the soil surface is predominantly negative, cations will accumulate on or near the soil surface producing a high concentration of positive ions. The cations try to diffuse away from the surface, but are held back by the negative forces from the soil particles. This produces a differential distribution of anions and cations in the surrounding soil solution. This effect can be described by the Donnan equilibrium and is also the basis of the double layer theory. (Wolt, 1994)

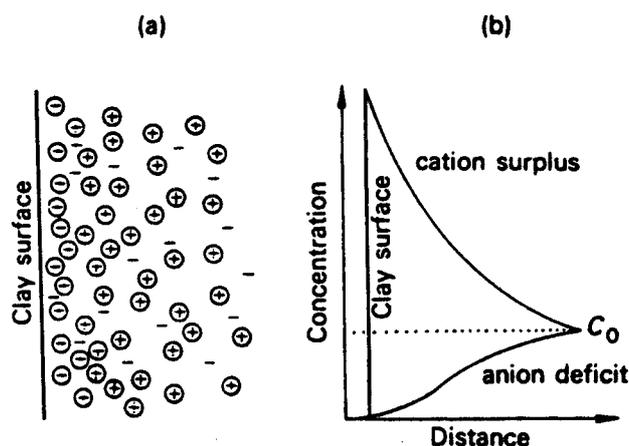


Figure 6: a) Ion distribution at a negatively charged clay surface. b) The concentration profiles associated with differential anion and cation distribution with distance from the clay surface (from Wolt, 1994)

In Figure 6 it is seen that the concentration of ions is highest around the clay surface, thus, the electrical resistance will be low. This means that an applied current to the soil will pass in this area. This is appropriate because, according to Hansen et al. (1997b) this is where the highest concentration of heavy metals is found.

4.6 Influence on the remediation with objects in the soil

Introducing a soil solution sampler in the electro-dialytic cell could influence the remediation. Previous investigations (Ottosen et al. 1999 and Ottosen et al., 2001b) showed that the copper removal was disturbed in a soil containing construction refuse, such as a stone, screw, brick or concrete. This is due to changes in the electric field when a large object is placed in the electro-dialytic cell, especially if the object has conducting properties. In Figure 7 the electric field lines are shown for a soil without large objects in the soil, with a conductor in the soil (e.g. a screw) and an isolating object in the soil (e.g. a stone).

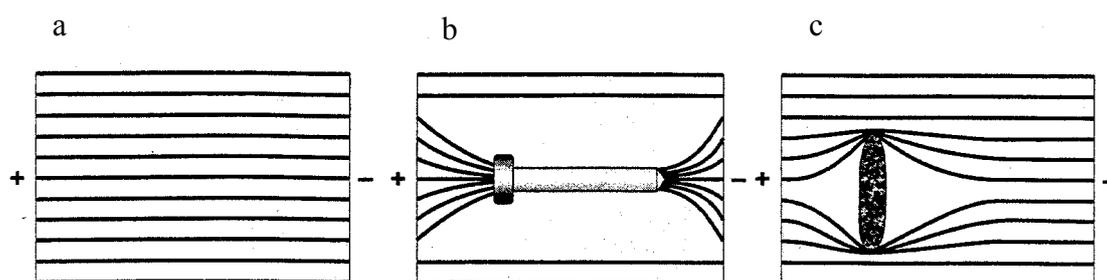


Figure 7: Simplified picture of the electric field lines in the three cases: (a) no larger object in the soil, (b) a screw in the soil and (c) a stone in the soil (from Ottosen et al., 1999).

The conductor (a screw) in Figure 7b has a low electrical resistance and the field lines will tend to pass through the conductor instead of through the soil. When the electric field is passing a conductor, electrode reactions can take place and the object can be reduced or oxidised. The field lines will pass next to the isolator (the stone) in Figure 7c and the field lines will lie close to the isolator, when passing. Obviously, both these

objects will disturb the remediation; the extent will depend on the size of the object and the number of objects in the soil.

4.7 Enhanced electrodialytic soil remediation

4.7.1 Addition of desorbing agents

Addition of desorbing agents to the soil for enhancement of the remediation is commonly used in electrodialytic remediation. The desorbing agent should make the electrodialytic remediation cost-effective and at the same time not create a new pollution problem in the soil. There are three significant advantages by adding desorbing agents to the soil:

1. The release of the heavy metals from the soil to the soil solution is accelerated and not dependent on the acidic front
2. Heavy metals, which are not desorbed by the acidic front, can be mobilised
3. Carbonate will stay precipitated if the desorbing agent has a high pH

Acid

Acid has been used as a desorbing agent in electrodialytic remediation. The acid is very effective for lowering the pH in the soil and thus, the heavy metals will be mobile. The problem is though, that the acid is not selective for desorbing the heavy metals only but also other cations, and the H^+ - ion will be present in the soil solution, ready for electromigration. This means long remediation times, because Ca^{2+} and H^+ will carry the current in a calcareous soil. It is also experienced that not all heavy metals will be mobile in an acidic environment (Ottosen et al., 1998).

Base

Ammonia can be used as a desorbing agent. Ammonia with its high pH is especially effective in calcareous soils, because the carbonate will stay precipitated. Copper will readily make $[Cu(NH_3)_4]^+$ - complexes with ammonia and since this complex is charged it will be mobile in the electric field. When ammonia is added to the soil the removal of copper will be faster and the energy consumption will be lower compared to remediation without ammonia addition (Ottosen et al., 1998). Copper will precipitate at high pH as $Cu(OH)_2$ and to prevent this from happening it is important to keep the ammonia concentration high in the whole soil volume during the experiment (Ottosen et al., 2000a). During the electrodialytic experiment, the acidic front will develop from the anionexchange membrane through the soil, even if the initial pH is high. It seems from previous investigations that if pH in the soil is lowered to 8.5 – 9, copper will precipitate and the soil can not be remediated further (Ottosen et al., 1998, Nyström, 2000). In (Ottosen et al., 2000a) the anionexchange membrane is changed to a passive membrane closest to the soil. This prevents the development of an acidic front from the anionexchange membrane, because the pH in the electrolyte can be adjusted. This will furthermore keep the pH in the soil high, if the electrolyte should enter the soil due to electroosmosis. The passive membrane also allows continuous addition of ammonia to the soil.

Experience has shown that chromium will not be remediated if ammonia is added to the soil (Ottosen, 2001a).

Present work at the Environmental Electrochemistry group, DTU includes the use of desorbing agents, such as ammonium citrate, citric acid and oxalic acid for different polluted medias. Several experiments with ammonium citrate addition to soil have been made. The preliminary experiments show that both copper and chromium are removed from the soil, if ammonium citrate is added to the soil (Ottosen, 2001b) and the results from the some of the experiments are enclosed in Appendix 2. The behaviour of the heavy metals in the soil is still investigated, as is optimisation of experimental set-up when ammonium citrate is used as desorbing agent.

4.7.2 Ammonium citrate

Ammonium citrate with the chemical formula, $C_6H_8O_7 - 2NH_3$, is a salt where two H^+ ions in the carboxyl groups of the citric acid are replaced by ammonium.

Ammonium citrate will dissolve in water, forming citrate and ammonium ions. In Table 3, the dissociation constants for citric acid and ammonia are shown (Zumdahl, 1992).

Chemical	Dissociation constant
Citric acid	$pK_1 = 3.1$
	$pK_2 = 4.7$
	$pK_3 = -5.4$
Ammonia	$pK_b = 4.7$

Table 3: Dissociation constants for citric acid and ammonia at 25 °C (Zumdahl, 1992)

Copper

Ammonium will dissociate to ammonia, which will readily make the mobile copper-tetra-ammin-complex, $[Cu(NH_3)_4]^+$ ($pK_c = -12.08$) with copper.

In Table 4, the possible complexation formations of Cu^{2+} and citric acid are shown, together with the stability constants (Martell, 1974).

Complex equilibrium	pK at 20°C, 0.1 ionic strength	Charge of complex
$M + L \leftrightarrow M.L$	- 5.90	-1
$M + HL \leftrightarrow M.HL$	- 3.42	0
$M + H_2L \leftrightarrow M.H_2L$	- 2.26	+1
$M + L \leftrightarrow M(H_{-1}L).H$	- 4.34	-1
$M_2 + L \leftrightarrow M.L.M$	- 2.20	+1
$M_2 + L_2 \leftrightarrow M^2L^2$	- 13.2*	-2
$M_2 + L_2 \leftrightarrow M_2(H_{-1}L)_2.H^2$	- 8.03*	0

*ionic strength is 1.0. $M=Cu^{2+}$, $L=C_6H_5O_7^{3-}$, $HL=C_6H_6O_7^{2-}$, $H_2L=C_6H_7O_7^-$, $(H_{-1}L).H=C_6H_5O_7^{3-}$ and $(H_{-1}L)_2.H^2=2 \times C_6H_5O_7^{3-}$

Table 4: Stability constants for copper complexation with citric acid and charge of complexes

It can be expected that copper will form both positively and negatively charged complexes that will be mobile in an electric field. At the same time, copper will form some uncharged complexes that will most likely be dissolved in the soil solution, but

not be mobile. Ammonium citrate has been used for soil washing, and investigations showed that up to 88% of the copper was removed by adding ammonium citrate to the soil (Wasay et al., 1998). Shiao et al. (2000) showed that citric acid removed 80% of the copper from polluted wood waste.

Chromium

Chromium (III) can form complexes with ammonium salts and citrates, whereas chromium (VI) will not (Pourbaix, 1974). Shiao et al. (2000) found that citric acid removed chromium from wood waste, but at lower levels than for copper.

Identification of the complexes and stability constants are not found and simple modelling in Visual MINTEQUE indicates that chromium makes positively charged complexes with 4, 5 and 6 ammonia groups, but not with citrate at pH 8, see Appendix 3. Previous investigations show that chromium also forms negatively charged species in ammonium citrate, see Appendix 2

Soil solution sampling



In this chapter, the use of suction cups for soil solution sampling for field sampling and properties for different suction cups are described. The theory of suction cups in field sampling, and here especially the sampling radius, will be applied to the electro-dialytic experiments in later chapters.

5 Soil solution sampling

Measurements of contamination in soil solution, are of great interest for both agricultural and pollution purposes, to survey concentration variations and movement of the contaminant in the soil matrix. There is a vast range of soil solution sampling methods for field sampling, including:

- zero – tension sampling (lysimeters, wick sampling systems and other passive sampling systems)
- tension sampling (different suction cells)
- others (extraction and centrifugation).

The most widely used non-destructive sampling system is tension sampling with suction cups, which has been used especially to investigate nutrient mass balances in agriculture and for metal contaminations (Kjærgaard et al., 2000), which will be described in the following.

5.1 Suction cups

Suction cups, used as soil solution samplers, have the advantage of being easy to install and allows sampling at the same location over time. Suction cups are made of hydrophilic materials with fine pores and can be made of different materials, most frequently of ceramics, aluminium oxide, glass, nylon, plastic and Teflon/PFTE (polytetrafluoroethylene). In Table 5 physical, physio-chemical and chemical properties for different suction cups are shown.

Material	Maximum pore diameter (μm)	Bubbling pressure (hPa)	Permeability ($\text{mL}/(\text{mPa s})$)	CEC (meq/cup)	Wall thickness (mm)	Elemental composition
Ceramic	1	140 – 4000	4.2	0.40 – 0.65	2.4 - 4	Si, Na, K, Ca, Mg, Fe, Al, can contain heavy metals
Aluminium-oxide	0.50 – 20	35 – 6000	6.7	0.39	2.4	Na, K, Ca, Mg, Fe, Al, Fe, al, can contain heavy metals
Nylon	0.2 – 0.5	200 – 2100	290	0.06 – 0.1	0.19	
Teflon		3 – 12			4	
Fritted glass	0.9 – 1.4	140 – 2500			3	

Table 5: Physical, physio-chemical and chemical properties for different suction cups (modified from Wenzel and Wieshammer, 1995)

The maximum pore diameter of the cup, the cup material and the cups bubbling pressure is highly interlinked. When the cup is placed in distilled water and put under increasing pressure, the bubbling pressure (or air entrance value) is the pressure when the first bubble appears. Hydrophilic materials (e.g. ceramic and Al_2O_3) show higher bubbling pressures than more hydrophobic materials (e.g. Teflon and plastic). The difference in bubbling pressure for a specific material, seen in Table 5, is due to different pore size for different tested cups. The bubbling pressure decreases for a

specific material, with increasing pore size. Because the soil tension should be lower than the bubbling pressure to collect a sample, use of suction cups in unsaturated soils can be difficult if the chosen cup is made of a more hydrophobic material, like Teflon (Wenzel and Wieshammer, 1995). Sampling in almost dry soil is impossible due to the low maximum vacuum of the suction cups (1 bar). For comparison, trees can produce a maximum vacuum of 15 bar during dry periods (Kjærsgaard et al., 2000).

5.1.1 Sampling

The sampling system for field sampling of soil solution consists of three functional units: the suction cup, the sampling bottle and the suction container, see Figure 8.

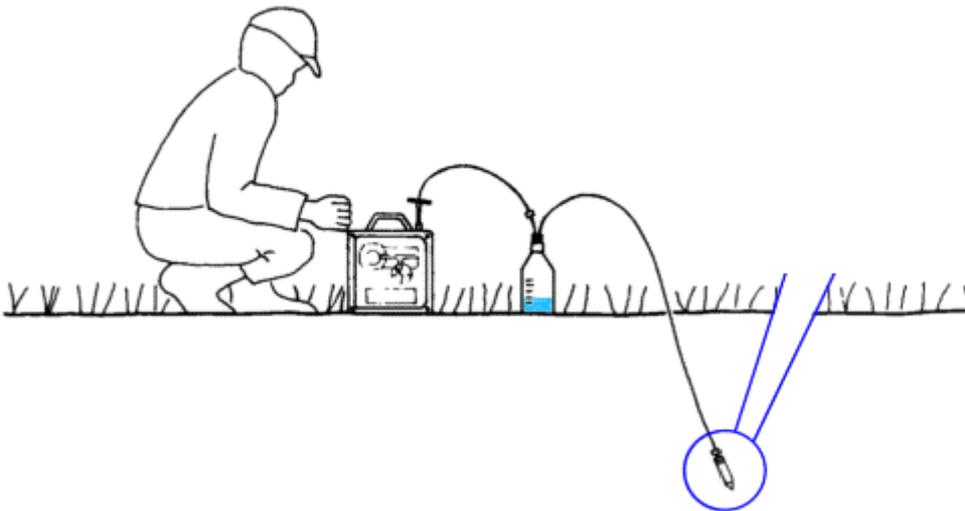


Figure 8: The sampling system for field sampling with suction cups (from Prenart, 2001).

Vacuum is applied to the suction cup by the suction container and the sample will be collected in the sample bottle. The amount of sample needed for later analysis, depends on the type of contamination and for which purpose the sample shall be used, but is normally in the range of 0.5 – 1 L (Kjærsgaard et al., 2000).

When applying vacuum, the vacuum shall be greater than the tension in the soil, to extract soil solution. The hydraulic conductivity for the porous cup is determining the ease of sampling. A high hydraulic conductivity due to the cups pore size, hydrophobic character and the capillary contact between the cup and the soil, will require greater vacuum to collect a sample. The moisture content in the soil, is limiting the amount of water that can be extracted for sampling. The soil water is held by capillary forces in the space between the soil particles or is adhered on the soil particles (Kjærsgaard et al., 2000).

There are three different systems to apply vacuum, to allow sampling, for suction cells. Sampling can be made with vacuum until the desired amount of sample is obtained, without vacuum between sampling (sudden tension), with continuous or variable constant vacuum, or as continuous sampling. There are different problems with all the

types of sampling systems, but the most prominent is, that ceramic cups tend to dissolve easier with sudden tension sampling (Kjærgaard et al., 2000).

5.1.2 Sampling radius

The sampling radius, or the area of the soil from where the soil solution is extracted, is of great interest. One limitation in the use of suction cups is the inability to determine the exact sampling radius of the cup. This is especially relevant for in situ measurements where the water flow in the soil, moisture content and percolation changes over time. The main problems for determining the sampling radius, are the inhomogeneous properties of the soil and the irregular flows and water content in the soil.

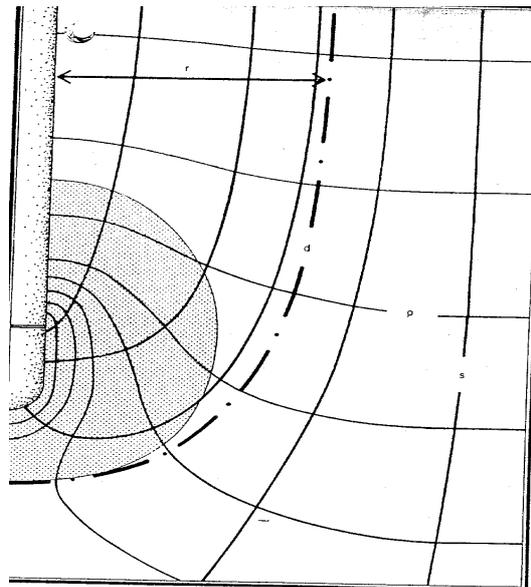


Figure 9: Potential field around a suction cup in homogeneous soil (from Grossmann and Udluft, 1991)

Figure 9 shows the idealised potential field (the area under influence when a sample is collected) around a suction cup for completely homogeneous sediment with stationary flow conditions. The dotted field is the area from where the sample is taken. It is also seen, that the sampling influences a greater area, for instance are the flow lines disturbed outside the sampling area. The actual potential field disturbance for inhomogeneous soils can be as extensive as one meter around the cup, but the actual sampling area is smaller, according to Grossmann and Udluft (1991).

Warrick and Amoozegar-Fard (1977) made a mathematical description of the maximum sampling radius (r_{\max}) under steady – state conditions:

$$r_{\max} = \left(\frac{\alpha^2 q}{4\pi K_0} \exp(-\alpha h) \right)^{1/2} \quad \text{Equation 1}$$

Where α is a constant for the actual soil (kPa^{-1}), q the flow into the cup (m^3/s), K_0 the saturated hydraulic conductivity for the specific soil (m/s) and h , the pressure head occurring outside of the sphere of influence of the cup.

Equation 1 is only valid for steady – state conditions when $\alpha(h - h_{\text{sampler}}) > 5$. Warrick and Amoozegar-Fard (1977) also suggest that transient –state systems will approach a steady state over time, especially if the collection rate of solution is slow. This means that the equation also can be interpreted in real cases.

Hart and Lowery (1997) compares the sampling radius found by the Warrick – Amoozegar –Fard model with two of their own quantitative models. One of their models is based on a mass balance approach of the total volume of soil solution sampled:

$$r_{\text{max}} = \left[\frac{\sum_{i=1}^n V_{wi}(z)}{D_w(z)} \frac{1}{\theta(z)} \frac{1}{\pi} \right]^{1/2} \quad \text{Equation 2}$$

Where V_w is the volume of soil solution sampled at a specific depth z , D_w is the depth of water drained past depth z , θ is the volumetric water content at depth z and n the number of samples.

The other model is based on the mass of bromide (Br^-) (bromide is used because it is a conservative tracer) collected in soil solution samples at a specific depth, after bromide was applied to the soil in the beginning of the experiment:

$$r_{\text{mas}} = \left[\frac{\sum_{i=1}^n M_i(z)}{L_{\text{Br}}(z)} \frac{1}{\theta(z)} \frac{1}{\pi} \right]^{1/2} \quad \text{Equation 3}$$

Where M is the mass of Br^- collected by the sampler and L_{Br} is the mass of Br^- leached past the sampler at depth z .

The second term of each of the two equations is the effective porosity of the soil, which is included to give a reliable estimate of the sampling radius.

The aim of the investigations of Hart and Lowery (1997) was to examine the axial – radial sampling radius under falling vacuum and transient flow conditions and comparison of the performance of two different porous cups in a sandy soil. The results showed that the sampling radius was in the magnitude of about 30 mm, but there were large differences for the different samplers and at different depths. This indicates variations in the performance of different samplers and care should be taken when choosing a sampler for investigations. The simple models presented by Hart and Lowery (1997), equation 2 and 3, were comparable with the Warrick and Amoozegar-Fard model, equation 1. The most important difference between the three models was, that the Warrick and Amoozegar-Fard always resulted in slightly larger sampling radius.

Morrison and Lowery (1990) used tensiometers in a defined unsaturated soil column and a bromide tracer, to measure the size of the radius of influence. The sampling was continuous, with a constant vacuum at 70 kPa. Their results showed a sampling radius in the order of centimetres as shown in Figure 10.

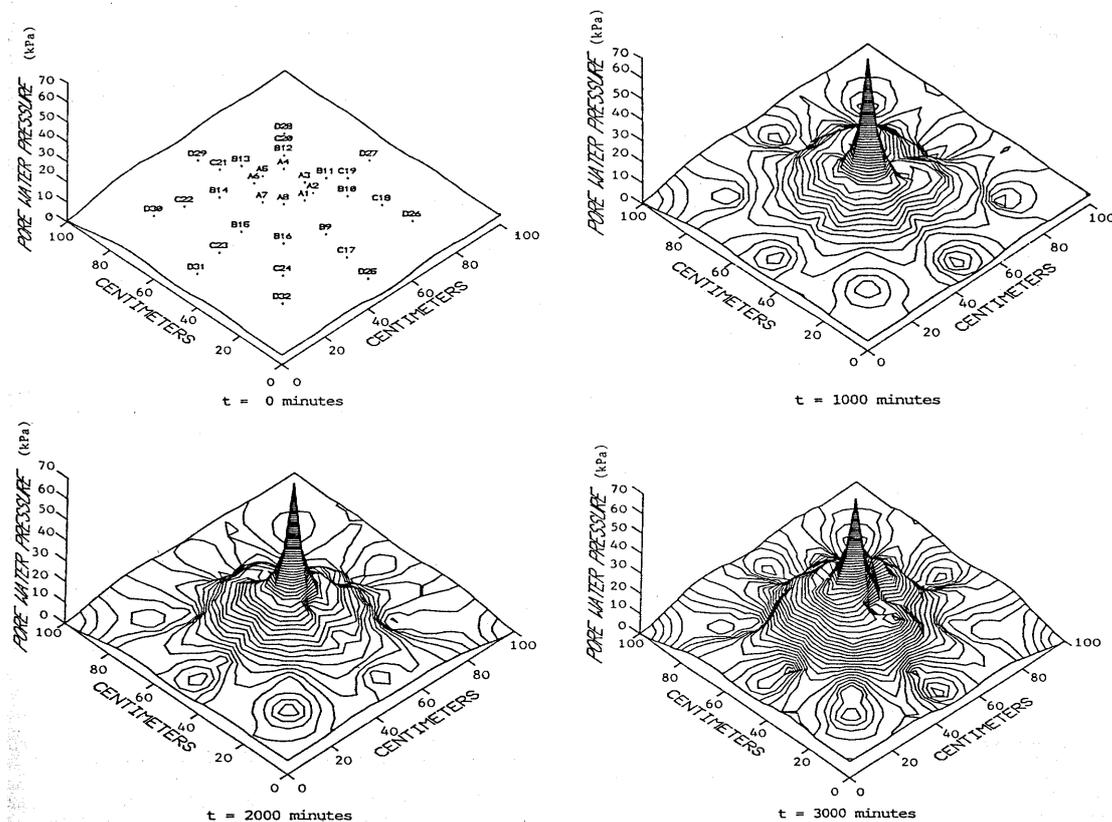


Figure 10: Change in matric potential for a test cell experiment at time (t)= 0, 1000, 2000 and 3000 minutes. The soil solution samples are sampled in the middle of the test cell (from Morrison and Lowery, 1990).

Figure 10 shows the change in matric potential for one of the experiments from the beginning of the experiment until 3000 minutes. The dramatic head loss is most likely due to the desaturation of the soil closest to the sampler. This indicates that the sample taken in the beginning of the experiment represents solution from the soil adjacent to the sampler and with time, the sample is collected from the soil further from the sampler.

5.1.3 Micro/macro pores

The potential gradient generated by the suction cup, will act on all the pores and movement of water will occur in all pores influenced by the sampling. The bigger pores can exhibit a kind of channelling effect on the water movement, but there is no reason to believe that a sample only will be collected from the bigger pores (Grossmann and Udluft, 1991). Morrison and Lowery (1990) suggest that the samples taken in the period from 0 – 1000 min represents water from the largest pores nearby and that after longer time the sample will represent water from both the micro - and the macropores.

5.1.4 Sampling flow rate

The flow rate during sampling depends on the applied suction, the permeability of the cup and the unsaturated permeability of the soil. To achieve an optimal sampling rate, perfect contact between the soil and the suction cup is necessary and the permeability of the suction cup should preferably be higher, than for the saturated soil (Grossman and Udluft, 1991).

5.1.5 Problems connected with suction cups

In Table 6 advantages and disadvantages for some porous cup materials are listed.

Material	Advantages	Disadvantages
Ceramic	Cheap Widely used / well known	Retains P May weather / release ions Not frost resistant Relatively fragile High ionexchange capacity
Teflon	Chemical inert Easy to install Robust Frost resistant	Expensive
Glass	Cheap	Very fragile Adsorption/desorption of C, N, Na Does not sample under dry conditions
Nylon	Low ionexchange capacity	Fragile May release N – compounds Expensive Do not sample under dry conditions
Plastic	No adsorption/desorption	Some retains Al Do not sample under dry conditions

Table 6: Advantages and disadvantages for different suction cup material (modified from Kjærsgaard et al., 2000)

Ceramic cups and Teflon cups are the most used porous cups. The use of ceramic cups should be avoided in investigations involving measurements of P, or if the soil pH is acidic, which will lead to dissolution of the cup. Teflon cups are chemically inert, which is their greatest advantage compared to other cups. Glass cups are fragile, which limit the use in the field and this cup is also believed to release Na. The pore size of a glass cup are large, which means that only a small vacuum can be applied and therefore no samples can be collected under dry conditions. Nylon and plastic cups are also assessed to be functional materials for collecting soil water samples. (Kjærsgaard et al., 2000)

Chemical stability of suction cups

Ceramic cups are widely used, but the disadvantages are many such as, retention of elements, release of elements due to weathering and high ionexchange capacity (Kjærsgaard et al., 2000, Ribeiro, 1998, Wenzel and Wieshammer, 1995). The ceramic cup will dissolve under acidic conditions and the rate of dissolution depends on the mineralogical and chemical composition of the cup material and the pH of the soil solution. Suction cups can contain different amount of heavy metals, which can be released to the soil solution and give alternated results. Especially sintered nickel cups contains high concentrations (10^6 mg Ni/kg cup), and under acidic conditions, nickel will be released and precipitate as $\text{Ni}(\text{OH})_2$. This precipitation will change both the soil

solution and the properties of the sampler. Ceramic cups also contain heavy metals in variable concentrations, which will be released under acidic conditions (Wenzel and Wieshammer, 1995).

Adsorption and desorption

McGuire et al. (1992) summarize previous investigations of adsorption to soil solution samplers. Several investigations found that NH_3 , NH_4^+ , P and K were adsorbed by ceramic cups, and ceramic cups were evaluated to be too reactive. Teflon cups and cups of fritted glass, showed a significant lower adsorption of similar compounds and a lower reactivity than the ceramic cups and were therefore to be preferred. Flushing of the cup with acid before installation, could lead to a potential increase in the adsorption.

The significance of metal sorption processes depends on the cation exchange capacity (CEC) of the cup material, the reversibility of metal specific adsorption and the concentration of the metal in the soil solution. Adsorption to cup material is highly dependent on pH of the soil solution (Wenzel and Wieshammer, 1995). Grossmann and Udluft (1991) found that in a solution at pH 4, 100% of the initial concentrations of Cd, Cu, Pb and Zn were recovered after flushing cups made of nylon, Al_2O_3 and ceramic, but at pH 8, less than 10 % of the initial concentrations were recovered for the Al_2O_3 and the ceramic cup. For the nylon cup, more than 80 % of the concentrations were recovered, except for Pb, where 50% was recovered.

McGuire et al. (1992), made investigations where different porous cups were placed in simulated soil solutions containing Zn, Co, Cr and Cd. These investigations showed that the adsorption of heavy metals to porous cups was in the following order:

Ceramic > stainless steel >> fritted glass = Teflon

And the investigated metals adsorbed to the suction cups in the following order:

Zn >> Co > Cr > Cd

Chromium sorbed to all the cups in a range of 40 – 50 $\mu\text{g Cr(III) /kg cup}$. Different methods for pre – cleaning the cup, the number of pore volumes of simulated soil solution drawn through the samplers, and the time of equilibrium with the simulated soil solution, were factors that influenced the magnitude of the observed adsorption. The investigations also showed that at high pH (> 8) in soil solution, the metals would sorb to silica.

Clogging

Clogging of the pores in a porous cup may occur through precipitation of compounds from the soil solution supersaturated with respect to the solid phase. Especially phosphates and aluminium hydroxy sulphates can clog the pores and filtration of colloids and macromolecules can also give clogging problems (Wenzel and Wieshammer, 1995).

5.1.6 Using suction cups in the laboratory

Suction cups are normally used in field investigations, but in this thesis, suction cups will be used in laboratory scale. The great advantages of using suction cups are, they can be installed without destroying the soil and the soil solution samples are collected from the same area of the soil.

5.1.7 Soil solution sampling and the effect on the electrical double layer

The effective thickness of the electrical double layer is of practical significance for soil solution sampling. The thickness is in the range of nanometers and is dependent on the dominant solution phase electrolyte and the ionic strength of the bulk soil solution and the effect is stronger for dilute soil solutions (Wolt, 1994). If a powerful extraction method for obtaining soil solution is used, like centrifugation or high pressure vacuum extraction, parts of the electrical double layer can be removed by the forces. The fraction of sampled electrical double layer may increase with higher centrifugation speeds, longer centrifugation times and reduced soil solution content. Due to this, centrifugation or other high-pressure vacuum extraction, the methods can give misrepresentative composition of the soil solution (Wolt, 1994).

5.2 The Prenart sampler

The chosen suction cup used in this study, is the Prenart super quartz mini, see Figure 11.



Figure 11: The Prenart super quartz mini soil solution sampler (from Prenart, 2001)

This is a suction cup made of Teflon and quartz. This combination keeps the chemically inert properties of a Teflon cup, but also removes the hydrophobic characteristic of Teflon. The Prenart super quartz mini is especially made for laboratory experiments due to the small size and is recommended for nutrient and heavy metal measurements. The detection limit for copper is < 0.01 mg/L, which was found by sucking 0.1 N HCl through the sampler and measure the copper concentration in the extracted solution by ICP-AES (Inductively coupled plasma- atomic emission spectrometry), to see if the sampler released the metal (Rasmussen, 2001a). The detection limit for chromium was not measured.

In Table 7 the physical properties of the sampler are listed (Prenart, 2001), more details are presented in Appendix 4.

Property	<i>Value</i>
Dimensions	OD 12mm, length 65mm*
Pore size	2 μm
Hydraulic conductivity	3.31×10^{-7} cm/s
Bubbling pressure	400 – 500 hPa

*Table 7: The physical properties of the Prenart super quartz mini soil solution sampler (from Prenart, 2001) * the pores are not covering the whole length of the sampler, but 45 mm.*

From Table 5, it was seen that the bubbling pressure of the tested Teflon cup was between 3 – 12 hPa and that the Prenart sampler has a considerably higher bubbling pressure, which means that it should be possible to collect samples from unsaturated or barely saturated soils. The small pore size of the sampler also means that the collected sample needs not to be filtered. This is a great advantage when the volume of the sample is small, since some sample will be retained in the filter if the sample is filtered.

5.2.1 Experiences with use of the Prenart sampler

Different research institutes in Denmark and other countries use the Prenart soil solution sampler. Normally, the sampler is used for investigations of soil and groundwater pollution, fertilizer application in agriculture, soil surveys and forestry. (Prenart, 2001) There are not many publications about the Prenart soil solution sampler. Andersen et al. (1996) used the Prenart sampler for collecting soil solution samples from CCA contaminated soil in situ and Beier et al. (1992) used it for collecting soil solution for nutrients in an agricultural soil and compared the results obtained with soil solution collected with a ceramic cup. There are not any publications about testing the Prenart sampler for adsorption/desorption of heavy metals and most probably this has not been done (Rasmussen, 2001a and Rasmussen, 2001b). This would be interesting to know, but will not be done in this thesis.

In the following sections the Prenart soil solution sampler will be called the soil solution sampler or the sampler.

Soil solution composition



In this chapter, the composition of soil solution under unpolluted conditions is presented and which changes there will be in the composition of the soil solution, if the soil is polluted with heavy metals.

6 Soil solution composition

6.1 Soil solution in unpolluted soils

It can be difficult to describe the soil solution in practise because it is impossible to measure the chemical components in situ and the soil solution will vary over the year because of different moisture content which changes the chemical composition. The composition of soil solution is dependent on the interaction between the different phases in the soil and the chemical and biological reactions taking place in the soil (Wolt, 1994). The major ions in soils, which are determining the soil solution composition, are (Wolt, 1994):

- Major exchangeable cation (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , Al^{3+} , H^+)
- Major anions (NO_3^- , SO_4^{2-} , Cl^- , HCO_3^- , CO_3^{2-})
- Weakly soluble anions (H_2PO_4^- , HPO_4^{2-} , H_2AsO_4^- , AsO_2 , H_3BO_3 , H_2BO_3^- , $\text{Si}(\text{OH})_4$, MoO_4^{2-})
- Transition metals and aluminium (Al^{3+} , Al hydroxides, Fe^{2+} , iron hydroxides, Mn^{2+} , Cu^{2+} , Zn^{2+})
- Toxic ions (Cd^{2+} , Al^{3+} , Pb^{2+} , Hg^{2+} , Hg , Be^{2+} , AsO_4^{3-} , CrO_4^{2-})
- Ions active in oxidation-reduction reactions (C, O, N, S, Fe, Mn, Se, Hg)

Different extraction methods will give different compositions of the soil solution. Therefore it is important to use only one extraction method for the same investigations and choosing the one, which seems to disturb the investigated object, the least possible. Mixing of soil and water in a known ratio cannot be interpreted as soil solution, because a dilution of soil solution has an uncertain effect on solubility, ion exchange and sorption (Wolt, 1994). The typical values of the chemical components of soil solution are seen in Table 8. The values are from different soils and from different extraction methods.

Chemical component	Concentration range	Typical values
pH	3.5 – 8.3	
EC	0.05 – 140 dS/m	
Ca	0.05 – 42 mmol/l	
Mg	0.05 – 13 mmol/l	0 – 2 mmol/l
K	0.05 – 7 mmol/l	0 – 3 mmol/l
Na	0.05 – 5 mmol/l	0.1 – 0.7 mmol/l
NH_4	0.05 – 5 mmol/l	0.05 – 0.5 mmol/l
Al	0.0004 – 0.1 mmol/l	
Si	0.05 – 0.5 mmol/l	
HCO_3	0.05 – 4 mmol/l	0.05 – 0.2 mmol/l
SO_4	0.02 – 2 mmol/l	0.02 – 0.6 mmol/l
Cl	0.04 – 5 mmol/l	0.04 – 1 mmol/l
NO_3	0.05 – 12 mmol/l	0.05 – 0.7 mmol/l
DOC	0.6 – 7 mmol/l	
Ionic strength	< 1 – 15 mmol/l	

Table 8: Typical values of the chemical components of soil solution (modified from Wolt, 1994)

Normally, Ca^{2+} is the major cation in soil solutions and NO_3^- is the major balancing anion. For describing the soil solution composition, total concentrations of Ca, Mg, K, NO_3^- , Cl and SO_4^{2-} , along with pH is sufficient, since these ions are dominating the soil solution composition (Wolt, 1994).

6.2 Soil solution for heavy metal polluted soils

Information of soil solution composition of polluted soil has not been found. Percival et al. (1999) added heavy metals in different concentrations in the form of nitrate salts to different soils. The soil solution was obtained by centrifugation and the soil solution was measured for the concentration of heavy metals, along with the major cations and anions. These experiments showed that at higher concentrations of heavy metals in the soil, the heavy metal concentration in the soil solution also increased. The increase in the concentration in the soil solution was higher than the amendment rates. The investigations showed that the amount of heavy metal in the soil solution was dependent on the CEC of the soil and the pH. Changes in the major cation concentration was distinct, the concentration increased because the heavy metals competed for the sorption places in the soil. The concentrations of heavy metals in the soil solution ranged from 0 – 200 mmol/l.

6.3 Storage of soil solution samples

To prevent changes in the composition of the sampled soil solution, care should be taken when storing the samples. Normally, samples can be refrigerated, frozen or conserved by addition of chemicals, in order to inhibit biological activity or changes in the soil solution. Preferably, the samples should be analysed immediately after sampling, or the same kind of conservation or storage should be used for all the samples, to limit different alterations due to different storing. The effects of different storage of soil solution samples with heavy metals have not been investigated in the literature.

Soil characterisation



In this chapter, the soil is being characterised and extraction experiments with different extractors are made. The electroalytic experiments in the following chapter will be performed based on the results from this chapter.

7 Soil characterisation

7.1 Description of the soil and its origin

The polluted soil is from the former wood impregnation site, Dansk A-træ. The wood impregnation took place in the years 1961 – 1981, though with a break in the years 1967 – 1974. The topsoil at the site is heavily polluted with arsenic, copper, chromium, coal tar, oil and organic impregnation preservatives. The heavy metals originate from the traditional impregnation method, where the impregnation preservative, Boliden K33, which contains 34 % arsenic, 26 % chromium and 15 % copper, was used. The wood poles were pressure-treated in this solution and let to dry in tanks or directly on the ground (Falkenberg, 1994). The soil is mostly polluted with arsenic (20 – 2570 mg/kg) (Falkenberg, 1994), which is also the most mobile of the three metals, but will not be treated in this thesis because there is not access to Induced Coupled Plasma, for arsenic measurements. The soil used in the experiments is from an area on the site, where the impregnated wood was stored. In Figure 12 it can be seen that the soil is polluted with chromium (yellow stone, circled) and copper (green/blue).



Figure 12: Clear evidence of copper (green/blue) and chromium (yellow stone, circled) pollution in the soil at the Dansk A-træ site

The experiments in this thesis will all be conducted with soil from Dansk A-træ. Originally, the soil used was collected the 21st of September 2000. Unluckily, there was not enough soil to perform all the wished experiments, so more soil was collected at the exact same site the 15th of May 2001. The same characteristics were determined for the latter soil as for the former, except CEC and sequential extraction. Soil Dansk A – træ 210900 is used for electro-dialytic experiments 1-4 and for the preliminary extraction experiments and is called soil 1. Soil Dansk A – træ 150501 is used for the electro-dialytic experiments 5 and 6 and for the extraction experiment with the soil solution sampler, and is called soil 2. The electro-dialytic experiments and the extraction experiment with the soil solution sampler will be described in a later chapter.

7.2 Physical and chemical soil parameters

7.2.1 Analysis

To characterise the soil pH, carbonate content, electrical conductivity, cationexchange capacity, organic matter content, copper and chromium concentrations are measured for the soil and sequential extraction and grain size are also determined. In Table 9 the method for the analyses is briefly described, for more detailed information see Hansen et al. (1999a).

Characteristic	Method number	Procedure
pH	4	1.0M KCl is added to soil in a 1:2.5 ratio, shaken for 1 hour and the pH is measured with a Radiometer pH electrode.
CaCO ₃ content	1	Scheibler apparatus is used for measurement of CO ₂ – formation when 2.500 g of soil react with 10% HCl. The CaCO ₃ content is calculated after a standard curve.
Electrical conductivity	17	Distilled water is added to the soil in a 1:2.5 ratio, shaken for 30 minutes, left for 20 minutes and measured with a Radiometer equipment. The temperature was manually adjusted for the equipment, since the electrical conductivity is highly temperature dependent.
Organic matter*	16	2.500 g soil is ignited at 550°C for 30 minutes.
CEC*	14 B	10 g of soil is treated with ammoniumacetate at pH 7 and NaCl. Measurements on flow injection.
Heavy metal content		Danish Standard 259, 20 ml 1:1 HNO ₃ is added to 1 g soil and heated at 200 kPa (125°C) for 30 minutes. Samples measured by AAS (Atomic absorption spectrophotometry)
Sequential extraction*	13 B	Addition of different extractors (acetic acid, hydroxylamine hydrochloride, hydrogen peroxide, nitric acid) to determine how strongly the heavy metals are bound to the soil.
Grain size*	6+7	100 g of soil is sieved through metal sieves for 15 minutes.

Table 9: Methods used for soil characterisation (from Hansen et al., 1999a)

* made by laboratory technician Ebba Cederberg Schnell.

7.2.2 Results

The results from the soil characterisation are seen in Table 10, these are based on the analysis previously described in Table 9. The calculations and the measurement results are seen in Appendix 5.

Characteristic	Soil 1	Soil 2
pH	7.82	7.02
CaCO ₃ content (%)	3.2	2.7
Electrical conductivity (uS/cm)	174.7	179.1
Organic matter (%)	3.23	2.08
CEC (meq/100 g DM)	6.28	n.m.
Copper concentration (mg/kg)	(1598 – 7857)	(1570 – 1664)
Chromium concentration (mg/kg)	(1125 – 1737)	(879 – 941)
Clay (%)	3.61	1.84
Silt (%)	19.14	18.65
Sand (%)	61.16	59.02

Table 10: Result of the soil characterisation of the two Dansk A-træ soils, soil 1 (collected 210900) and soil 2 (collected 150501) n.m. – not measured

pH

The speciation of a heavy metal in soil is highly pH – dependent. Cu^{2+} is the mobile form of copper in natural soils and copper will be released from the soil at $\text{pH} < 3.5$. Chromium (III) will be mobile if $\text{pH} < 4$ or if chromium is present as chromium (VI) it will be mobile at $\text{pH} > 4$ (Kjeldsen and Christensen, 1996). The pH in the soils from Dansk A-træ is neutral to alkaline and at this pH – level, neither copper nor chromium will be mobile, except Cr (VI) if present, but most likely copper and chromium will be sorbed to the soil or precipitated.

CaCO₃ content

The carbonate content in a soil is an indication of the soils buffering capacity. When an acidic front is developing through the soil in electrodynamic soil remediation, carbonate will dissolve and Ca^{2+} - ions will compete with copper and chromium ions in the electromigration. In Ottosen et al. (2001a) it was shown, that the acidic front is developing faster in a non-calcareous soil, than in calcareous soils and that the original pH of the non-calcareous soil is also lower than for the calcareous soils. The carbonate content of the soil influences the remediation and the calcareous soils will need a longer remediation period than the non-calcareous soil for removing the metals copper and zinc. By adding base to the soil, carbonates will stay precipitated in the soil and thus, current will not be wasted by removing calcium – ions from the soil (Hansen et al., 1999b). The soils from Dansk A-træ contain carbonate, so considerations should be taken when performing electrodynamic experiments on this soil.

Electrical conductivity

The electrical conductivity for a solution gives an indication on how the current will pass through the soil. If the electrical conductivity is high, it means that there will be low resistance in the soil and the current will pass easily through the soil. The electrical conductivity in this soil is relatively low; other soils from Dansk A-træ can have electrical conductivity values up to three times the found value (Nystrøm, 2000).

Organic matter

The sorption distribution coefficient is dependent on the content of organic matter in the soil, because the heavy metals tend to sorb to the organic matter. Copper is specifically sorbed to organic matter, which makes it difficult to mobilise. There is organic matter in the Dansk A-træ soil, indicating that the heavy metals could be sorbed to organic matter in the soil.

CEC (Cation exchange capacity)

CEC is defined as the soils capacity to absorb and exchange cations. Since most heavy metals exist as cations in the soil solution, the amount of negatively charges sites in the soil is determining for the extent of adsorption. Ion exchange is defined as the exchange between the cations adsorbed on the soil and the cations in the soil solution. The parameters normally determining the size of the CEC are the organic matter content and the clay fraction (Alloway, 1995). The CEC is high in the Dansk A-træ soil, which is partly due to the high content of organic matter.

Heavy metal concentrations

There is a varying heavy metal concentration in the two soils, especially in soil 1. Small green lumps, containing copper, are seen in parts of this soil. According to the limiting values set by Frederiksberg kommune et al. (2001), see Table 1 and Table 2 in chapter 3.6 Copper in soil and 3.7 Chromium in soil, respectively, both soils are very polluted with both copper and chromium

Sequential extraction

Sequential extraction is performed on soil 1. There are four steps in the sequential extraction, determining in which phase of the soil the heavy metal will occur. The sequential extraction also indicates the availability of the heavy metal in the soil. In the method, different extractors are used, which has increasing strength to selectively remove the heavy metals from the given phase. The four steps of the sequential will remove the heavy metals from the following phases:

- | | | |
|---------|--|------------------------------|
| Step 1: | Exchangeable and carbonatic phase | decreasing availability
↓ |
| Step 2: | Easily reducible phase (e.g. oxides) | |
| Step 3: | Oxidisable phase (e.g. sorbed to organic matter) | |
| Step 4: | Residual phase | |

The results from the sequential extraction are shown in Figure 13.

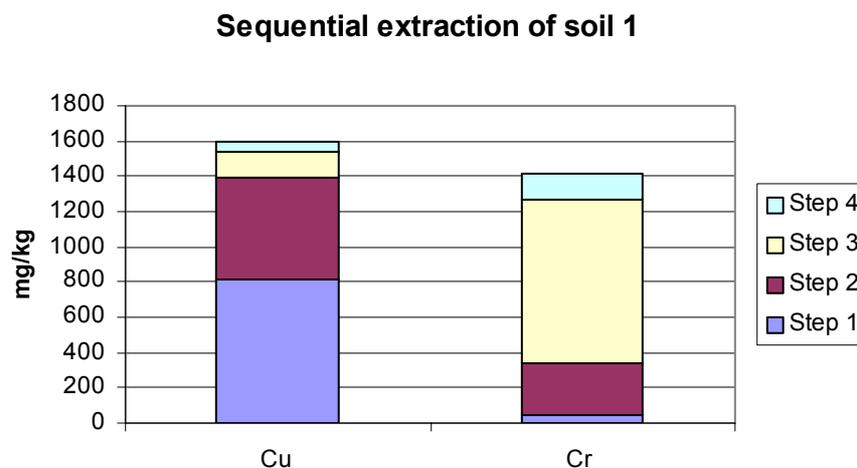


Figure 13: Results of the sequential extraction of copper and chromium for soil 1

The distribution of copper in the soil is mainly in the relatively mobile phases, as seen in Figure 13. Over 50 % of copper is in the exchangeable and the carbonatic phase of the soil, even though the carbonate content of the soil is low. Over 35 % of copper is in the easily reducible phase. Chromium shows a different behaviour. Only 3 % of the chromium is found in the exchangeable and the carbonatic phase and 20 % is found in the carbonatic phase. The largest fraction of chromium is found in the oxidisable phase and is thus, strongly attached to the soil, but this fraction can be oxidised to the mobile Cr (VI).

Redistribution towards the more available phases after electro-dialytic remediation has been reported for copper, chromium and arsenic (Ribeiro, 1998) and for lead (Pedersen

and Jensen, 1999). Sequential extraction can thus be seen as a tool to evaluate leaching ability from the soil after the remediation.

Grain size

The two soils are classified as sandy, with silt. The clay fraction in the soil is low, though higher for soil 1 than soil 2. The highest concentrations of copper and chromium are expected to be in the smallest fractions in the soil.

7.2.3 Comparison of the two soils

From Table 10 the greatest differences between soil 1 and 2 are the concentrations of copper and chromium. High concentrations of copper and chromium in the soil will result in longer remediation, than lower concentrations of copper and chromium in the soil. The higher pH in soil 1 is probably due to the higher carbonate content in this soil, which indicates that the buffering capacity of soil 1 is slightly higher than for soil 2 and due to this, the development of the acidic front could be slower in soil 1. The results from the sequential extraction show that copper will be easier mobilised in the electrodynamic experiments than chromium. Soil 1 has a slightly higher pH, organic matter and carbonate content, but the differences are evaluated to be small enough so the results from the electrodynamic experiments can be treated as being from the same soil.

7.3 Extraction experiments

Extraction experiments are made to investigate the availability of the heavy metals when the soil is mixed with a chemical. The liquid phase in the experiments should resemble the soil solution as much as possible and thus, it would be possible to get an insight in the behaviour of the soil solution. These experiments are also valuable for determining how effective the chosen extractor is to desorb the given heavy metal from the soil to the soil solution. Desorption should be as high as possible to result in a high desorption distribution coefficient, which is in these experiments defined as desorbed concentration/ total concentration in soil.

The extraction experiments are made to decide which extractor that shall be used for the electrodynamic experiments and to assess the advantages/disadvantages for the different extractors. The experiments are made with different extractors, see Table 11, and the liquid/solid ratio is 2 for all the experiments.

Extractor	Concentration
Ammonia	1.25%, 2.5 % and 5%
Ammonium citrate	0.25 M, 0.5 M and 1.0 M at pH 5, 8 and 9
Citric acid	0.25 M and 0.5 M at pH 8 and 9

Table 11: Overview of the parameters for the extraction experiments

7.3.1 Procedure

10.0 ml of extractor is added to 5.0 grams of soil. The suspensions are shaken for 48 hours to make sure equilibrium is reached. Electrical conductivity and pH are measured in the suspension, the suspension is centrifuged at 3000 ppr for 15 minutes and filtrated through a 45 µm filter. Thereafter the heavy metal concentration of the suspension is measured by AAS.

7.3.2 Results

The results from the extraction experiments are presented as the desorbed amount of heavy metal from the soil to the suspension in relation to the total amount in the soil, C/C_0 . Measurement results are presented in Appendix 6.

Ammonia

The extraction experiments with ammonia show a small fraction of extracted copper, (10 %) and hardly any extracted chromium, (< 0.03 %) in the suspension as shown in Figure 14. Copper will form complexes with ammonia, such as copper-tetra-amin. Chromium can also form complexes with ammonia, but this is not happening to any larger extent and the reason for this is not known. The lowest concentration of ammonia give the lowest extraction of copper, and the concentration of extracted copper is increasing with increasing ammonia concentration. The same behaviour is seen for chromium, though at much lower concentrations.

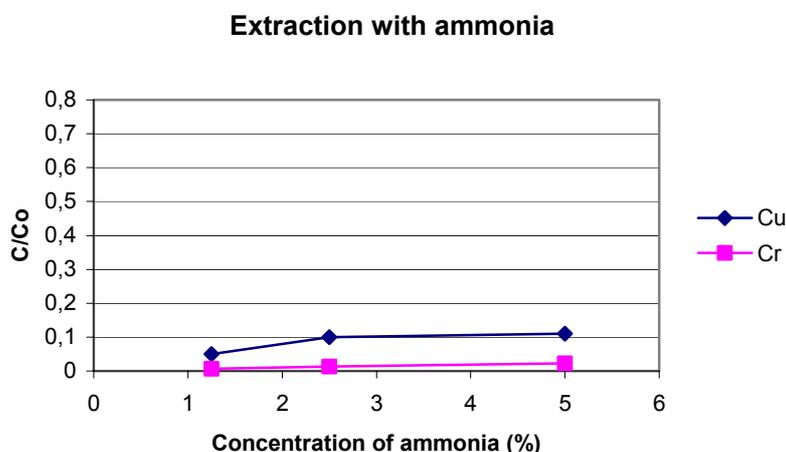


Figure 14: Extraction of copper and chromium with different concentrations of ammonia

In Table 12, the electrical conductivity for the suspensions with different concentrations of ammonia is shown. The variations in the electrical conductivity for the suspensions are limited, but a small increase is seen. The increase in electrical conductivity can be related to the increase in the copper concentration in the suspension.

Concentration of ammonia (%)	Electrical conductivity (mS/cm)
1.25	1.93
2.5	2.18
5	2.3

Table 12: The electrical conductivity in the suspension for different concentrations of ammonia

Citric acid

The results for extraction with citric acid are shown in Figure 15. Citric acid extracts both more copper and chromium than ammonia. The copper extraction is almost equal for the two concentrations (> 50%), and the pH does not seem to influence the extraction. Chromium extraction seems more dependent on the concentration of citric acid, at a citric acid concentration of 0.25 M, over 30 % of chromium is extracted, and

at a concentration of 0.5 M, the extraction is increased to over 50%. The extraction of chromium does not seem to be pH dependent for the two investigated pH values.

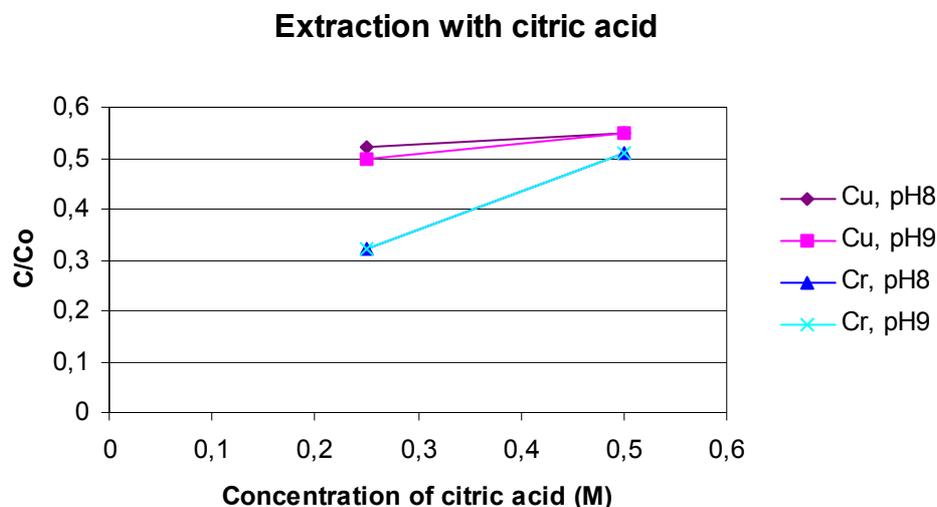


Figure 15: Extraction of copper and chromium with different pH and concentrations of citric acid

The electrical conductivity in the suspensions is seen in Table 13. Different pH does not affect the electrical conductivity, but an increase in the concentration will increase the electrical conductivity. The magnitude of the electrical conductivity is much higher than for ammonia.

Concentration of citric acid	pH	Electrical conductivity (mS/cm)
0.25	8	23.5
0.25	9	23.6
0.5	8	35.7
0.5	9	35.9

Table 13: The electrical conductivity in the suspension for different concentrations and pH of citric acid

Ammonium citrate

The results for the extraction of copper and chromium in ammonium citrate are shown in Figure 16. The extraction of copper is higher than the extraction of chromium. The extraction for copper seems dependent on the concentration of ammonium citrate and the pH. The extraction of copper is increasing with increasing concentration, 50 – 60 % is extracted at the lowest concentration, and 70 – 80 % at the highest concentration of ammonium citrate. There is also an indication that at pH 5, the extraction is lower than at the higher pHs. The chromium extraction is highly dependent on the concentration. About 25 % is extracted at 0.25 M and over 55 % is extracted at 1 M. Chromium extraction does not seem to be pH dependent.

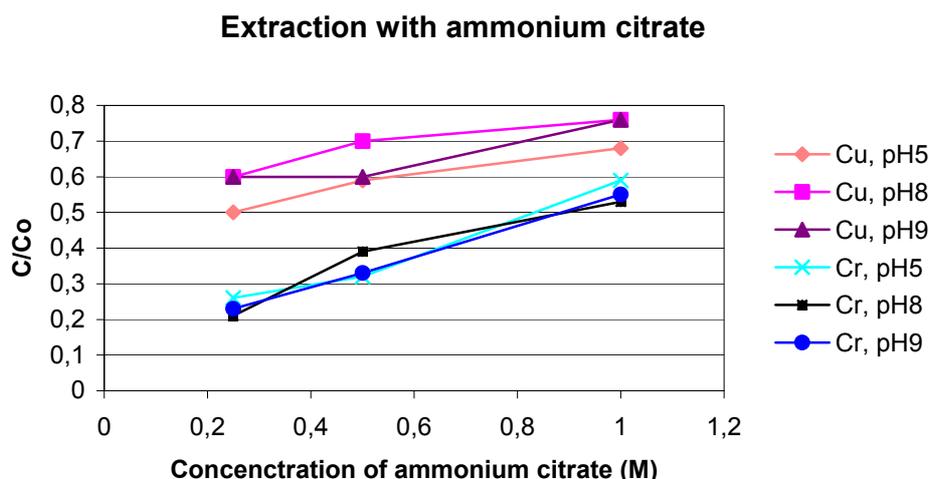


Figure 16: Extraction of copper and chromium with different concentrations and pH of ammonium citrate

In Table 14, the electrical conductivity in the suspensions with different concentrations and pH of ammonium citrate is seen. For the same concentration of ammonium citrate, the electrical conductivity is dependent on pH, where higher pH means higher electrical conductivity. The electrical conductivity also increases when the concentration of ammonium citrate increases.

Concentration of ammonium citrate (M)	pH	Electrical conductivity (mS/cm)
0.25	5	23.5
0.25	8	34.1
0.25	9	36.2
0.5	5	48.5
0.5	8	63.1
0.5	9	63.7
1	5	60.4
1	8	97.3
1	9	97.3

Table 14: The electrical conductivity in the suspension for different concentrations and pH of ammonium citrate

7.3.3 Extractor used for the electrodynamic experiments

Ammonium citrate pH 8 is chosen for the electrodynamic soil remediation experiments because ammonium citrate gives the highest extraction of both copper and chromium. The disadvantage of using ammonium citrate is the high electrical conductivity. The high pH will also keep the carbonate immobile. Ammonium citrate pH 5 cannot be used in experiments with this soil, because of the carbonate content. In the extraction experiments, the soil expanded due to dissolution of the carbonate and if pH 5 of ammonium citrate would be used in the electrodynamic experiments the soil would expand in the cell.

Experiments



In this chapter, all the experiments made, are described, which are extraction experiments with the soil solution sampler and different electrodynamic experiments.

8 Experiments

The experiments that are described in this part of the thesis are planned on the basis of the soil characterisation. Six electrolysytic soil remediation experiments are made. Extraction experiments with lower L/S ratio than used in the soil characterisation are made, in order to predict the behaviour of the soil solution. One experiment is made to investigate where the soil solution is sampled from in the electrolysytic cell, and three experiments are made in order to try to identify the charge of the copper ammonium citrate complexes.

8.1 Extraction experiments with soil solution sampler

The experiments should resemble the actual soil solution as it would be in electrolysytic experiments and furthermore, the results should be comparable with the results from the electrolysytic experiments. Therefore the same L/S ratio is chosen for these experiments as is used in the electrolysytic experiments, which is when the soil is saturated. The saturation is obtained by mixing the soil with the liquid, manually. The extraction experiments are also made to investigate the equilibrium time for copper and chromium in the soil solution. If the heavy metals charge is known, measurements of the electrical conductivity in the soil solution makes it possible to estimate the ratio the heavy metal contributes to the electrical conductivity. This ratio should preferably be as high as possible to ensure that the current during the electrolysytic remediation is used to remove heavy metals from the solution and not wasted on other ions. The ideal extractor is selective for desorbing the heavy metals only. Three extraction experiments with ammonium citrate pH 8 as desorbing agent are made:

- Experiment A: with 0.25 M
- Experiment B: with 0.5 M
- Experiment C: with 1.0 M

8.1.1 Procedure for extraction experiments with L/S 0.16 – 0.18

500 grams of soil was mixed with 80 – 90 ml of ammonium citrate pH 8, to reach saturation as used in the electrolysytic remediation experiments. The soil solution sampler was placed in the middle of a 500 ml glass and the soil was packed manually as it normally is for the electrolysytic experiments. Plastic film kept the experiment airtight and the temperature was kept constant at 29 °C during the experiment. The experiment lasted 48 hours and about 1 ml of soil solution sample was collected at time 0, 30 minutes, 60 minutes, 4 hours, 24 hours and 48 hours. The heavy metal concentrations were measured in all the samples and the electrical conductivity for the last sample in each experiment.

8.2 Electrolysytic soil remediation experiments

Six electrolysytic soil remediation experiments were in total carried out. Ammonium citrate was used as electrolytes and mixed with the soil. The parameters for the different experiments are seen in Table 15. Ammonium citrate pH 8 is used for all the experiments.

Experiment	Soil	Current (mA)	Current density (mA/cm ²)	Duration (days)	Q _{tot} (mole)	Voltage range	Cell
1	1	10	0.2	21	0.188	2.1 – 2.6	15 cm glass
2	1	10	0.2	21	0.188	3.0 – 3.3	15 cm glass
3	1	10	0.2	21	0.188	2.3 – 2.5	15 cm glass
4	1	50	1	21	0.940	4.5 – 5.1	15 cm plastic
5	2	50	1	42	1.880	3.9 – 5.0	15 cm glass
6	2	75	1.5	42	2.821	5.2 – 23.9	15 cm glass

Table 15: Parameters for the electrodynamic soil remediation experiments

The start concentration of copper and chromium and ammonium citrate in the soil, is in Table 16 showed for all the experiments.

Experiment	Initial Cu concentration in soil (mg/kg)	Initial Cr concentration in soil (mg/kg)	Ammonium citrate concentration (M)
1	3569	1088	1
2	3337	1115	0.25
3	7857	1737	0.5
4	4091	1137	1
5	1664	941	1
6	1574	879	1

Table 16: Initial copper and chromium concentration in the soil as well as ammonium citrate concentration for the electrodynamic soil remediation experiments.

Experiments 1 – 3 were made to determine which concentration of ammonium citrate would be the most efficient for desorbing the heavy metals from the soil and thus give a high concentration of the heavy metals in the soil solution. Secondly, experiments 4 – 6 were made to investigate how different current densities and a longer clean-up period would effect the remediation and the concentration of the heavy metals in the soil solution.

8.2.1 The experimental cell

The experimental set-up is shown in Figure 17.

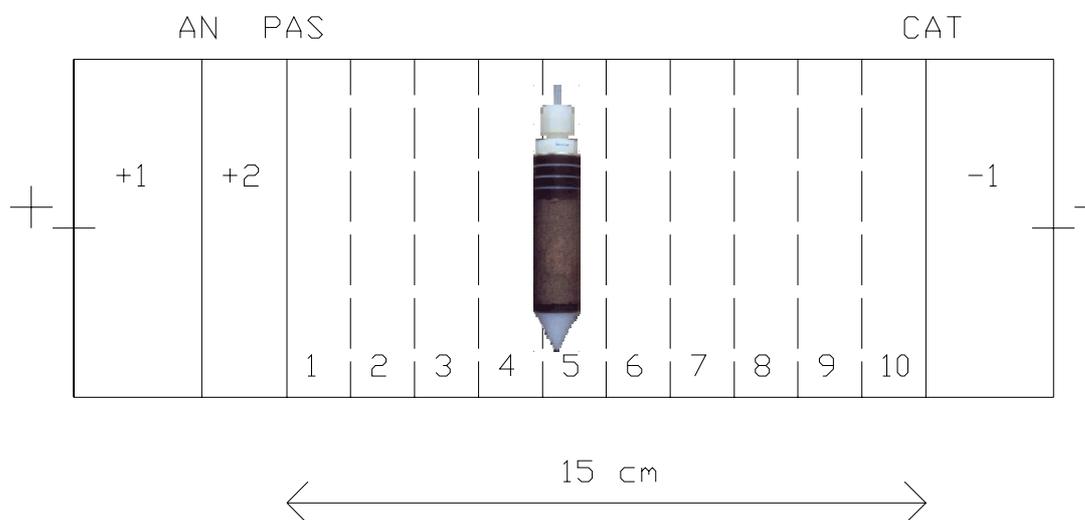


Figure 17: The experimental set-up for the electrodynamic soil remediation experiments

The cell consists of four compartments, two electrolyte compartments, the anolyte (+1) and the catholyte (-1), one middle compartment containing the polluted soil (15 cm long) and one extra compartment (+2) (1.5 cm long). The inner diameter of the compartments is 8 cm. The size of the soil solution sampler is deciding the size of the cell. The soil solution sampler is placed in the middle of the soil compartment because the cell is made in such a shape, that it could be placed here. The cathode compartment is separated from the soil with a cationexchange membrane (CAT) and an anionexchange membrane (AN) separates the anode compartment and the extra compartment. A passive membrane (PAS) separates the soil compartment and the extra compartment. The extra compartment is included in the set-up to allow continuous adding of electrolyte to the soil. This should prevent the soil from being desaturated. The extra compartment will in the following be called the liquid compartment.

When inserting the liquid compartment in the cell, it is possible to collect soil solution samples from electrodynamic experiments, this was seen in the pre-investigations for this thesis, see Appendix 1.

Experiment 4 was made in a plastic cell, also 15 cm long with an inner diameter of 8 cm, with inert reference electrodes, to measure if the soil solution sampler disturbed the electric field in the soil. 4 reference electrodes (on the top, front, bottom and back of the cell) were placed in 6 rows as seen in Figure 18, three rows on each side of the sampler.

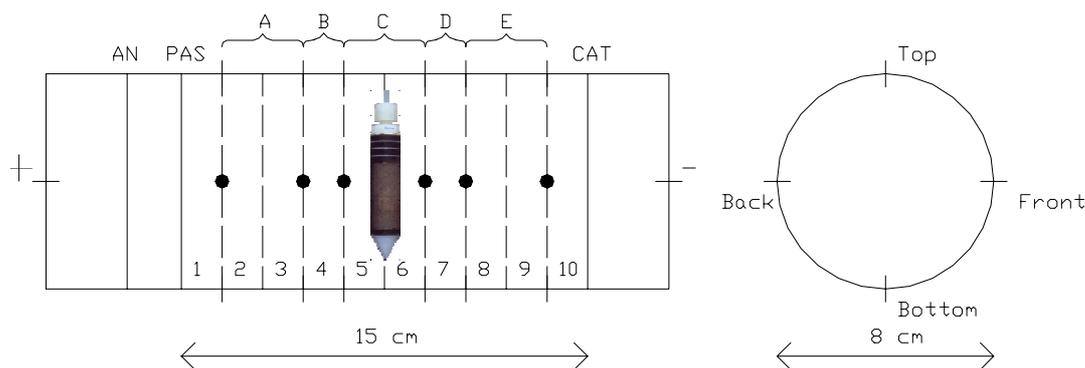


Figure 18: The laboratory cell used for experiment 4

The voltage from the anode and cathode to the reference electrodes was measured with a multimeter immediately before and after soil solution sampling.

Table 17 shows the apparatus used for the experiments.

Apparatus	Manufacturer
Pumps	Pan World Magnet Pump Model NH -5PX
Power supply	Hewlet Packard E3512 A
Anionexchange membrane	Ionics AR-204-SZRA-7639
Cationexchange membrane	Ionics CR67-HMR-166A
Passive membrane	Piece of laboratory coat and filter paper
Working electrodes	Platinum coated from Bergsøe Anti Corrosion
Reference electrodes	Silver
Soil solution sampler	Prenart super quartz mini

Table 17: The manufacturers of the used apparatus for the electroalytic experiments

Pre-treatment of the soil solution sampler

The soil solution sampler was, as suggested from the manufacturer, pre-treated, see Appendix 7. This was done by mixing a thin slurry of soil and water and in which the sampler was placed. Then, suction was put on the sampler for about 10 minutes. This procedure fills the biggest pores of the sampler, to ensure a tight capillary contact with the soil and is suggested by Grossmann and Udluft (1991) to avoid the strong sorption effect new sampler can have. The manufacturer also suggests that the slurry can be made of silica flour and water, but McGuire et al. (1992) found that chromium sorbs to silica when the pH is above 8, and thus, the use of silica flour could make errors in the results.

Set-up

The soil used in all the experiments was dried at 105°C and then sieved through a 4 mm sieve, to remove rocks and debris. Then, the soil was saturated with ammonium citrate in concentrations from 0.25 – 1 M depending on the experiment, to a total humidity content of 11 – 15 %. The soil was then packed manually in the cell and the soil solution sampler was placed in the middle of the soil compartment, in the distance 6 – 8 cm from the passive membrane on the anode side, as seen in Figure 17.

Initial pH in the soil was measured in duplicate on wet soil. Soil samples in triplicate were dried at 105 °C to measure initial humidity. Copper and chromium concentrations were thereafter measured on the dry soil according to Danish Standards 259, see Table 9.

Electrolytes

Ammonium citrate was used as electrolytes. In the pre-investigations (Appendix 1) a sizable water flow in the direction from the anode to the cathode was observed and thus bringing the undesired electrolyte into the soil. It was therefore decided, that the same chemical should be used as electrolyte as was mixed with the soil, also to ensure a continuous adding of the desorbing agent to the soil. The electrolytes circulated in all the experiments. The concentration of the anolyte and catholyte was 0.25 M in all the experiments, and the concentration in the liquid compartment was the same as the concentration of the solution mixed with the soil, see Table 16 for details. The initial volumes were 1.0 L for the anolyte and catholyte and 0.5 L for the liquid compartment.

Thereafter the pumps were started and the experiment was allowed to equilibrate overnight before start samples from the electrolytes and soil solution were taken and the current was applied.

8.2.2 During the experiment

pH, current, voltage drop and volumes of the electrolytes were measured every week day for all the experiments. The pH of the electrolytes should exceed 8 at all time. The pH would only drop under 8 in the anolyte and the extra compartment and if the pH drops under 8, it was adjusted with NaOH tablets, to keep the pH over 8.

Soil solution samples

The soil solution samples were taken three times a week. The sampling procedure was based on sudden tension as follows, see: Figure 19.



Figure 19: The sampling method for soil solution sampling

A small piece of soft plastic tubing was attached to the smaller tube from the soil solution sampler to be able to attach a syringe to the tube. It is important that this connection to be absolutely airtight in order to collect the sample.

1. A 20 ml plastic syringe was attached to the tube from the soil solution sampler and the syringe was extended between 10 – 120 minutes to create the necessary vacuum to collect the amount of sample needed.
2. After sampling, the amount of sample was measured and the colour was noted.
3. The sampler was left without vacuum until next sampling.

The amount of sample needed, is depending on the number of analysis that shall be performed on the sample. It is desirable to extract the smallest possible volume because:

- To be able to collect sample throughout the experiment, even if the total solution content in the soil is low.
- To limit the disturbance on the experiments.

Measurements of electrical conductivity require at least one ml sample, and for pH measurements almost ten ml are needed (pH indication paper could not be used, because the soil solution coloured the paper). The most important measurements in this study are the concentrations of copper and chromium, determined by Atomic absorption spectrometry (AAS). This measurement method requires about 2 – 3 ml of sample for each metal. Thus, the number of elements that should be measured is determining for the needed sample volume. On the other hand, the standard range of measuring copper and chromium by AAS is 1- 5 mg/l, so dilution of the samples is most likely necessary and this will mean that a smaller sample volume is needed.

From experiments 1 and 2 about 5 ml sample was taken and the samples were conserved with 1:1 HNO₃ for AAS measurements. From experiments 3 – 6 between 2 – 3 ml of sample was collected. These samples were kept in the refrigerator until AAS measurement, to keep the samples unaltered. For all samples, electrical conductivity was measured and pH was measured for some of the experiments, but with uncertainties, because the sample volume was not sufficient.

Collecting the sample with the use of a larger syringe (50 ml) and a vacuum device was also tested, to see if this would shorten the sampling time, but it did not.

8.2.3 Observations during experiment

The electrolytes +1 and +2 quickly (after 5 – 10 days) changed colour in all the experiments from yellow through orange to dark green. The catholyte became slightly green or blue in all the experiments and precipitation of copper on the cathode was observed early in the experiments (after one week). The soil solution samples were coloured in all the experiments, ranging from transparent green in experiment 2 and 3, through dark green/black in experiment 1 and 4 and being green/brown/black in experiment 5 and 6. Other observations during the experiments are presented in Table 18.

Experiment	Observations/irregularities
1	None
2	Air is coming into the liquid compartment Leakage from liquid compartment Passive membrane changed and 200 ml ammonium citrate added to liquid compartment
3	None
4	None
5	Electrolytes changed after 21 days
6	Passive membrane changed Electrolytes changed after 21 days, after this, the soil collapsed partly

Table 18: Observations and irregularities for the electrodialytic experiments

8.2.4 After experiment

When the experiment ended, samples from the electrolytes were taken and the volumes of the electrolytes were measured. The soil volume was divided into ten slices that were about 1.5 cm thick each. Slice 1 corresponds to the soil closest to the anode and slice 10 corresponds to the soil closest to the cathode, see Figure 17. Care was taken when removing the soil solution sampler. pH was measured in duplicate on the wet soil for each slice and the rest of the soil was dried at 105°C to measure the humidity. The heavy metal concentrations were measured after Danish Standard 259 on the dry soil, see Table 9. The membranes and the sampler were put in 1 M HNO₃ for 24 h and the electrodes were put in 5 M HNO₃ for 24 h to remove the metals. For experiment 1, carbonate content was also measured for each slice.

8.3 Electrodialytic experiments with liquid

In order to specify the charge of copper in ammonium citrate, three electrodialytic experiments with copper nitrate dissolved in ammonium citrate were made. The copper concentration in the solution was 500 mg/l for the three experiments, with ammonium citrate concentrations 0.25 M, 0.5 M and 1.0 M at pH 8. The experimental set-up is seen in Figure 20.

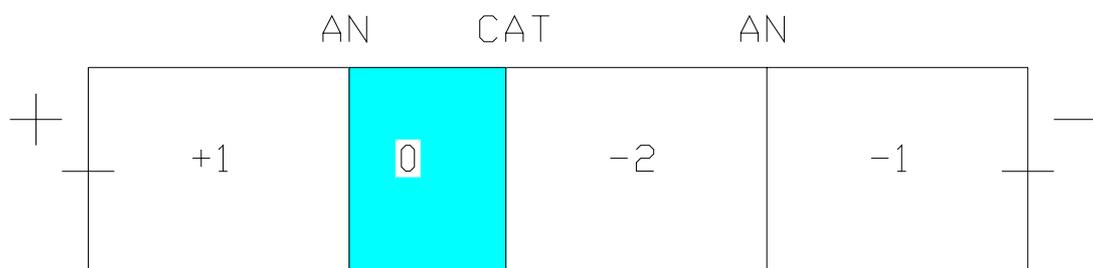


Figure 20: The electrodialytic cell used for the desalination of copper-containing ammonium citrate. AN is the anionexchange membrane, CAT is the cationexchange membrane, +1 the anolyte, -2 and -1 the catholytes and 0 the contaminated ammonium citrate.

The cell consisted of four compartments. The compartments all had an inner diameter of 4 cm and the length was 5 cm except for compartment 0, which length was 2 cm. The electrolytes in compartments +1, -2 and -1 were filled with 0.25 L of ammonium citrate pH 8, with different concentrations for the three experiments. The electrolyte in compartment 0 was 0.1 L 500 mg/l copper in ammonium citrate pH 8, at respectively concentrations for the three experiments. The electrolytes in all compartments were circulating using Masterflex pumps. The electrolytes circulated for 15 minutes, start samples from compartment +1 and -2 were taken and then a 250 mA current was applied. Samples were afterwards collected from compartments +1 and -2 throughout the experiment. In Table 19, duration and number of samples taken for the different experiments are shown.

Experiment	Ammonium citrate concentration (M)	Duration (h)	Number of samples
A	0.25	21.5	23
B	0.5	21	6
C	1.0	30	8

Table 19: Parameters for the different experiments for desalination of copper-containing ammonium citrate

The experiments ended when the voltage had reached maximum (137 V) for the power supply, which indicates that all the ions in the solution are removed. Experiment C ended before the voltage reached its maximum because compartment 0 was emptied, due to electroosmosis.

8.4 Electrodialytic soil experiment to test the sampling radius of sampler

In order to investigate the sampling radius of the soil solution sampler during the electro-dialytic experiment, a test experiment was made. The set – up used, was the same as used for the other electro-dialytic soil remediation experiments, as seen in Figure 19. The electrolytes + 1 and -1 were 0.01 M NaNO₃ pH 2 and the electrolyte +2 was green fruit syrup. The soil was unpolluted kaolin, which is white. The applied current was 10 mA. Soil solution samples were taken occasionally, with the same procedure as for the other electro-dialytic experiment. The experiment lasted for one week. The aim of the experiment was to see whether the collected soil solution samples would be green, because if so, the sample could be from compartment + 2 and not the representative solution in the soil.

8.5 Uncertainties in analysis

Working with soil and soil analysis can be challenging. Due to the inhomogeneous and complex properties of the soil, uncertainties in connection with analysis cannot be avoided. Therefore, this is probably the reason for any unexplainable difference in the results.

Ammonium citrate has the unfortunate ability to evaporate and this will mean that the concentration of heavy metal in the upper part of the dried soil is higher than in the lower part, the difference can be as much as 100 %, see Appendix 8. As dried ammonium citrate gets caramelised, it is not easily crushed and thus, an evenly mixed crushed soil sample can be difficult to obtain. There was not found any difference in the

difficulty of crushing the soil if it was air-dried or oven dried. The crushing is done manually for all the samples.

The total concentration of heavy metals in the soil can vary a lot. For this analysis, only 1 gram of soil is used and a soil slice from the treated experiment weighs about 100 grams. For the total concentration in the soil, a duplicate determination was made primarily. If this gave recovery results for 95 – 105% for copper and 90 – 110% for chromium for the whole experiment, the results were accepted. If any deviation from this occurred, any distinct errors would be looked for. Then the start concentrations would be measured again and the concentration in the soil slice if the concentration deviation was large. If this would not help on the recovery balance, the obtained results would anyway be accepted.

The measuring procedure for the AAS also changed while the project was running. For the first two experiments the soil solution samples was conserved with acid to be measured within an acidic standard range. After this, a 0.25 M ammonium citrate pH 8 standard range was made, and the soil solution samples were hereafter kept in the refrigerator until measurement. This change of procedure should not mean any change in the measured concentrations.

Results



In this chapter, the results from the experiments described in the previous chapter, are presented.

9 Results

9.1 Extraction experiments with soil solution sampler

In Figure 21, the concentration of copper in the soil solution, collected from the extraction experiments with the soil solution sampler, is shown. Measurement results are seen in Appendix 9. It can be seen from the figure that desorption of copper starts immediately after the ammonium citrate has been mixed with the soil, at time 0. Equilibrium for desorbed concentration of copper in 0.25 M ammonium citrate is reached quickly, already after four hours. Coppers desorption in 0.5 M and 1M ammonium citrate increases rapidly in the first four hours, but is still increasing until the end of the experiment. Since there are not collected any samples between 24 and 48 hours, it is impossible to predict if the concentration measured at 48 hours is the equilibrium concentration.

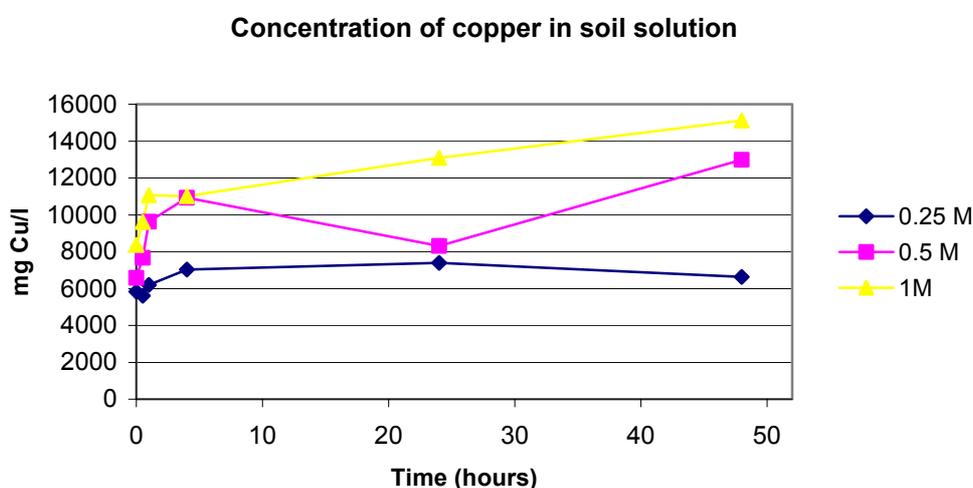


Figure 21: Concentration of copper in the soil solution extracted from three experiments with different concentrations of ammonium citrate pH 8

In Figure 22 the chromium in the soil solution collected from the extraction experiment is shown and measurement results are seen in Appendix 9. Chromium desorption is clearly dependent on the concentration of ammonium citrate in the soil. As for copper, the chromium desorption starts immediately after the ammonium citrate is mixed with the soil, at time 0. The desorption at 0.25 M reaches equilibrium already after four hours, but the concentration of chromium in the soil solution is low, < 150 mg/l. The chromium concentration in 0.5 M ammonium citrate barely exceed 500 mg/l after 48 hours and the chromium concentration in 1 M ammonium citrate is as high as 1800 mg/l after 48 hours. As for copper, it is impossible to predict if equilibrium for desorption is reached after 48 hours for 0.5 M and 1 M ammonium citrate.

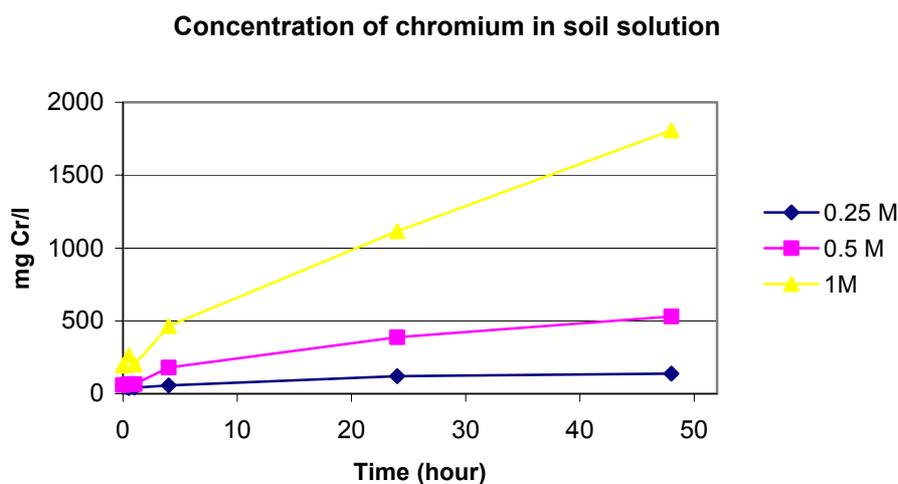


Figure 22: Concentration of chromium in the soil solution extracted from three experiments with different concentrations of ammonium citrate pH 8

In Table 20 the electrical conductivity for the last sample (at 48 hours) with different concentration of ammonium citrate is shown. The electrical conductivity could not be measured for the other samples due to the low sample volume. The part of the electrical conductivity that originate from the heavy metals, K_{Me} , are shown in Table 20. K_{Me} was estimated for different charge composition, see Appendix 10.

Concentration of ammonium citrate pH 8 (M)	Electrical conductivity (mS/cm)	K_{Cu}	K_{Cr}
0.25	26.5	0.4 – 0.8	0.01 – 0.02
0.5	47.5	0.5 – 0.9	0.03 – 0.04
1	80.7	0.3 – 0.6	0.06 – 0.09

Table 20: Electrical conductivity of the last sample for the three experiments with ammonium citrate concentration of 0.25M, 0.5M and 1M.

The calculations of K_{Me} are made to get an idea of the percentage of the current being used for transporting the heavy metals in the soil solution. The fact that copper and chromium are forming both negative and positive complexes with ammonium citrate, makes it difficult to predict the composition of the charges. The K_{Cu} is high for all the given concentrations of ammonium citrate, which indicates that a large percentage of the current should be used to remove copper from the soil solution. Opposite, the K_{Cr} is very low, indicating that hardly any current will be used to remove chromium from the soil solution. Therefore, the magnitude of the electrical conductivity is dependent on the copper concentration in the soil solution. If the obtained values for K_{Cu} are somewhat correct, the use of ammonium citrate should be very efficient for copper removal. The opposite applies to chromium. The K_{Cr} is low, which means that the use of ammonium citrate to remove chromium could be insufficient because the current must be high in order to remove it. Even though the concentration of copper and chromium in the soil solution will increase with higher concentration of ammonium citrate, this will also mean that the electrical conductivity in the soil solution will increase. So it is necessary to balance these two parameters to find the optimum for electrodynamic remediation.

9.2 Electrodialytic soil remediation experiments

The results for the electrodialytic remediation experiments are presented experiment by experiment. Mass balances for the copper and chromium are presented as recovery percentage and removal percentage. The removal is furthermore specified as removal to the cathode or anode side of the cell. The volumes of the electrolytes during the experiment are presented. pH, humidity, copper and chromium concentrations before and after the experiments, are thereafter presented. At last the pH, electrical conductivity, copper and chromium concentrations in the soil solution, along with the sampling rate for the soil solution are presented. Results and measurement results for the six electrodialytic experiments are presented in Appendix 11, I-VI.

9.2.1 Definitions

The sampling rate is calculated as amount of ml sample / the time of the sampling. The sampling rate is not exact, because neither the measurement of the sampled volume nor the sampling time is precise.

The recovery is defined as total amount of heavy metal found after the experiment / total amount of heavy metal in the soil before the experiment.

The removal is defined as total amount of heavy metal in electrolytes, membranes and electrodes after experiment / total amount of heavy metal found after the experiment

The removal can be either to the cathode or the anode side of the cell and the percentages for this are based on the removal as 100 %.

The soil solution sampler is found mainly in slice 5 but also in slice 4 for all the experiments, except experiment 4 where it was found equally in slice 5 and 6.

The conditions for the different experiments are seen in Table 15 and Table 16 in chapter 8.2 Electrodialytic soil remediation experiments.

9.2.2 Experiment 1

The results for experiment 1 are presented in Appendix 11 I. The recovery rates are for copper 96 % and for chromium 88 %, as seen in Table 21. The total removal for copper is 11 % and for chromium, 6%. Both metals have mainly migrated towards the anode, indicating that both copper and chromium are forming negatively charged compounds in the soil with citrate. Copper has also formed some positively charged compounds with ammonia, which are migrating towards the cathode.

	Recovery	Removal	Removed to cathode side	Removed to anode side
Cu	96 %	11 %	20 %	80 %
Cr	88 %	6 %	5 %	95 %

Table 21: Mass balance and removal for copper and chromium in experiment 1

Electrolytes

The volumes of the electrolytes during the experiment are seen in Figure 23. A decrease in the volume of the anolyte is followed by an increase in the volume in the liquid compartment. Nearly 300 ml of anolyte is disappearing indicating that the anionexchange membrane is not 100 % effective. This volume is not found as extra

volume in the liquid compartment. Some of the liquid is being transported into the soil due to electroosmosis, for compensation for the about 50 ml extracted for soil solution samples. A large part may have evaporated, the temperature of the pumps gets high during the experiment, and the experiment was performed in early spring and the sun was shining directly into the laboratory, causing condensation on the inside of all the electrolyte flasks.

Volumes of electrolytes during experiment

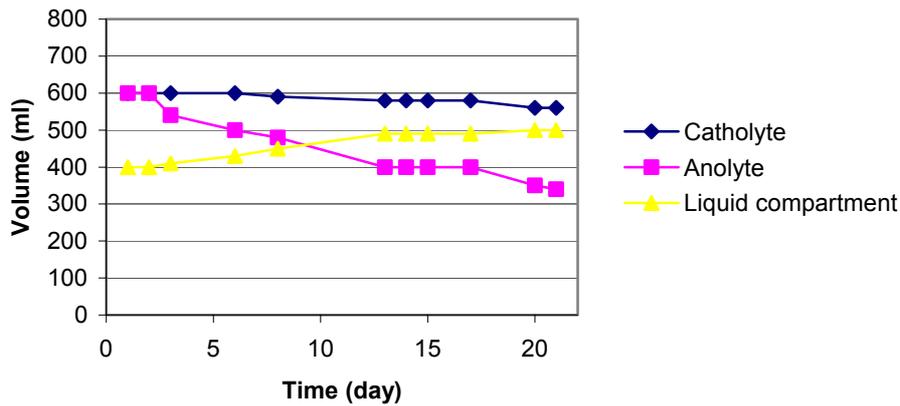


Figure 23: Volumes of the electrolytes during experiment 1

Soil

Figure 24 shows the pH and the humidity in the soil before and after the experiment. The pH in the soil is not changing during the experiment, because there is no development of an acidic front, since the anionexchange membrane is not in contact with the soil. The sampler does not seem to have any influence on the pH in the soil. The humidity is decreasing over the whole soil during the experiment, especially in slice 6. This could be due to the soil solution sampling. It is also seen that the humidity in the slice closest to the passive membrane is higher than for the other slices, indicating a transport of electrolyte into the soil through the passive membrane.

pH and humidity in the soil

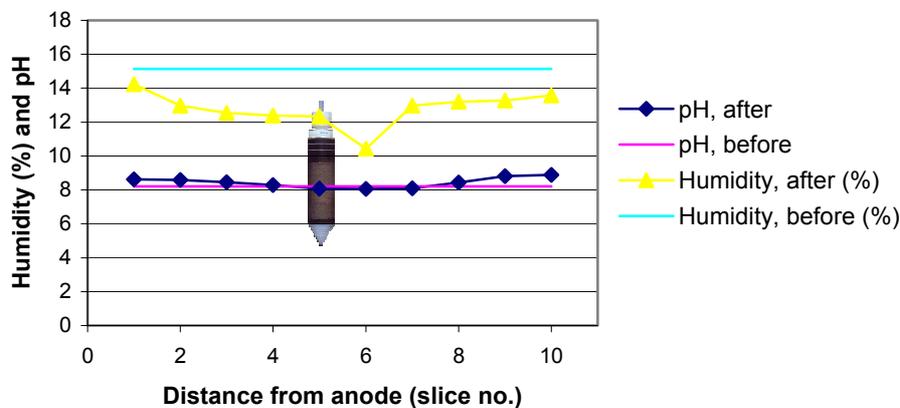


Figure 24: pH and humidity in the soil sliced before and after experiment 1

The concentrations for copper and chromium in the soil before and after the experiment are seen in

Figure 25. The start concentration for chromium is much lower than for copper in the soil. The soil is not remediated to a level where the soil can be regarded to be cleaned for neither copper nor chromium, which means a concentration below 500 mg/kg. The remediation of copper seems to be most extensive in the slices closest to the electrodes, and the lowest concentration obtained is 1300 mg/kg. The concentration profile does not give any clear indication on how copper is moving in the soil. Clearly, there is migration towards both electrodes. The peak in the middle of the soil can be a point where the negatively and positively ions are meeting in the migration through the soil. The recovery rate of chromium is lower than for copper, which can be seen in Figure 25, where a removal of chromium is indicated, but this is due to a high start concentration, which is due to the inhomogeneities of the soil. The concentration profile for chromium does not give any clear indications on how chromium is moving in the soil. The sampler does not seem to have any influence on the copper and chromium concentrations in the soil.

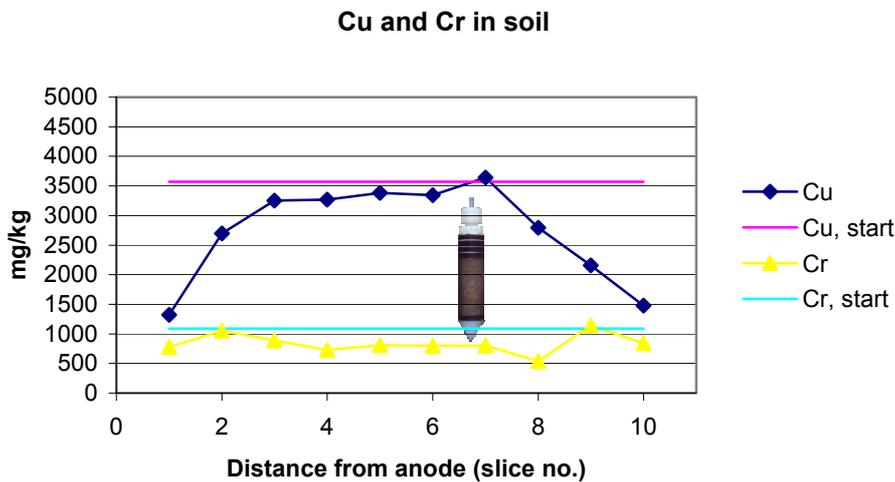


Figure 25: Copper and chromium concentrations in the soil slices before and after experiment 1

The carbonate content in the soil was measured before and after the experiment, see Figure 26. It is seen that the carbonate is not dissolving in the soil, due to the high and stable pH in the soil, and that it stays immobile as expected. The variations in the carbonate content are probably due to inhomogeneities, since small carbonate lumps can be seen in the soil, more than an actual movement of the carbonate in the soil.

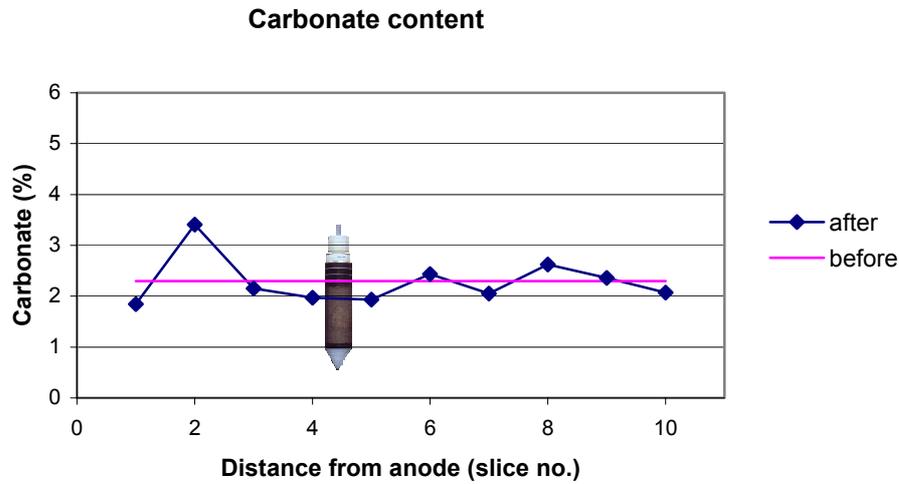


Figure 26: Carbonate content in the soil slices before and after experiment 1

Soil solution

The concentrations of copper and chromium in the soil solution during the experiment are seen in Figure 27. The copper concentration starts at a high level, 12000 mg/l and is decreasing throughout the experiment to 9000 mg/l in the end. The chromium concentration in the soil solution is lower than the copper concentration. The chromium concentration starts at 1300 mg/l and is increasing until the 15th day, when it starts decreasing. The increase is due to the slower equilibrium between the soil and soil solution for chromium than for copper. The copper and chromium concentrations are still high compared to natural concentration of copper and chromium in soil solution, which indicates that they are still mobile in the soil solution and the soil is not fully remediated. This is also in agreement with the high concentrations of copper and chromium in the soil slices surrounding the sampler.

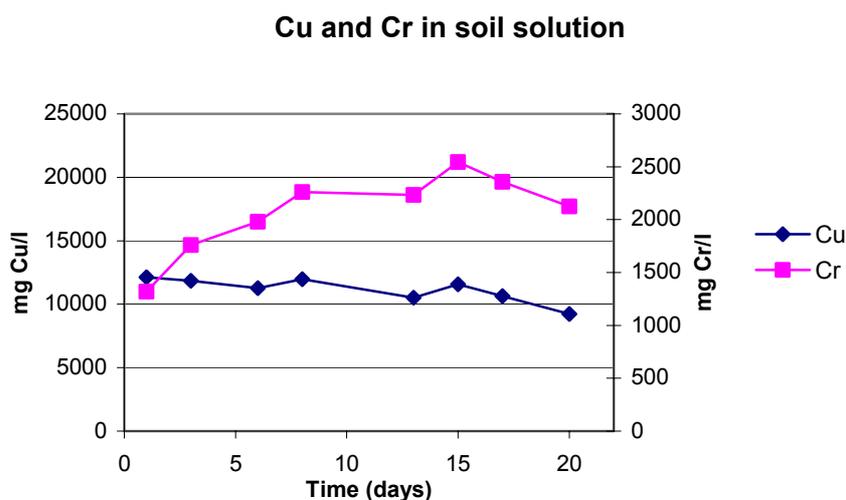


Figure 27: Copper and chromium concentrations in the soil solution in experiment 1

The electrical conductivity and pH of the soil solution are seen in Figure 28. The electrical conductivity is stable until 12 days of remediation, where after it starts to decrease. This indicates that the number of ions in the soil solution is decreasing. The pH in the soil solution remains stable throughout the experiment, always over 8.5.

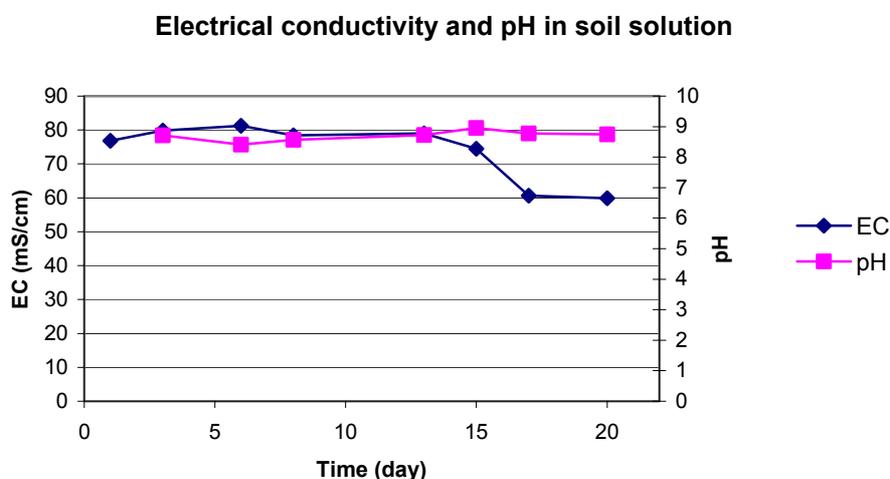


Figure 28: Electrical conductivity and pH in the soil solution in experiment 1

In Figure 29 the sampling rate of the soil solution is seen. The rate is indicating a slow sampling. This is probably due to bad contact between the sampler and the soil because of the packing of the soil around the sampler. In this experiment, 5 ml of soil solution was sampled each time, with sampling times up to 2 hours. Neither disturbances in the voltage nor bubbles in the liquid compartment from the soil were observed during sampling. Thus, the effect on the system equilibrium of such a long sampling time seems to be low.

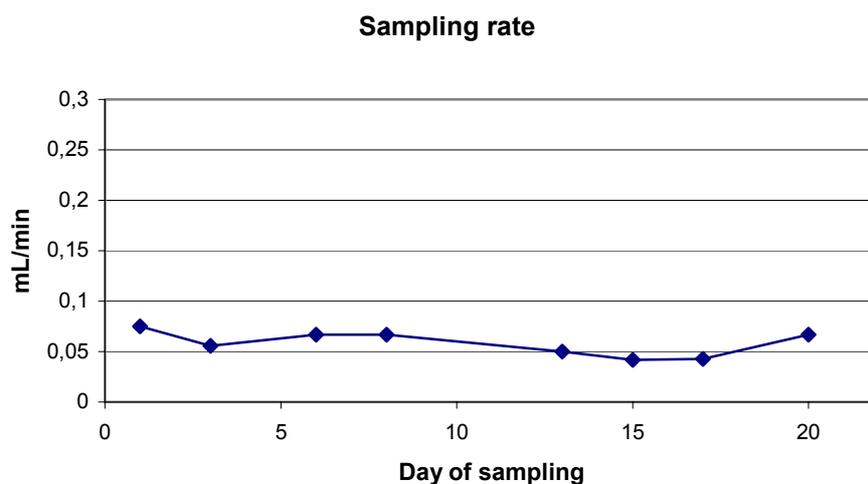


Figure 29: Sampling rate of soil solution samples collected from experiment 1

9.2.3 Experiment 2

The results for experiment 2 are presented in Appendix 11 II. The recovery rates for copper and chromium is 98 % and 114 % respectively and only 4% copper and 3% chromium is removed from the soil during the experiment, as presented in Table 22. Chromium measurements were made twice, both for the start concentrations and for some of the slices, but this did not make the recovery rate lower. The removed copper is found in both the cathode side and the anode side of the cell. Chromium on the other hand is mainly being transported towards the anode.

	Recovery	Removal	Removed to cathode side	Removed to anode side
Cu	98 %	4 %	45 %	55 %
Cr	114 %	3 %	10 %	90 %

Table 22: Mass balance and removal for copper and chromium in experiment 2

Electrolytes

The volumes of the electrolytes during the experiment are shown in Figure 30. The electrolyte in the liquid compartment is disappearing throughout the experiment. This is partly due to a leakage from the cell. When the liquid compartment was almost empty, the experiment was stopped and the passive membrane was changed and the leakage stopped. The increase in the volume of catholyte indicates electroosmosis.

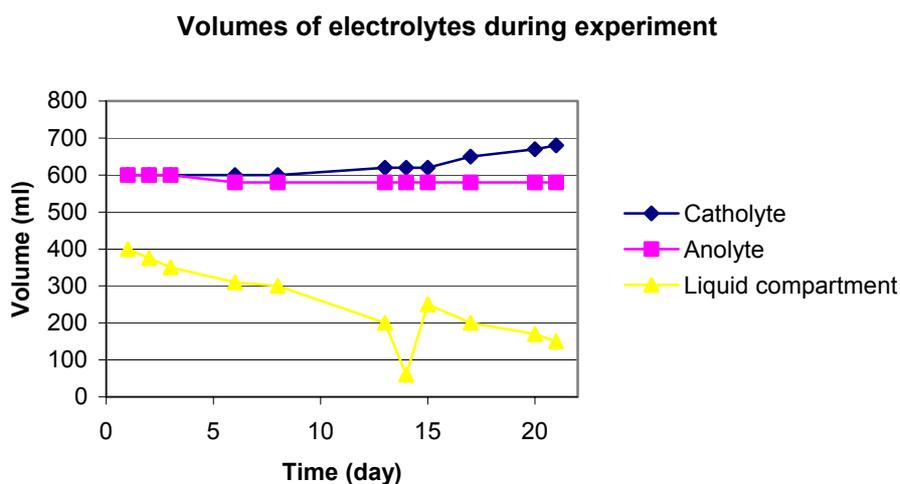


Figure 30: Volumes of the electrolytes during experiment 2

Soil

The pH and the humidity in the soil before and after the experiment are shown in Figure 31. The humidity is not changing in the soil during the experiment, which indicates that the liquid compartment is functioning as desired, to ensure that the soil is not drying and the soil solution sampler is not draining the soil in any area. The pH is also stable in the soil throughout the experiment.

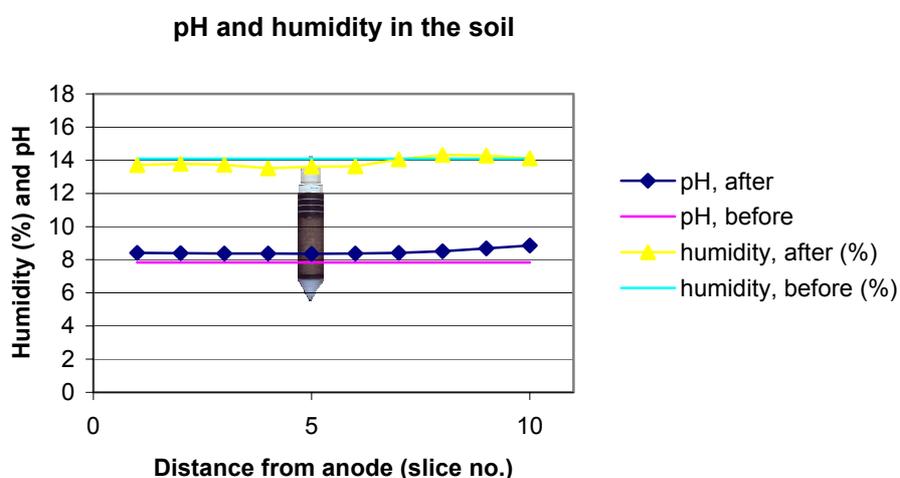


Figure 31: pH and humidity in the soil sliced before and after experiment 2

The concentrations of copper and chromium in the soil before and after the experiment are seen in Figure 32. There is an indication of removal of copper, especially in the slices closest to the electrodes and again as for experiment 1, a distinct peak in the middle of the soil is seen. None of the slices are remediated to a clean level for copper. The removal of copper seems higher than it actually is, this is due to the amount of copper extracted in form of soil solution samples, which is higher than the amount removed by electromigration. The concentration profile for chromium does not have the same characteristic shape as for copper, but removal of chromium in the slices closest to the electrodes is indicated. The recovery rate of chromium is high in this experiment,

which is indicated by the fact that the concentration in the slices is often higher after the experiment than before.

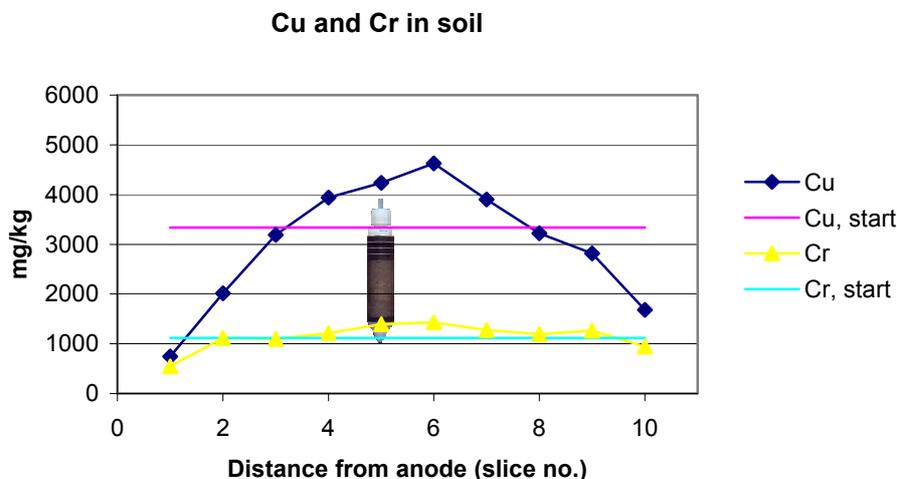


Figure 32: Copper and chromium concentrations in the soil slices before and after experiment 2

Soil solution

The concentrations of copper and chromium are shown in Figure 33. The concentration profiles are strikingly alike, though in different concentration intervals and lower concentrations than for experiment 1. The concentrations are low in the beginning of the experiment and are increasing steadily until day 17, where a pronounced increase is seen. Since these measurements are from the last soil solution sample, it is impossible to predict if the concentrations would continue to raise, stabilise or even decrease again. If the last measurement is not considered, interpreted as a deviation from the other samples, it seems as the concentrations are reaching a stable level after 12 days.

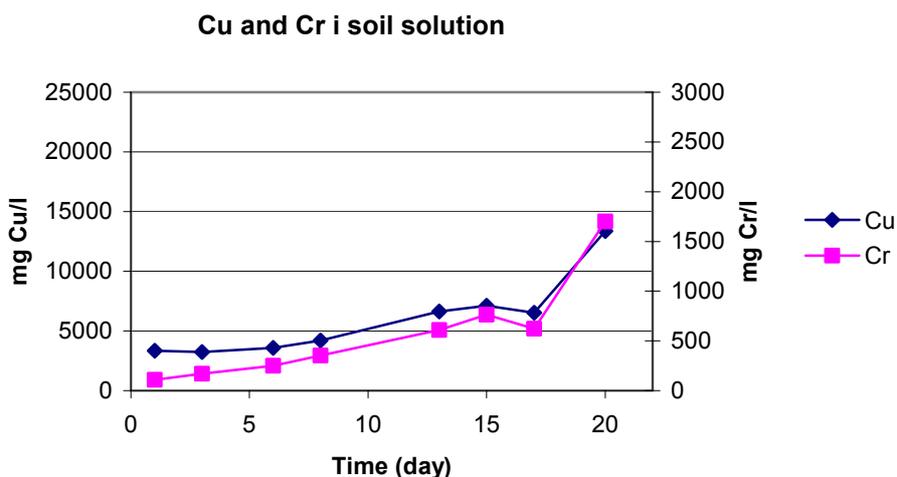


Figure 33: Copper and chromium concentrations in the soil solution in experiment 2

The pH and electrical conductivity in the soil solution are seen in Figure 34. The pH in the soil solution is not changing during the experiment. The electrical conductivity is stable in the beginning of the experiment and is slightly decreasing by the end of the experiment. The increase in the electrical conductivity could be due to the increase in the heavy metal concentrations as seen in Figure 33.

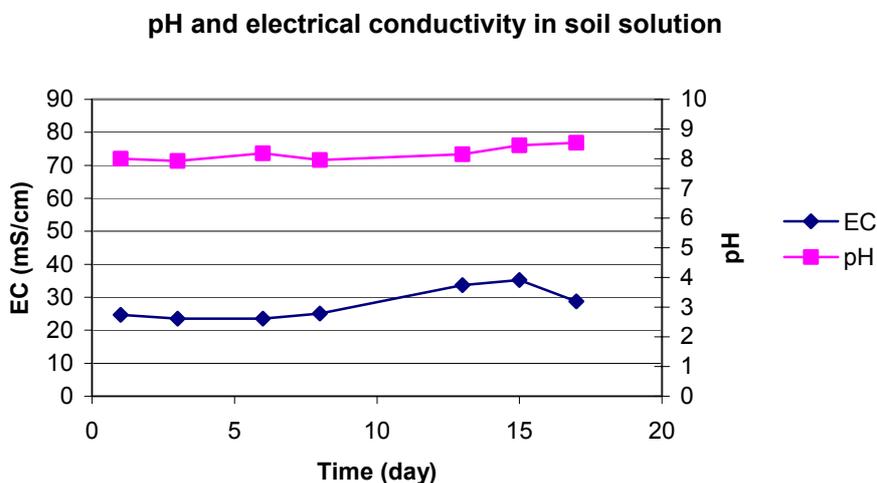


Figure 34: Electrical conductivity and pH in the soil solution in experiment 2

The sampling rate for the soil solution samples for experiment 2 is seen in Figure 35. The sampling rate is higher in the beginning of the experiment and is decreasing and sampling gets difficult by the end of the experiment. About 5 ml sample are sampled each time, with sampling times between 35 – 75 minutes. Only 1 ml of sample could be sampled on the last day of the experiment and this took 60 minutes.

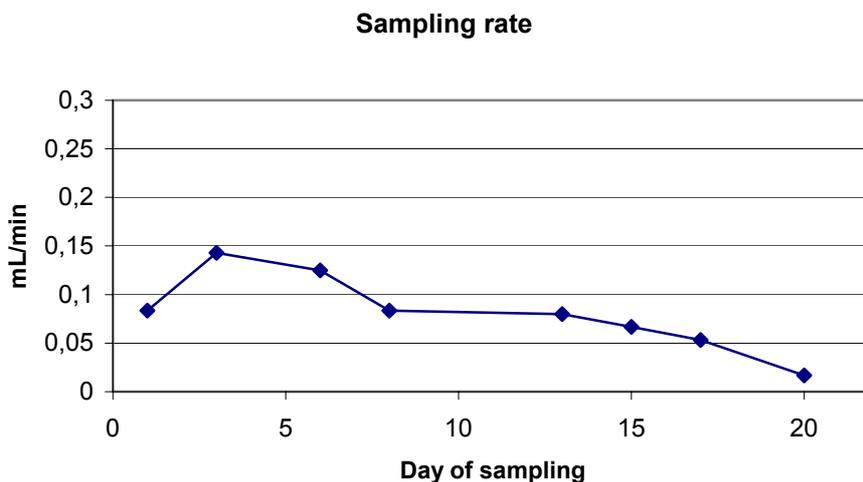


Figure 35: Sampling rate of soil solution samples collected from experiment 2

9.2.4 Experiment 3

The results for experiment 3 are presented in Appendix 11 III. The recovery rate for copper is 120% and for chromium 91%, as seen in Table 23. The high recovery rate for

copper can be explained by the soil containing a high copper concentration and small green lumps, containing copper, were seen in the soil. This makes copper measurements for this soil very uncertain, because the lumps will not be equally distributed in the soil. The soil samples were measured twice, but this did not change the result of the recovery. The small green lumps were also seen in the slices after the experiment. The copper removal from the soil was 12 % and the chromium removal was 3%. Both the metals were mainly removed towards the anode side of the cell indicating negatively charged species.

	Recovery	Removal	Removed to cathode side	Removed to anode side
Cu	120 %	12 %	10 %	90 %
Cr	91 %	3 %	2 %	98 %

Table 23: Mass balance and removal for copper and chromium in experiment 3

Electrolytes

The volumes of the electrolytes for experiment 3 are seen in Figure 36. A decrease in the volumes of the anolyte and the liquid compartment is seen, indicating transportation of electrolyte into the soil.

Volume of electrolytes during experiment

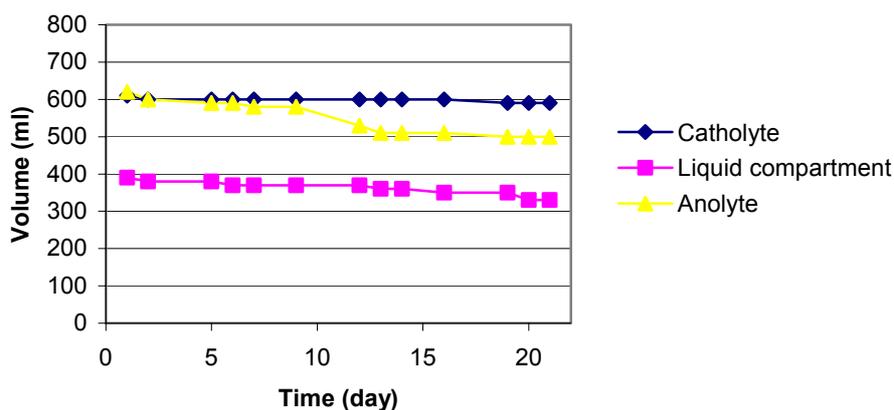


Figure 36: Volumes of the electrolytes during experiment 3

Soil

The pH and the humidity in the soil before and after the experiment are seen in Figure 37. The humidity has increased in all the slices, compared to the humidity in the beginning of the experiment, but the level seems to be stable for all the slices, although the humidity in slice 1 is slightly higher than for the other slices. The pH is slightly higher after the experiment, compared to the start pH in the soil, but the pH seems rather stable throughout the soil.

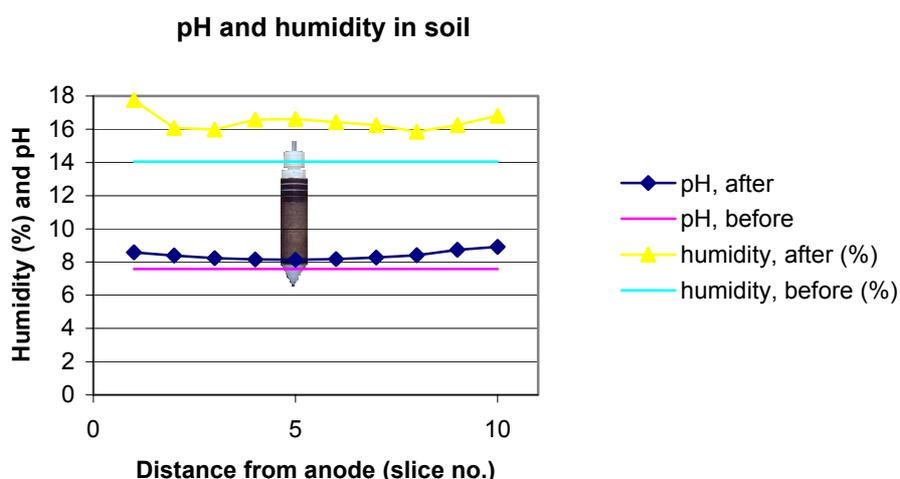


Figure 37: pH and humidity in the soil sliced before and after experiment 3

In Figure 38 the concentrations of copper and chromium in the soil before and after the experiment are seen. It can be seen that the copper concentration is much higher in this experiment than the first two and none of the slices are fully remediated. The distinct concentration profile with removal of copper near the electrodes and a peak in the middle of the soil is seen again. The concentrations in the peak area are much higher than the start concentration and this is due to the high recovery rate. The removal of chromium is not high and the concentration profile is not indicating how chromium is moving in the soil.

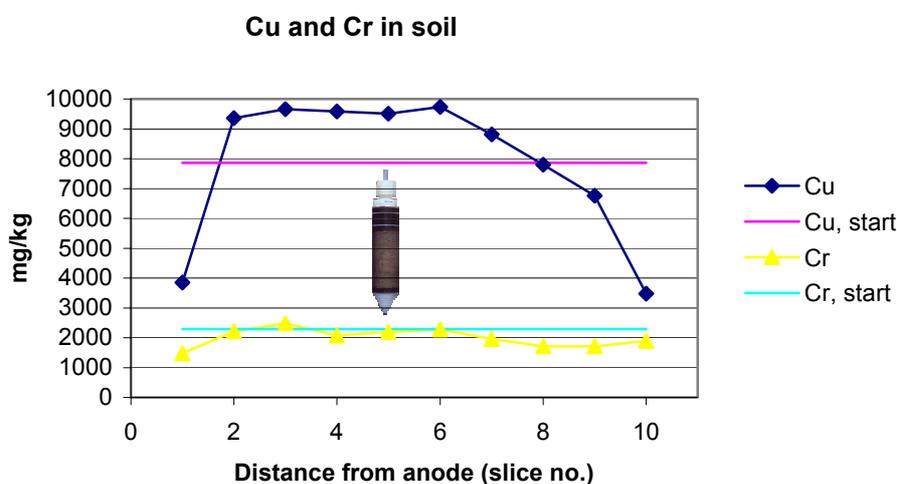


Figure 38: Copper and chromium concentrations in the soil slices before and after experiment 3

Soil solution

The concentrations of copper and chromium in the soil solution are seen in Figure 39. The concentrations for both the metals are increasing during the experiment, and by the end of the experiment, a stabilisation in the concentrations can be indicated. The copper concentration is much higher than in the other experiments, because of the high start concentration in the soil, and is much higher than the chromium concentration.

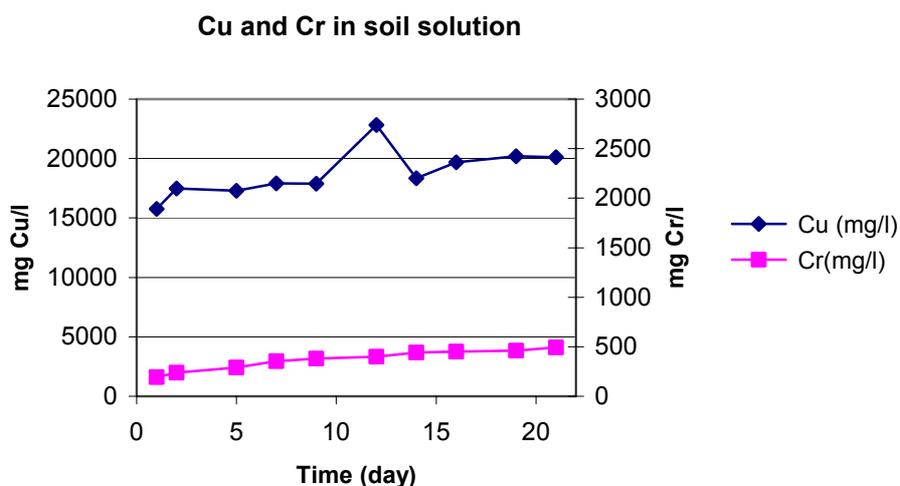


Figure 39: Copper and chromium concentrations in the soil solution in experiment 3

The pH and the electrical conductivity of the soil solution are seen in Figure 40, and they are more or less stable throughout the experiment. Even though the copper concentration in the soil solution is considerably higher than for the other experiments, the electrical conductivity is not equally higher, indicating that the heavy metal concentration in the soil solution is not determining for the size of the electrical conductivity.

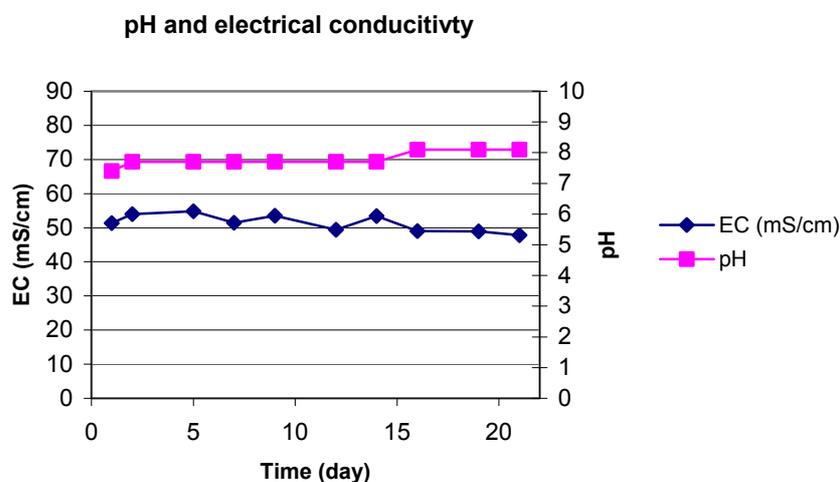


Figure 40: Electrical conductivity and pH in the soil solution in experiment 3

The sampling rate is seen in Figure 41 and about 2 ml of sample was sampled each time in this experiment. The sampling was easiest in the beginning of the experiment and the sampling rate is decreasing during the experiment. The sampling rates gives sampling times between 10 – 20 minutes for this experiment.

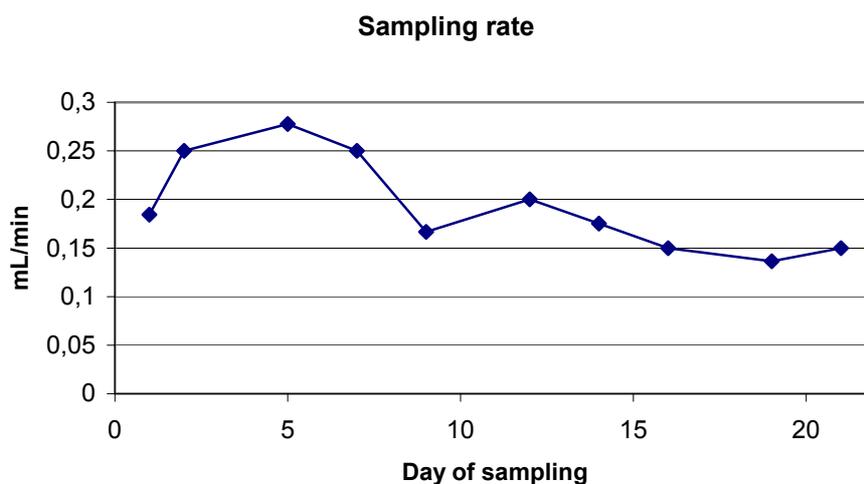


Figure 41: Sampling rate of soil solution samples collected from experiment 3

9.2.5 Experiment 4

The results for experiment 4 are presented in Appendix 11 IV. The recovery for copper and chromium is 107% and 101% respectively and the removal is 28 % for copper and 7 % for chromium as seen in Table 24. Thus, a higher current is clearly more effective for removing the heavy metals from the soil, compared to the first three experiments. Copper and chromium is mainly found removed in the anode side of the cell, although some copper is found precipitated on the cathode.

	Recovery	Removal	Removed to cathode side	Removed to anode side
Cu	107 %	28 %	20 %	80 %
Cr	101 %	7 %	5 %	95 %

Table 24: Mass balance and removal for copper and chromium in experiment 4

Electrolytes

The volumes of the electrolytes are seen in Figure 42. The increase in the catholyte is due to electroosmosis, as is the decrease in the anolyte. The decrease in the liquid compartment is mainly occurring by the end of the experiment, due to electroosmosis.

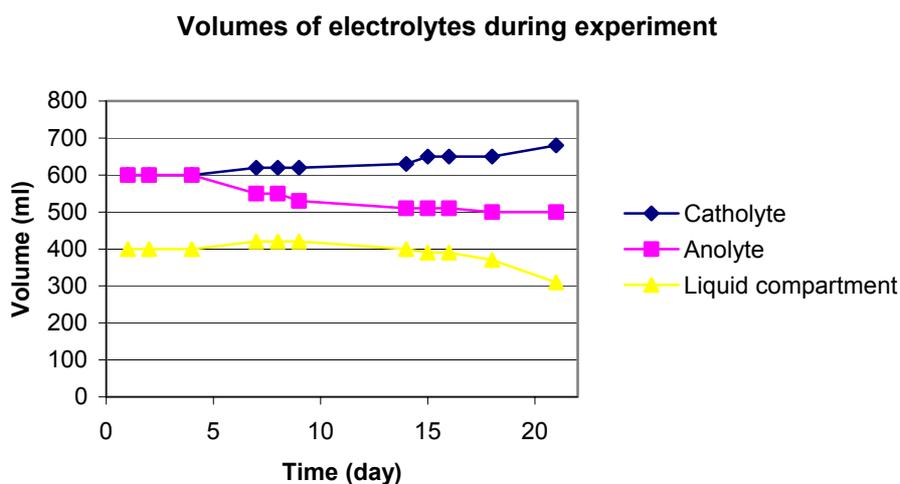


Figure 42: Volumes of the electrolytes during experiment 4

Soil

The pH and the humidity in the soil, before and after the experiment, are seen in Figure 43. The pH is stable in all the slices. The humidity is highest in the slices closest to the anode and is decreasing towards the cathode, but there are not any indications that this is caused by the soil solution sampling.

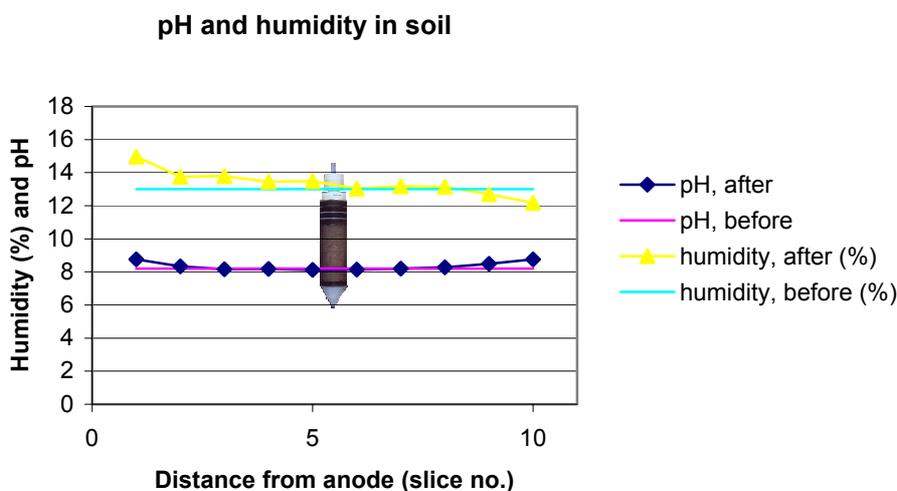


Figure 43: pH and humidity in the soil sliced before and after experiment 4

In Figure 44, the concentrations of copper and chromium, before and after the experiment, are shown. It is clearly seen that copper is being removed from the soil and the distinct peak has moved further towards the cathode side. Only in one slice is the copper concentration higher than the start concentration, indicating that copper is moving in the soil. Although there is a more clear removal of copper in this experiment, the concentrations are not low enough in any of the soil slices to be regarded as clean. The concentration profile of chromium indicates removal from the slices closest to the anode, and higher concentrations are seen in the slices closest to the cathode. The lowest concentration for chromium is still over 1000 mg/kg and the soil is not clean for either of the metals in any of the slices.

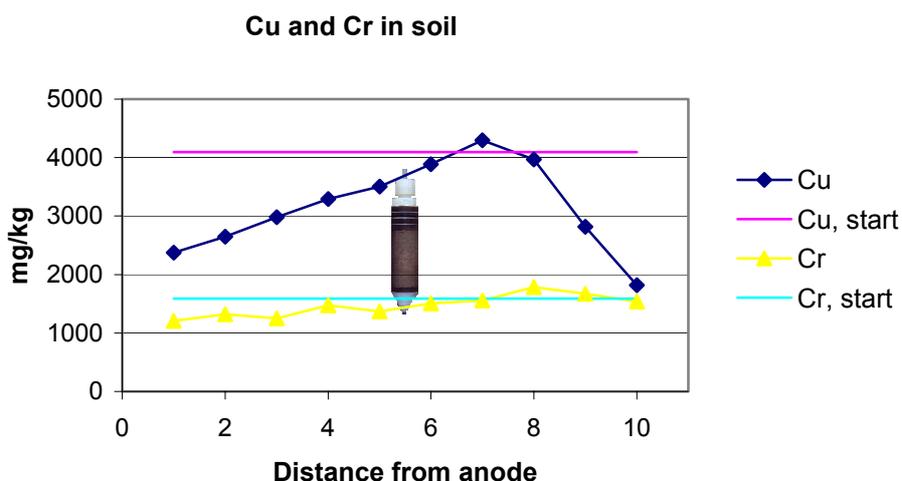


Figure 44: Copper and chromium concentrations in the soil slices before and after experiment 4

Soil solution

The concentrations for copper and chromium in the soil solution are shown in Figure 45. There is an increase in the concentrations for both of the metals until day 15, where there seems to be a decrease or at least a stabilisation of the concentrations.

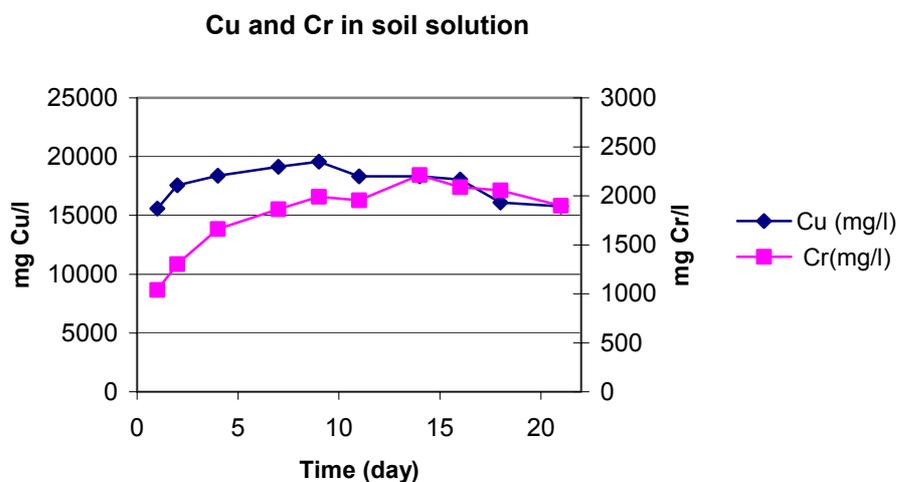


Figure 45: Copper and chromium concentrations in the soil solution in experiment 4

In Figure 46, the pH and the electrical conductivity of the soil solution is seen. The pH is again stable throughout the experiment. The electrical conductivity starts at a high level and is decreasing throughout the experiment, the decrease cannot mainly be due to removal of heavy metal ions, and since this concentration in the soil solution still is high.

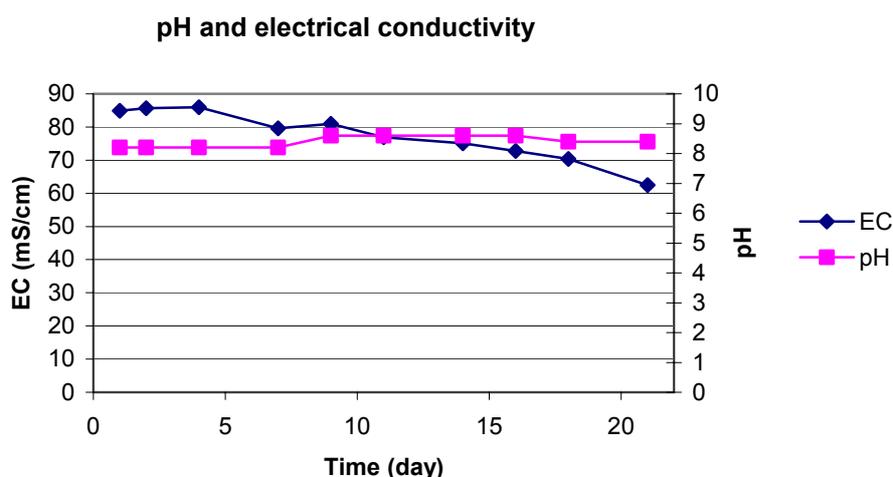


Figure 46: Electrical conductivity and pH in the soil solution in experiment 4

The sampling rate for the soil solution sampling is seen in Figure 47. The sampling rate is much more stable in this experiment than in the previous. About 2 ml sample was collected in this experiment on each sampling day, which gives sampling times between 10 – 20 minutes.

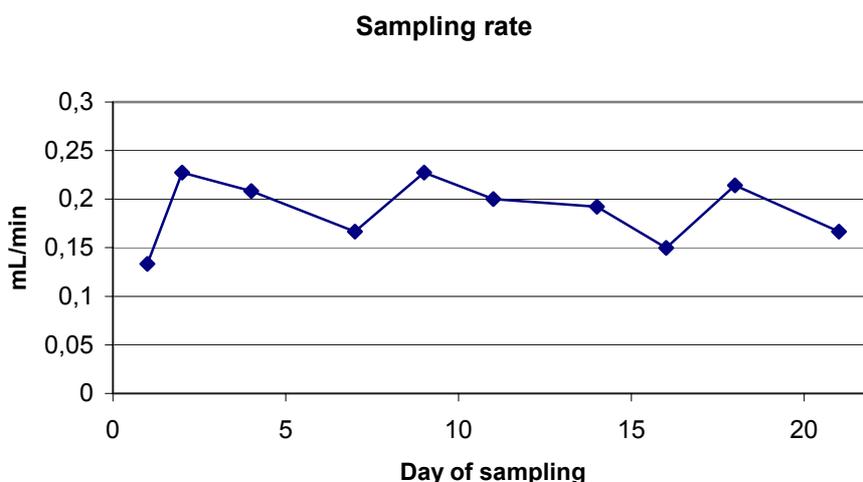


Figure 47: Sampling rate of soil solution samples collected from experiment 4

9.2.6 Experiment 5

The results for experiment 5 are presented in Appendix 11 V. The recovery for copper is 105 % and for chromium 103 % and the removal is 32% and 14 % respectively and the longer remediation time is clearly giving higher removals, especially for chromium, as seen in Table 25. All the removed chromium is found in the anode side of the cell and copper is found both in the anode and the cathode side.

	Recovery	Removal	Removed to cathode side	Removed to anode side
Cu	105 %	32 %	30 %	70 %
Cr	103 %	14 %	1 %	99 %

Table 25: Mass balance and removal for copper and chromium in experiment 5

Electrolytes

In Figure 48, the volumes of the electrolytes in experiment 5 are shown. The electrolytes were changed on day 21. The general trend is again a decrease in the anolyte and the liquid compartment, but the increase in the volume of the catholyte is greater in this experiment compared to the previous ones.

Volumes of electrolytes during experiment

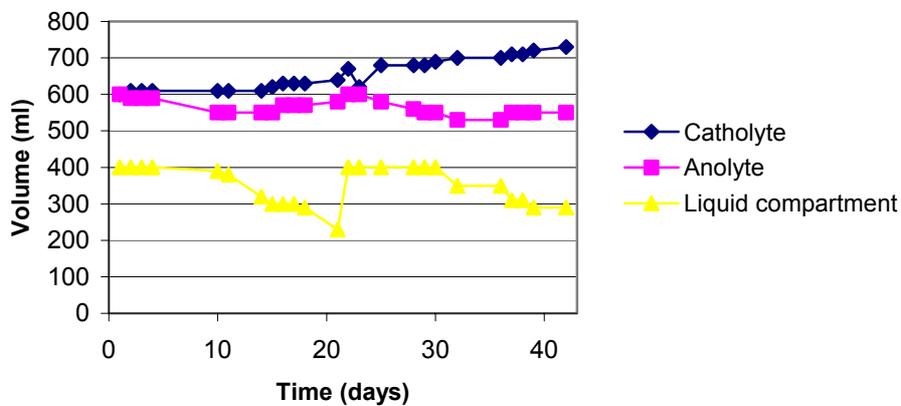


Figure 48: Volumes of the electrolytes during experiment 5

Soil

In Figure 49 the pH and the humidity in the soil before and after the remediation, are seen. The pH is stable in all the slices compared to the start level. The humidity has increased in the slices closest to the anode and is higher than the start level in all the slices except for the slice closest to the cathode, where the humidity is slightly lower.

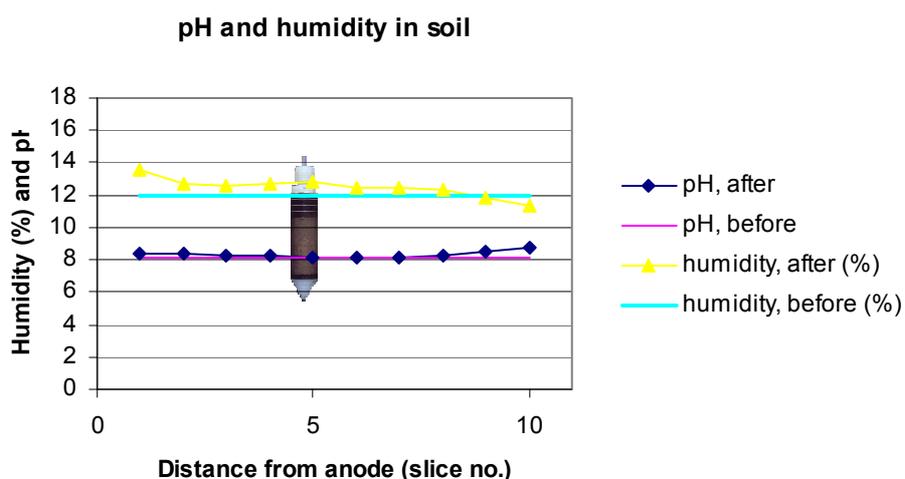


Figure 49: pH and humidity in the soil sliced before and after experiment 5

In Figure 50 the concentrations of copper and chromium in the soil before and after the experiment are seen. The copper profile shows removal from all slices in this experiment and there is still a peak but not as distinct as in the other experiments. The removal is greatest at the cathode side of the soil, even though copper is mainly found in the anode side of the cell. The soil is not fully remediated for copper in any of the slices. Removal of chromium is also seen, but not in all slices. The chromium profile indicates an accumulation of chromium in the slices closest to the cathode.

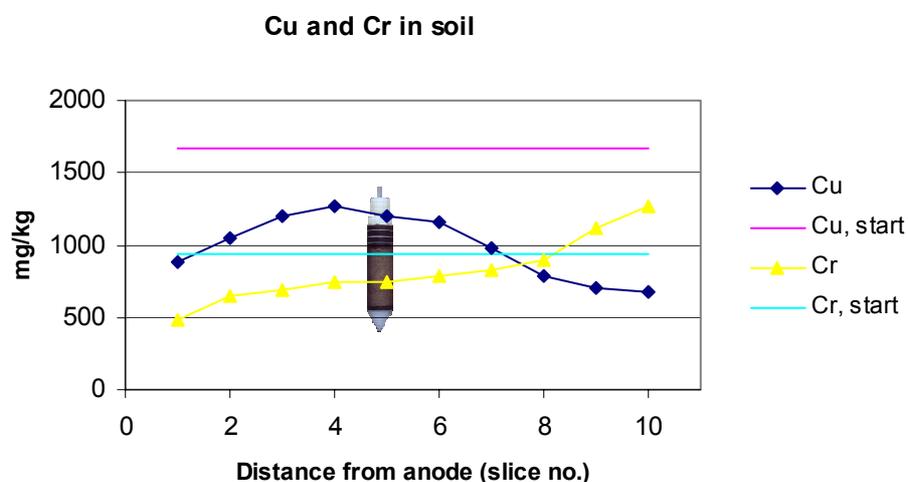


Figure 50: Copper and chromium concentrations in the soil slices before and after experiment 5

Soil solution

The concentrations for copper and chromium in the soil solution are seen in Figure 51. The copper concentration is increasing in the beginning of the experiment and then decreasing from day 15 and throughout the experiment. The concentration of chromium is also increasing in the beginning of the experiment and is more or less stable after 10 days of remediation. Again, the copper concentration is much higher than the chromium concentration.

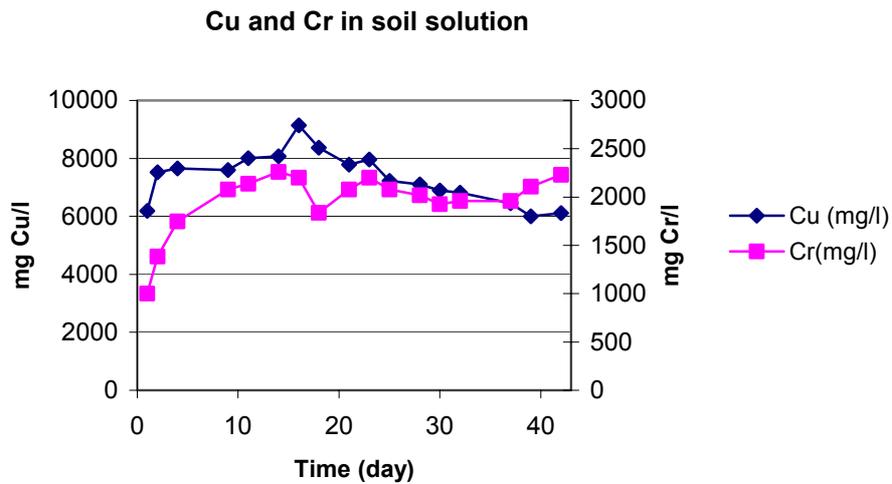


Figure 51: Copper and chromium concentrations in the soil solution in experiment 5

The electrical conductivity in the soil solution is shown in Figure 52. pH in the soil solution was not measured in this experiment. The electrical conductivity is high, although decreasing throughout the experiment, from about 90 mS/cm to less than 70 mS/cm.

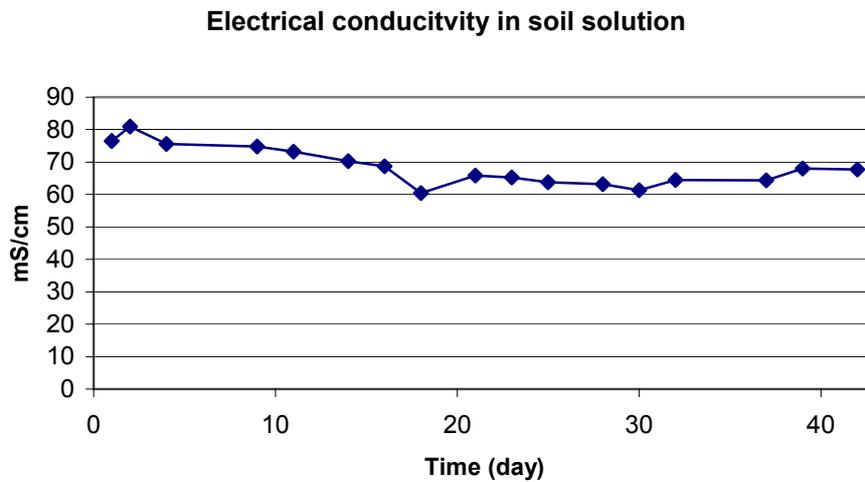


Figure 52: Electrical conductivity in the soil solution in experiment 5

The sampling rate for soil solution sampling is low in this experiment, as seen in Figure 53. Sampling of about 2 ml sample means sampling times between 20 – 50 minutes.

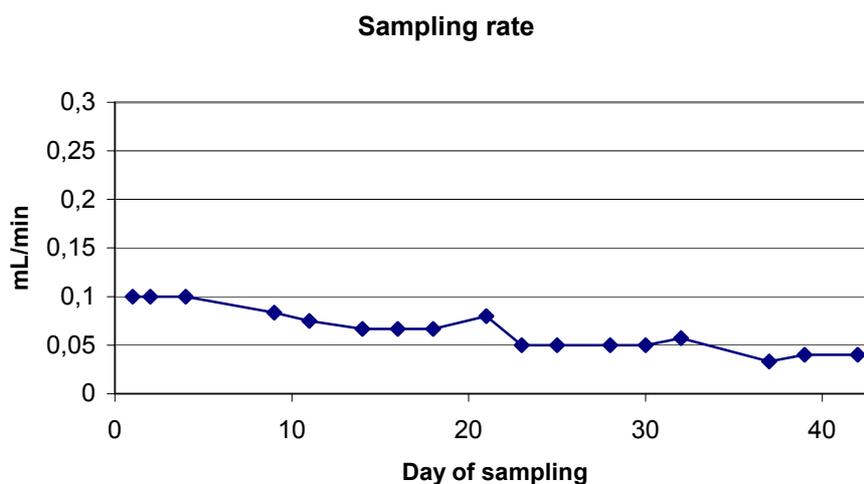


Figure 53: Sampling rate of soil solution samples collected from experiment 5

9.2.7 Experiment 6

The results from experiment 6 are presented in Appendix 11 VI. The recovery of copper is 115 % and for chromium 104 %, as seen in Table 26. 32 % of copper and 10 % of chromium are removed in the experiment. Chromium is only found in the anode side of the cell and copper is found in both the anode and the cathode side.

	Recovery	Removal	Removed to cathode side	Removed to anode side
Cu	115 %	32 %	40 %	60 %
Cr	104 %	10 %	0 %	100 %

Table 26: Mass balance and removal for copper and chromium in experiment 6

Electrolytes

The volumes of the electrolytes during the experiment are seen in Figure 54. The electrolytes were changed after 21 days. The anolyte volume remains constant during the whole experiment. The volume of the liquid compartment is decreasing during the experiment and some of the electrolyte can be found in the catholyte, where the volume has increased. The liquid compartment is almost emptied before the change of electrolytes and before the end of the experiment.

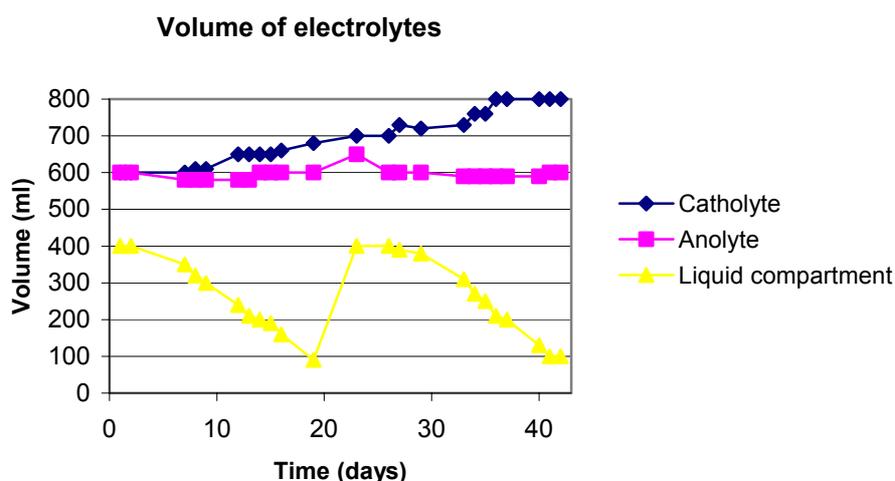


Figure 54: Volumes of the electrolytes during experiment 6

Soil

The pH and the humidity are seen in Figure 55. The pH is stable throughout the soil. The humidity is slightly higher in the slice closest to the anode and for the rest of the slices there are no considerable variations. The humidity is slightly lower in the slices where the soil solution sampler is found, but there are no indications that the sampling is drying the soil in any of the slices.

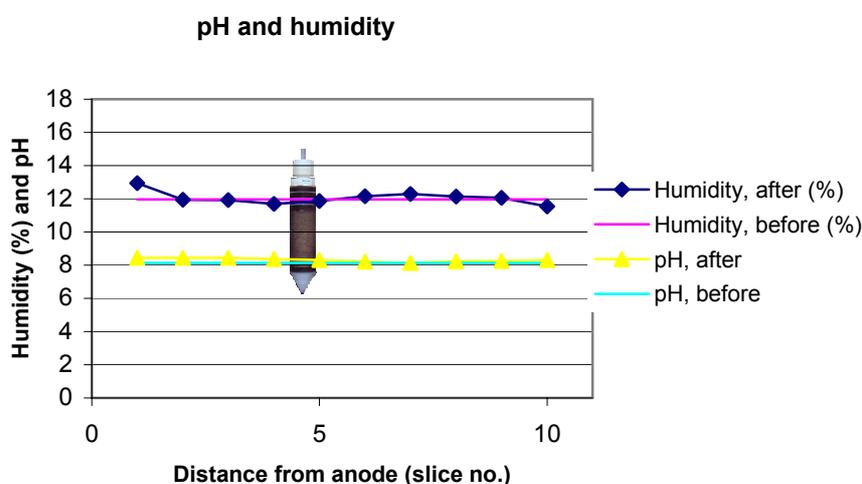


Figure 55: pH and humidity in the soil sliced before and after experiment 6

The copper and chromium concentrations in the soil before and after the experiment are seen in Figure 56. Copper is clearly removed from all the slices, although none are fully remediated. A distinct peak in the concentration is not seen in this experiment, although the concentration is higher in the slices closest to the soil solution sampler. Chromium is removed from the slices closest to the anode, but as for experiment 5 the high concentration of chromium in the slices closest to the cathode indicates accumulation, especially since chromium is not found in the cathode. The concentrations of chromium are not low enough in any of the soil slices to be regarded as clean.

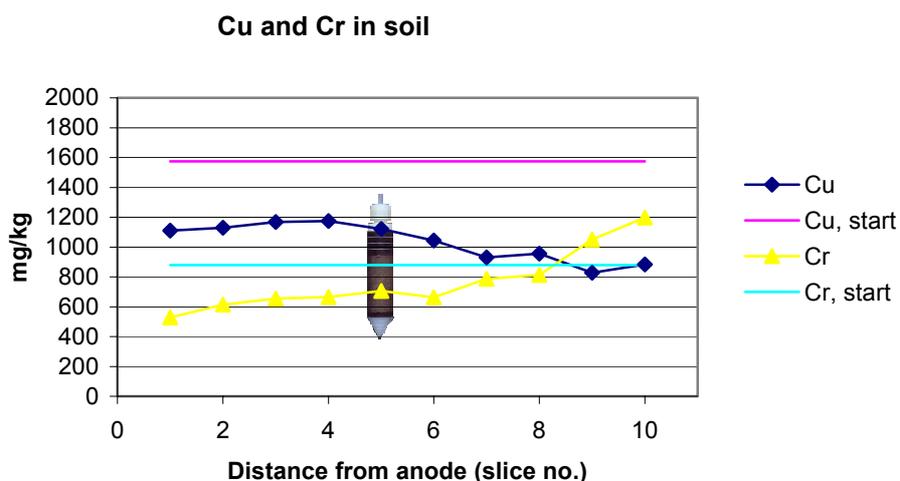


Figure 56: Copper and chromium concentrations in the soil slices before and after experiment 6

Soil solution

The copper and chromium concentrations in the soil solution are seen in Figure 57. The copper concentration is varying between 5500 – 7500 mg/l in the beginning of the experiment and the decrease seems first to be permanent in the last week of the experiment. The chromium concentration is increasing in the beginning of the experiment and reaches a stable level throughout the experiment, if the chromium concentration for day 23 is regarded as an exception.

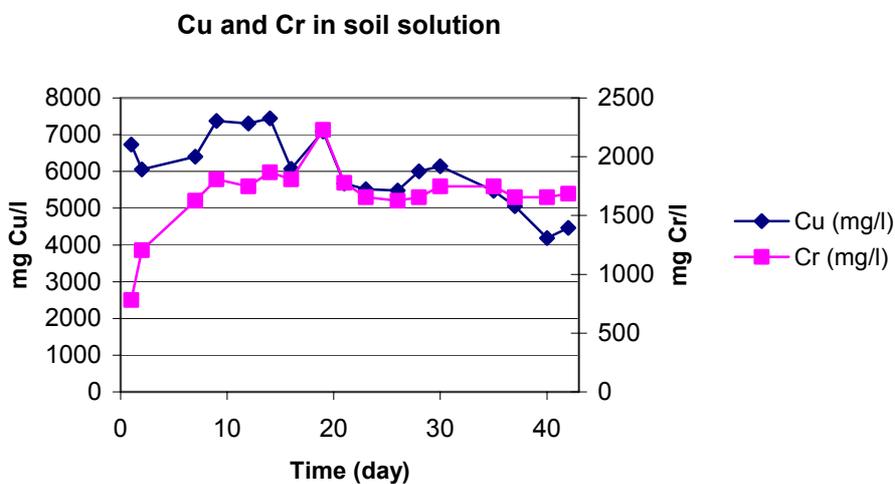


Figure 57: Copper and chromium concentrations in the soil solution in experiment 6

The electrical conductivity for the soil solution is seen in Figure 58, pH is not measured for this experiment. The electrical conductivity is around 90 mS/cm in the beginning of the experiment, decreases throughout the experiment to less than 60 mS/cm. The decrease in the copper concentration in the soil solution, as seen in Figure 57, could be one of the reasons why the electrical conductivity is also decreasing.

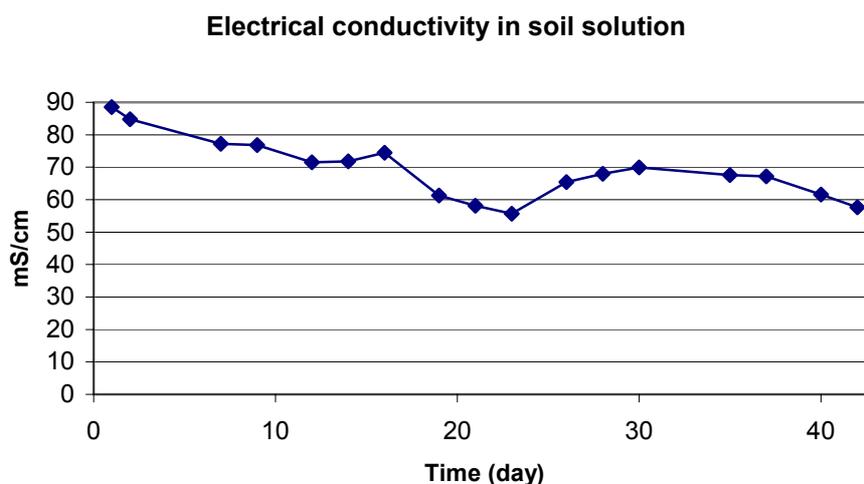


Figure 58: Electrical conductivity in the soil solution in experiment 6

The sampling rate for the soil solution sampling is seen in Figure 59. The sampling rate is decreasing throughout the experiment and about 2 ml of sample was extracted in this experiment, meaning sampling times between 15 – 45 minutes.

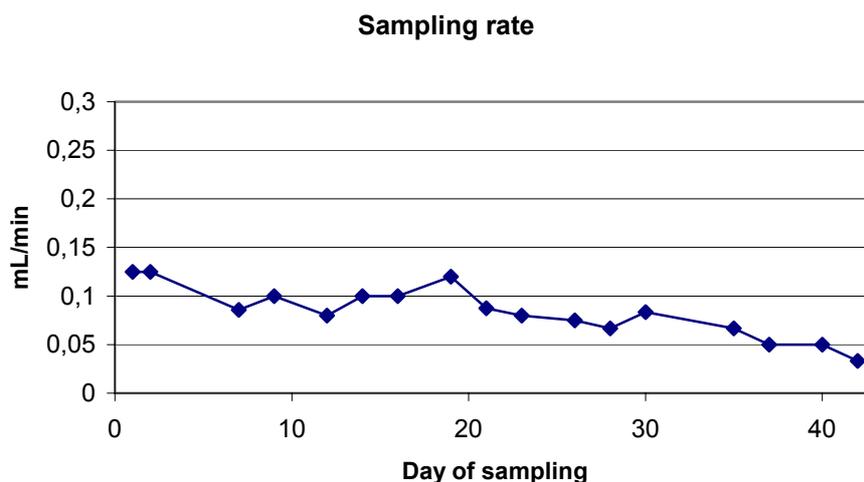


Figure 59: Sampling rate of soil solution samples collected from experiment 6

9.3 Electrodialytic experiments with liquid

The results from the electrodialytic experiments where $\text{Cu}(\text{NO}_3)_2$ and ammonium citrate were dissolved in water can be seen in Appendix 12. The results show that copper in ammonium citrate will migrate solely to the anode (between 96 – 100%) as negatively charged species. This indicates that when copper is dissolved in ammonium citrate as liquid it does not form the same complexes as when ammonium citrate is mixed in copper polluted soil.

9.4 Electrodialytic soil experiment to test the sampling radius of the sampler

9.4.1 Electrodialytic experiment with green fruit syrup

Soil solution samples were taken occasionally from the experiment and in the beginning the sampled soil solution was blank. After about one week the volume of the green fruit syrup started to decrease, and the green fruit syrup was entering the soil. When the soil solution samples were sampled after this, they were green and had the very distinct smell of the green fruit syrup. When the experiment was dissembled the green fruit syrup was found in the entire soil, indicating that it had been transported through the whole soil volume. This experiment indicates that the soil solution samples are sampled from an area in the soil, and is not being sampled from the liquid compartment, because the green fruit syrup is only detected in the samples after it started entering the soil.

9.4.2 Voltage measurements in experiment 4

The voltage over the slices in experiment 4 is shown in Figure 60 and the results are presented in Appendix 11 IV. Voltage measurements were taken immediately before and after soil solution sampling, to investigate if the sampling and the sampler resulted in disturbances in the experiment. Figure 60 a), b) and c) show the total voltage between the working electrodes, the voltage over the anionexchange membrane and passive membrane and finally over cationexchange membrane. The voltage over the membranes make up for the most of the voltage between the working electrodes, leaving 1.5 V to be distributed over the soil. How the soil is divided in slices is seen in Figure 18. In Figure 60 d), e), f), g) and h) the voltage over the slices are shown as voltage per centimetre, because the slices were not of the same size. There does not seem to be any irregularities in slice 2, 4 and 6, but there are some small differences in the voltage for the slices around the cell. This is most likely due to variable contact between the reference electrode and the soil than actual differences. The soil solution sampler is placed in slice 4 and both the sampling and the sampler do not seem to give disturbances in the voltage. There are some disturbances in slice 5, see Figure 60 g). This is probably due to the sampling, either sample is drawn from this area or more likely, the area is affected by the suction exerted by the sampler, which is oppositely directed from the electroosmosis and the electric field on this side of the sampler, see Figure 61.

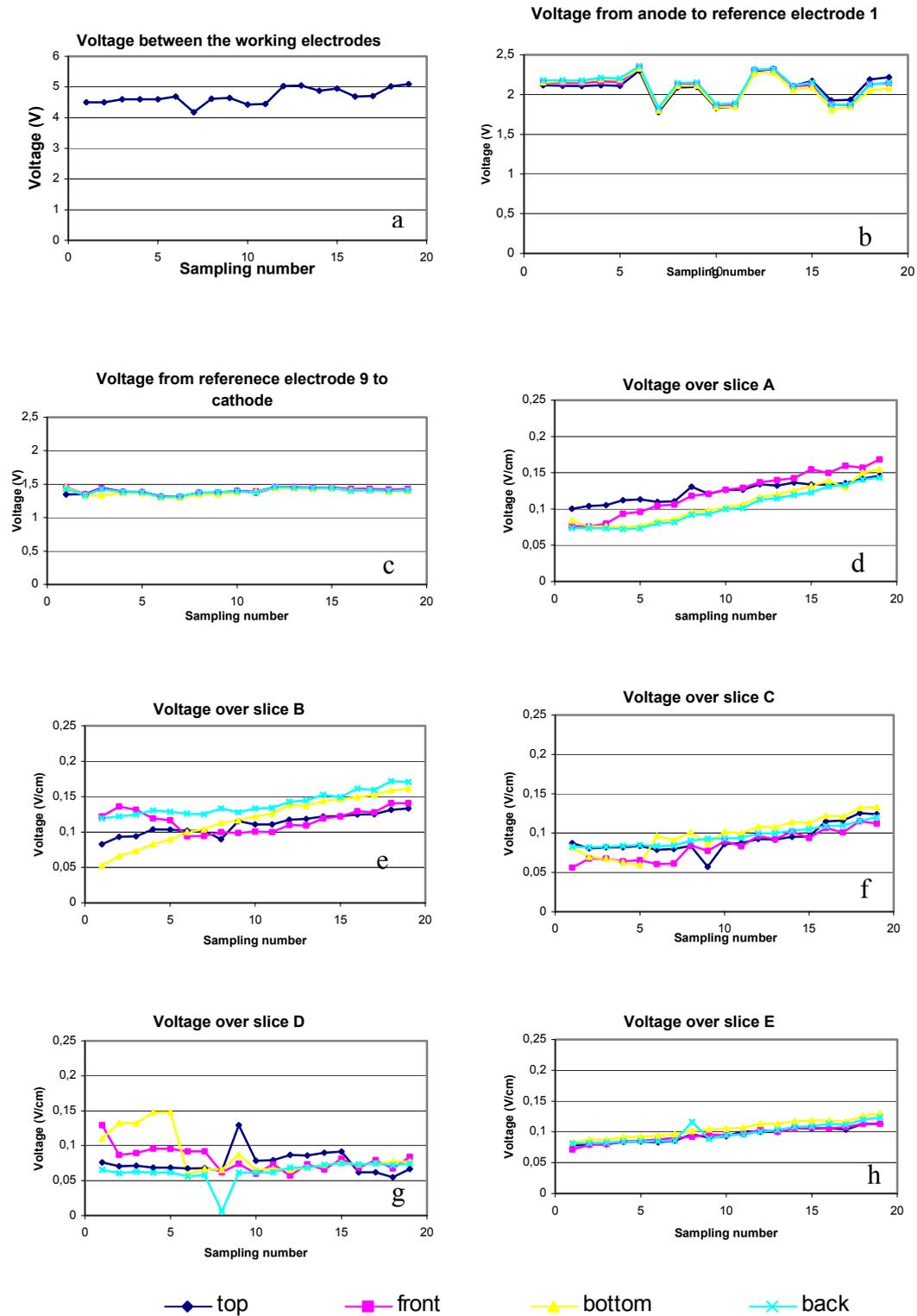


Figure 60: Voltage over the different slices in experiment 4, the soil solution sampler is placed in slice C.

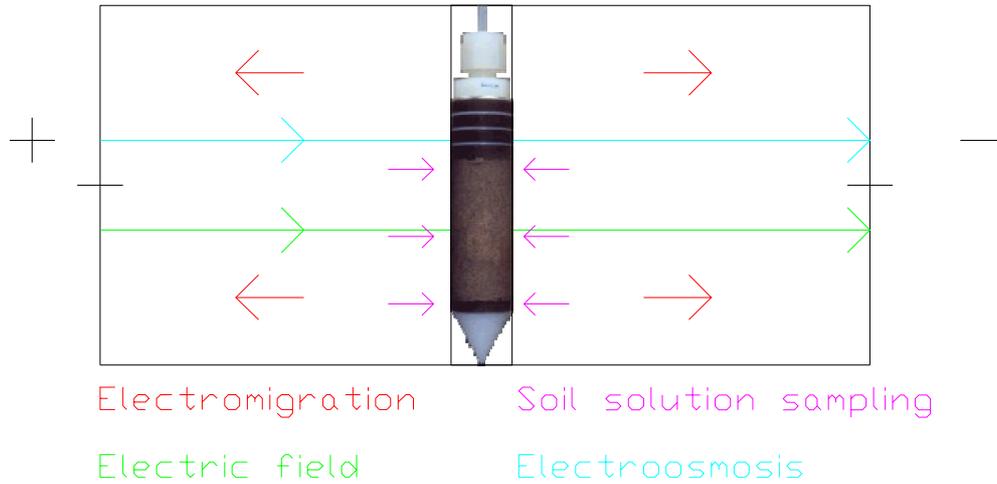


Figure 61: The samplings effect on the soil

Since there are not any disturbances in slice 6, this could mean that the sampling does not influence this part of the soil. This can also explain the smaller disturbances in slice 3 than in slice 5. If slice 3 is affected by the sampling, obviously, the disturbance should be smaller, because the forces from the electroosmosis and the electric field are mainly working in the same direction as the sampling. There does not seem to be disturbances in the slice 2 and 6, which implies that the sampling does not affect these slices. Slice 3 to 5 are in the range of 4.5 cm from the anode to 10.5 cm from the anode and is probably the area that is influenced by the sampling. The soil solution sample is collected from this area, 3cm on each side of the sampler, but most likely in a narrower area.

Discussion



In this chapter, the results from all the performed experiments are discussed. Since the soil is not fully remediated in any of the experiments, predicted soil and soil solution profiles from the beginning of the experiment until the soil is fully remediated, are made to evaluate how successful the experiments have been and how the set-up of the electrodynamic experiments can be optimised.

10 Discussion

10.1 Soil solution sampling

Soil solution samples have been collected three times a week during the six electroalytic experiments and the sampling has been without great difficulties. It was possible to collect soil solution samples from the electroalytic experiments, by keeping the humidity in the soil during the experiments. This was done by inserting an extra compartment, which was separated from the soil with a passive membrane, to allow continuous addition of ammonium citrate to the soil. Generally, it was hardest to collect the first sample from the experiments, meaning that it took 5 – 15 minutes before sample could be seen in the tube from the soil solution sampler. For the following sampling, the sample could be seen in the tube after 30 seconds – 1 minute. Sampling times in the different experiments were between 10 – 120 minutes, see Table 27.

Experiment	Sampling time (min)	Number of ml sampled
1	90 – 120	5
2	35 – 75	5
3	10 – 20	2
4	10 – 20	2
5	20 – 50	2
6	15 – 45	2

Table 27: Sampling times and volume of samples extracted from the electroalytic experiments.

The sampling time is dependent on the volume of the extracted soil solution sample. The smaller volumes requires a shorter the sampling time. Generally, it was easy to sample 2 – 3 ml of soil solution and the sampling went rather quickly, 10 – 30 minutes. However, if more than 2 - 3 ml sample was required, the sampling was harder and the sampling times longer, as seen for experiment 1 and 2. This could indicate that the sample was collected from the area closest to the sampler until there was not more sample to collect from this area, and thereafter, the sample had to be withdrawn further away from the sampler.

The differences in the sampling times between the different experiments, are probably due to how the contact between the sampler and the soil was in each experiment. Due to the manual packing of the soil, the contact between the soil and the sampler could be reduced. The sampling times increased during the experiment for some of the experiments. This is most probably due to clogging of the pores in the cup.

10.1.1 Humidity

It was seen for all the experiments, that the humidity in the soil did not decrease during the experiments. The humidity in the slice, where the soil solution sampler was placed, did not vary much from the other slices. This is due to transport of electrolyte from the liquid compartment into the soil towards the cathode, which means that the liquid compartment was working as intended, to keep the soil saturated, so that soil solution sampling could be possible during the experiment.

10.1.2 The sampling radius

If bubbles in the liquid compartment would be observed during soil solution sampling, it would indicate that the sampling radius could be as extensive as to the electrolyte. This did not happen during the sampling. The experiment with the green fruit syrup to test if the sample is collected from the liquid compartment also showed that this is not happening.

Experiment 4, where the voltage was measured from the working electrodes to reference electrodes (see chapter 9.4.2 Voltage measurements in experiment 4), showed that the area that was influenced by the sampling was about 3 cm on each side of the sampler. If the sampling radius is estimated from equation 2 by Hart and Lowery (1997), a sampling radius of under 1 cm would be found, see Appendix 13. The sampling area can also be estimated on the basis of the humidity in the soil. If it is assumed that the soil from where the sample is extracted from will be drained, the sampling area is also under 1 cm for different humidity in the soil and extracted volumes, see Appendix 13. This is a very rough estimation because the soil will probably not be drained in the area where the sample is extracted. For instance, the estimated sampling area will correspond to less than 2 cm of the soil in the cell, if only 1/5 of the liquid in the soil can be extracted. Comparison with the results found by Morrison and Lowery (1990), where the sampling radius was found in the order of centimetres for continuous sampling in a defined area, there is reason to believe that this will also happen in the electrodialytic experiments. Thus, the sample is collected in the area of a couple of centimetres around the sampler.

10.1.3 Evaluation of the samplings influence on the remediation

Placing a foreign object, such as the soil solution sampler, in the soil during the electrodialytic remediation must, to some extent, influence the electric field and the remediation. The sampler can also perform forces in the soil, which indicates even more that the remediation can be disturbed, although the sampling time is limited compared to the remediation period. To collect a soil solution sample, the forces from the applied vacuum working on the sampler must exceed the forces in the soil, such as soil tension and the electric field. When sampling, imagine that all the soil solution is being sucked inwards to the sampler. The remediation can be retarded because of this continuous withdrawal of sample, at least if the charged ions are being pulled back from the direction they are heading. On the other hand, it could also mean speeding up the migration for the ions moving in the same direction as the soil solution is sampled. Thus, short sampling times and small extracted volume of soil solution will limit the disturbances. The high electrical conductivity in the soil solution means that the resistance in the soil is low and that the current passes freely through the soil, which is reflected in the low voltages for the experiments, see Table 15. The voltage over the sampler is in the same order as for the other slices of the soil, see Figure 60, which indicates that the sampler does not disturb the current and thus, the disturbance in the remediation is limited. Another reason to believe that the sampler does not disturb the remediation considerably is, that there are not any sudden or different changes in pH, humidity or the copper and chromium concentrations in the soil, where the soil solution sampler is placed, as seen in the figures in chapter 9.2 Electrodialytic soil remediation experiments.

10.2 Soil and soil solution

10.2.1 Mass balances

The mass balance for copper is generally good in the experiments (96 – 107 %), except for experiment 3 (120 %) and 6 (115%). In experiment 3, small green lumps in the soil were observed before and after the experiment, meaning that large variations in the copper concentration could be expected. For experiment 6 there are no obvious reasons for the high recovery and the start concentrations were measured twice. The mass balance for chromium is very good for experiments 3, 4, 5 and 6 (91 – 104 %), but is low in experiment 1 (88%) and high in experiment 2 (114 %) and no apparent reason can be found for this.

The removal was calculated based on the amount of copper or chromium that was found after the experiment, which means that the recovery is not influencing the removal percentages. The percentage of the removal of copper was in the following order for the experiments:

Exp. 5 = exp. 6 > exp. 4 > exp. 1 > exp. 3 > exp. 2

and for chromium:

Exp. 5 > exp. 6 > exp. 4 > exp. 1 > exp. 2 = exp. 3

Obviously, the longer remediation time and higher current density gave higher removal for both the metals.

10.2.2 Speciation of the metals

In Table 28, the percentages of the removed metal found in the two sides of the cell are seen. The removal is mainly happening to the anode side of the cell for both copper and chromium, although copper is also removed to the cathode side, as precipitation on the cathode. This indicates that copper is forming both positively and negatively charged complexes. Chromium is mainly removed as negatively charged complexes. Chromium should form positively charged complexes with ammonia, but this does not seem to happen, because hardly any chromium is found in the cathode side of the cell.

Experiment	Cathode side		Anode side	
	Cu (%)	Cr (%)	Cu (%)	Cr (%)
1	20	5	80	95
2	45	10	55	90
3	10	2	90	98
4	20	5	80	95
5	30	1	70	99
6	40	0	60	100

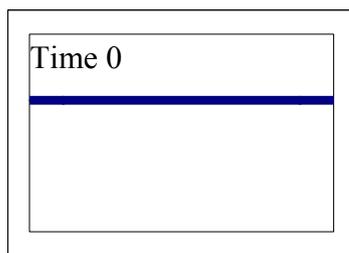
Table 28: The removal of copper and chromium in percentage that is removed to the anode and cathode respectively

10.2.3 Predicted soil and soil solution profiles

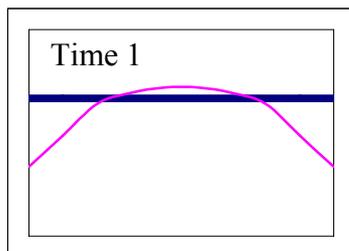
Soil and soil solution profiles for copper and chromium are made based on the empirical material from the results in this thesis and the experiments presented in Appendix 2. The profiles are made from the beginning of the experiment until the soil is remediated, i.e. the residual heavy metal in the soil cannot be mobilised. The profiles are made to predict the behaviour of copper and chromium in the soil and the soil solution when ammonium citrate is used as desorbing agent. Some assumptions are made:

- When the heavy metal forms a complex with either ammonia or citrate, the heavy metal will stay in this complex throughout the experiment
- Copper and chromium from both positively and negatively charged complexes
- The migration velocity of the positive and negative charged complexes is equal
- The soil solution samples are collected from the middle of the soil
- The start concentrations of copper and chromium in the soil are equal
- The experimental set-up is the same as used in the experiments conducted in this thesis
- 1 M ammonium citrate is used as desorbing agent

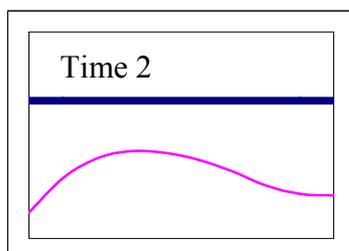
Copper in soil



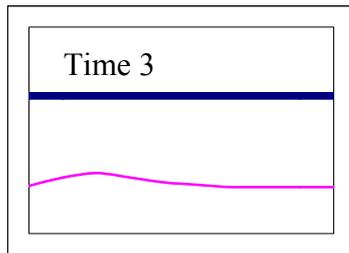
Start of experiment.



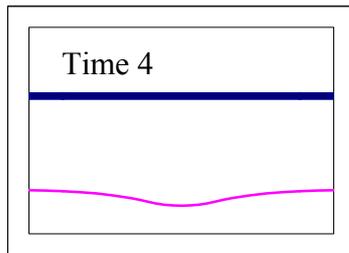
The removal of copper starts. In the soil slices closest to the electrodes the concentration will be low, due to removal of ions over the ionexchange membranes and migration into the soil, dependent on the ions charge. Since the ions are migrating into the soil, a peak area will be seen, where the concentration is higher than the start concentration of copper.



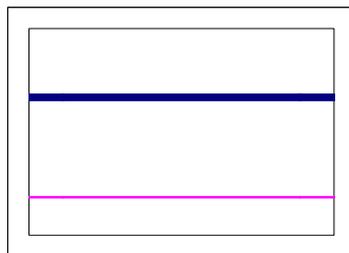
More copper is removed from the soil and the peak is smoother. The concentrations in the soil are lower or equal, than the start concentration, over the whole soil profile.



Even more copper is removed and the peak is less distinct. The concentrations are lower than the start concentrations over the whole soil profile.

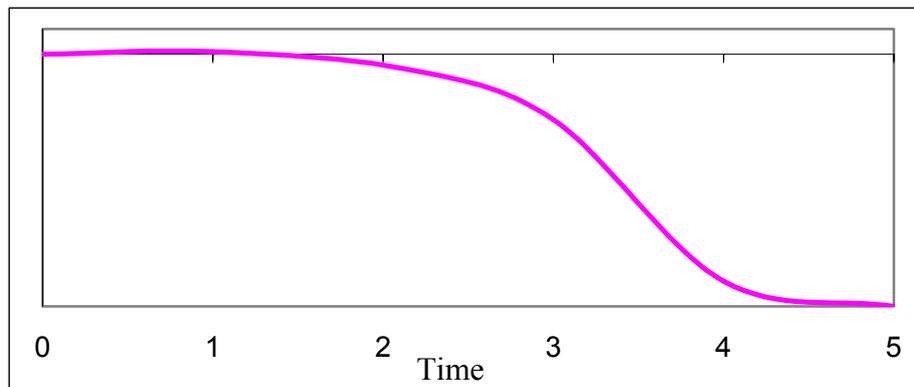


The first slice to be remediated will be in the middle of the soil, since all the available copper has been removed. Thereafter the slices towards the electrodes will be remediated, finishing with the slices closest to the membranes.



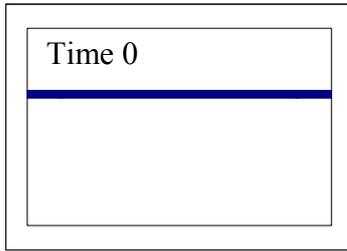
The soil is fully remediated

Copper in soil solution

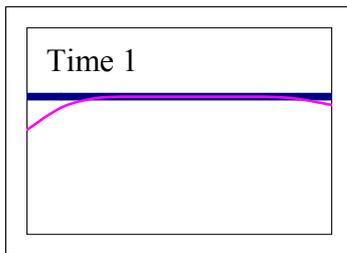


The copper concentration in the soil solution will be more or less constant during the experiment and will first decrease at the end of the experiment. The copper concentration will be in equilibrium when the experiment starts (time 0), because the equilibrium between soil and soil solution is fast. During the experiment the copper concentration in the soil solution is high because ions are being transported through the middle area of the soil and copper is released continuously to the soil solution (time 1 and 2). The concentration is not decreasing until the concentration in the soil is decreasing (time 3) and the fraction of available copper in the soil is getting smaller. From this point (time 3), the concentration in the soil solution will drop suddenly and stabilise on a low level.

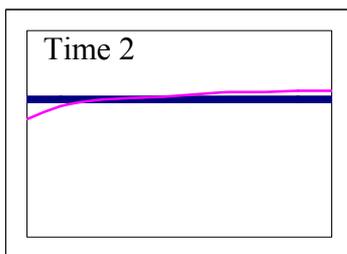
Chromium in soil



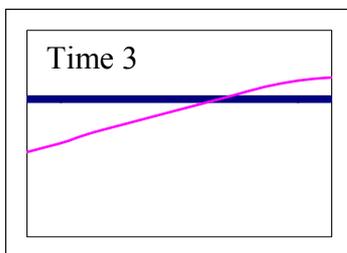
The remediation of chromium will be slower than for copper, since chromium is stronger bound to the soil.



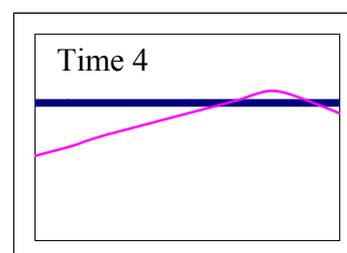
The removal of chromium is limited and there is no distinct concentration profile in the soil.



The removal of chromium is seen, still limited, towards the anode and a small accumulation close to the cationexchange membrane is observed

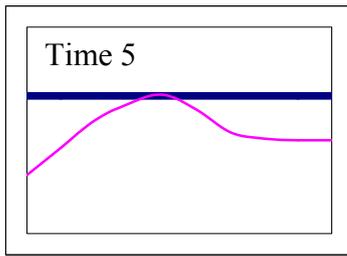


An even greater accumulation is observed close to the cathode and the removal of chromium is happening continuously towards the anode.

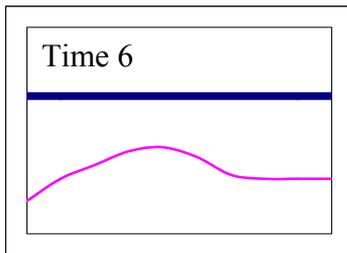


The accumulation of positively charged chromium complexes near the cathode means that they cannot pass the cationexchange membrane. One of the assumptions for the behaviour of copper and chromium in the soil was that they would not change complexes, and thus, charge. However, this is the only explanation to the removal of the accumulated chromium. In the soil there is a slow equilibrium between the different complexes and this equilibrium is much slower than the migration

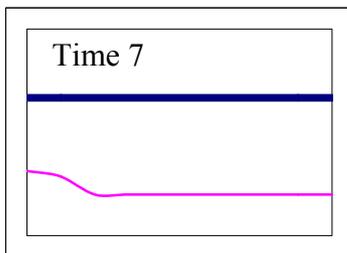
velocity. Thus, chromium will slowly change charge and be transported towards the anode. The concentration in the soil at the cathode side will then decrease. This can be assumed, because it is observed in the experiments presented in Appendix 2.



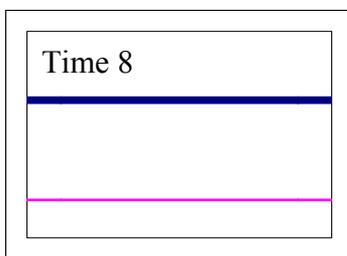
There will be an area in the soil, where the chromium concentration is higher and this area will move from the cathode to the anode.



Thus, the slice closest to the cationexchange membrane is first remediated.

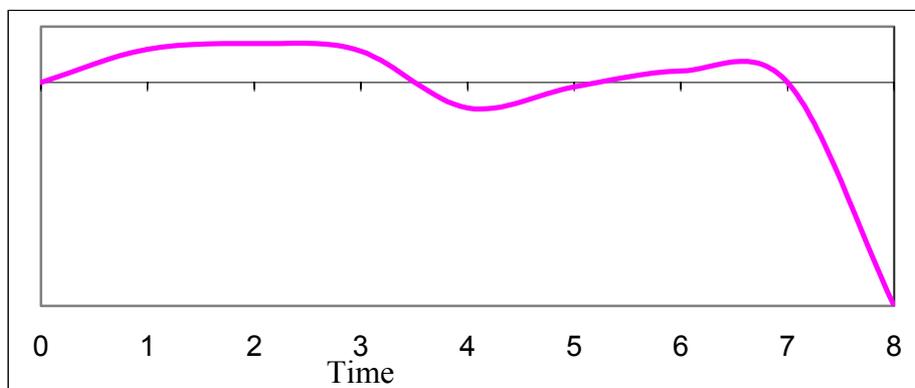


The middle of the soil is remediated



The soil is fully remediated

Chromium in soil solution



The development of the chromium soil solution profile is different than for copper. The concentration during the beginning of the experiment (time 1 and 2) is higher than the start concentration, because chromium is not as available as copper. The equilibrium between the soil and the soil solution is slow for chromium and not reached when the experiment starts. At time 3, a decrease in the concentration is seen due to the accumulation of cations in the slices at the cationexchange membrane and the removal of anions toward the anode, but the concentration is still high due to the continuous release of chromium to the soil solution. The concentration will rise again when the accumulated chromium will change charge and start migrating towards the anode. When all this chromium has passed the point in the middle of the soil, a sudden drop in the concentration will be observed and the concentration will reach a stable, low level.

The remediation for copper is faster than for chromium, much due to the observation that the negatively charged copper complexes cannot pass the cationexchange membrane. Even though the cationexchange membrane was changed for a passive membrane, the remediation for chromium would be slower. The concentration of copper is often twice or even three times the concentration of chromium in soils from polluted wood impregnation sites, which could imply that the soil could be remediated simultaneously for the two heavy metals. If soil solution extraction is used to assess when the soil is clean it is important to let the remediation continue even though the concentration in the soil solution suddenly is lower, because this only means that parts of the soil is fully remediated.

10.2.4 Comparison of actual soil and soil solution profiles

As described in chapter 8.2 Electrodealytic soil remediation experiments, experiments 1 – 3 are made to determine which concentration of ammonium citrate would be the most efficient for desorbing the heavy metals from the soil and thus, give a high concentration of the heavy metals in the soil solution. Secondly, experiments 4 – 6 are made to investigate how different current densities and a longer clean-up period will effect the remediation and the concentration of the heavy metals in the soil solution. The conditions for all the electrodealytic experiments are seen in Table 15 and Table 16.

The soil concentrations for the experiments lasting 21 days (experiment 1, 2, 3 and 4) are presented in the same figure. This is done to:

1. Compare how the different concentrations of ammonium citrate (experiment 1, 2, and 3) is affecting the remediation
2. Compare how a higher current density (experiment 4 compared to experiment 1) is affecting the remediation

The soil concentrations for the experiments lasting 42 days (experiment 5 and 6) are presented in a separate figure, together with the results from experiment 4. Experiment 4 only lasts 21 days, but have the same current density as experiment 5. These three experiments are compared to see:

1. How longer remediation times influences the soil concentrations
2. How a higher current density in experiment 6 compared to experiment 5, will affect the remediation.

The concentrations of copper and chromium in the soil solution are presented in two different figures, one for each heavy metal. The concentrations from all the experiments are presented in the same figure.

Copper

The normalised copper concentration profiles for experiments 1, 2, 3 and 4, lasting 21 days, are shown in Figure 62. The experiments have a characteristic profile with a peak in the middle of the soil and lower concentrations in the slices closest to the electrodes. The highest removal is seen in experiment 4, which has a higher current density than experiment 1. Since copper is forming complexes with both ammonia and citric acid, there are both negatively and positively charged complexes migrating through the soil. Thus, the peak is the area in the soil, where there the positively and negatively charged complexes meet in the migration through the soil. This is one of the reasons why there seems to be a bigger removal from the slices nearest to the electrodes than actually takes place. Another reason is the collection of soil solution samples, which is especially seen in experiment 2, where there seems to be a higher removal, but actually, the same amount of copper removed by electromigration is removed in soil solution samples. In experiment 4, over twice as much copper is removed as in experiment 1. Comparison of the profiles for these two experiments indicates that the peak is situated further towards the cathode when the removal increases. The higher concentration in slice 1 in experiment 4 also indicates that the migration of positively charged species has reach this part of the soil and that the migration velocity cannot be equal for the complexes of opposite charge. If this were true, the concentration would be lower in this slice than for the other experiments.

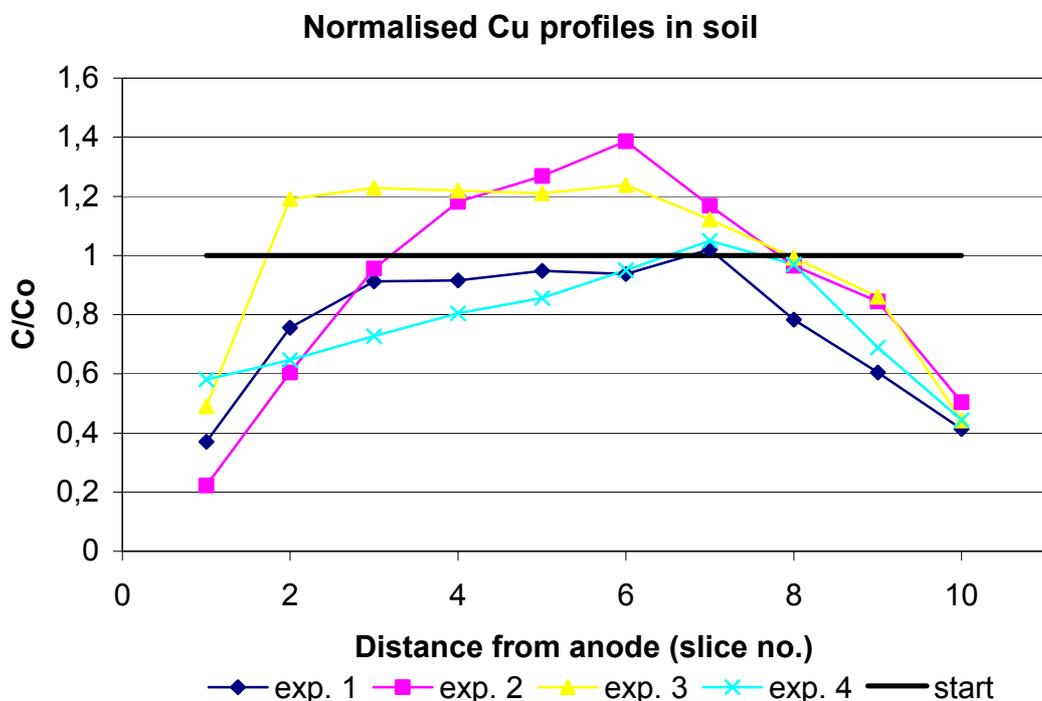


Figure 62: Normalised copper concentration profiles in the soil for experiment 1 (1M ammonium citrate and current density 0.2 mA/cm²), 2 (0.25 M and 0,2 mA/cm²), 3 (0.5 M and 0,2 mA/cm²) and 4 (1M and 1 mA/cm²)

Figure 63 shows the normalised copper concentration profiles in the soil for experiment 4, 5 and 6. The profiles in experiments 5 and 6 have a more smooth shape than the profile in experiment 4. The shape indicates that the peak has moved towards the anode and the peak is less distinct. The longer remediation time in experiment 5 compared to experiment 4 clearly increases the removal of copper. The higher current density in experiment 6 than in experiment 5, does not seem to improve the remediation, because the removal of copper is the same in these two experiments, see Table 28. From the figure it seems that the remediation in experiment 5 is better and that the higher current density in experiment 6 does not accelerate the remediation further. The recovery for experiment 6 was high, which means that the normalised concentrations are high.

Normalised Cu profiles in the soil

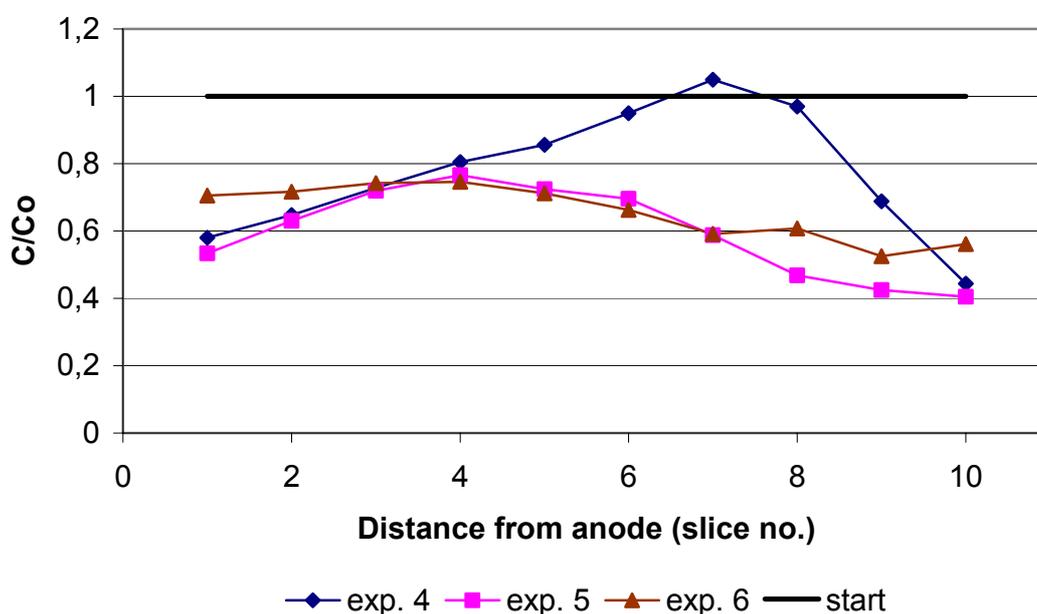


Figure 63: Normalised copper concentration profiles in the soil for experiment 5 (1 M ammonium citrate and current density 1 mA/cm²) and 6 (1M and 1.5 mA/cm²)

If all the soil profiles from Figure 62 and Figure 63 are compared with the predicted profiles, it can be seen that the distribution between the formation of positive and negative complexes is not equal. There seems to be more negatively charged complexes that are migrating towards the anode for experiment 4, 5 and 6, because the peak is highest in the anode side of the soil. A total removal of copper from the soil is not seen in any of the experiments and the concentration profiles in the experiments corresponds to the predicted profiles at time 1 (experiment 1, 2, 3 and 4), time 2 (experiment 5 and 6).

The copper concentrations in the soil solution for all the experiments are shown in Figure 64. The concentrations range from under 5,000 mg/l in experiment 2 to over 20,000 mg/l in experiment 3. The concentration in the soil solution is dependent on the concentration of copper in the soil and the concentration of ammonium citrate. The soil solution concentrations are highest in experiment 3 and 4. The copper concentration in

the soil in experiment 3 is much higher than for the other experiments, which explains the much higher concentrations, and from the extraction experiments in Figure 21, it is seen that desorption of copper is almost at the same level, when the ammonium citrate concentration is 0.5 M compared to 1 M. If comparing experiment 1 with experiment 4 the copper concentration in the soil is 3500 mg/kg and 4000 mg/kg, respectively and the concentration in the soil solution is 12,000 mg/l compared to 18,000 mg/l. The copper concentration in the soil for experiments 5 and 6 is about 1600 mg/kg, resulting in soil solution concentrations around 7,000 mg/l and for these two experiments with different current density, a higher current density does not result in higher concentrations in the soil solution. The release of copper to the soil solution follows the same pattern for all the experiments, except experiment 2. There seems to be equilibrium after a few days, the concentration stabilises at a concentration level close to the start concentration, and in the end of the experiments, the concentration is decreasing slowly. For experiment 2, the situation is different, the start concentration is lower and the concentration is increasing during the experiment. This is most likely due to the lower concentration of ammonium citrate in this experiments and is in agreement with the results from the extraction experiments in Figure 21, where the extraction is dependent on the ammonium citrate concentration.

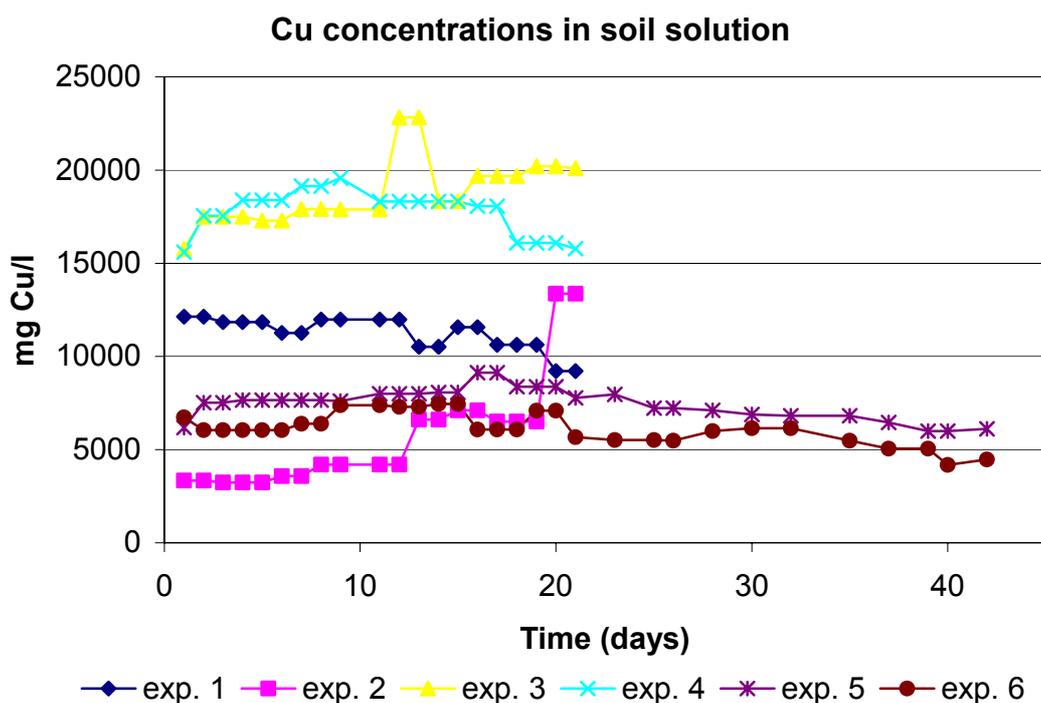


Figure 64: Copper concentrations in soil solution for all experiments. Experiment 1 (1M ammonium citrate and current density 0.2 mA/cm²), experiment 2 (0.25 M and 0,2 mA/cm²), experiment 3 (0.5 M and 0,2 mA/cm²), experiment 4 (1M and 1 mA/cm²), experiment 5 (1 M and 1 mA/cm²) and experiment 6 (1M and 1.5 mA/cm²)

The normalised concentration profiles for copper in soil solution are shown in Figure 65, where the concentrations are normalised by the start concentration in the soil solution. The largest variations from the start concentration are seen in experiment 2, where the concentration is increasing, compared to the start concentration, throughout the experiment. For the other experiments, the copper concentration during the

experiment is stable compared to the start concentration, which indicates that the soil is not remediated, at least not in the area where the sample is collected, where the soil is expected to first be remediated, see the predicted profiles.

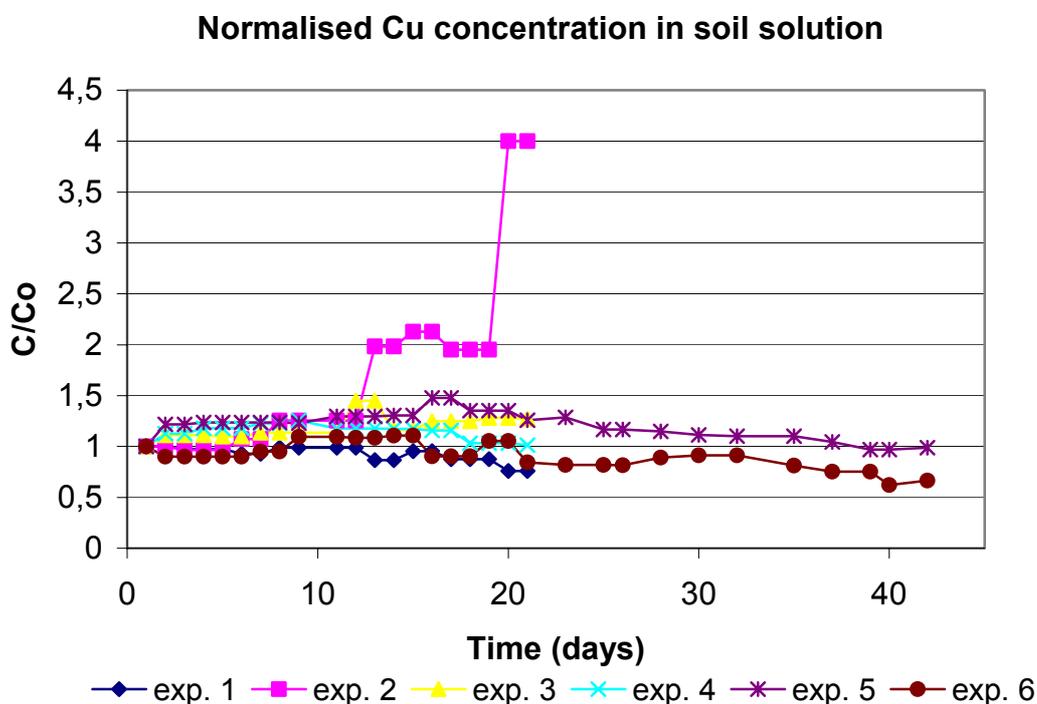


Figure 65: Normalised copper concentration profiles in soil solution for all experiments

When comparing the soil solution profiles with the predicted profiles for copper, the found profiles in the experiments fit with the stage, where copper is still being released to the soil solution. The soil solution concentration is starting to decrease in experiment 1, 4, 5 and 6, but the expected sudden drop in the concentrations is not observed. The concentration is stable and the concentrations in the soil solution do not indicate that the sudden drop will occur soon.

Chromium

In Figure 66 the normalised chromium concentration profiles in the soil for experiment 1, 2, 3 and 4, are seen. The removal in experiment 2 and 3 is limited to 3 %, but the shape indicates that chromium is being redistributed in the soil, since the concentration is not equal in the slices. For experiment 1 and 4 the removal is higher, about 6 %, and the higher current density in experiment 4 does not seem to increase the removal, although the profile is more distinct in experiment 4. The shape of all the profiles does not indicate the direction of the chromium migration, even though there seems to be an accumulation in the slices nearest to the cathode in experiment 4.

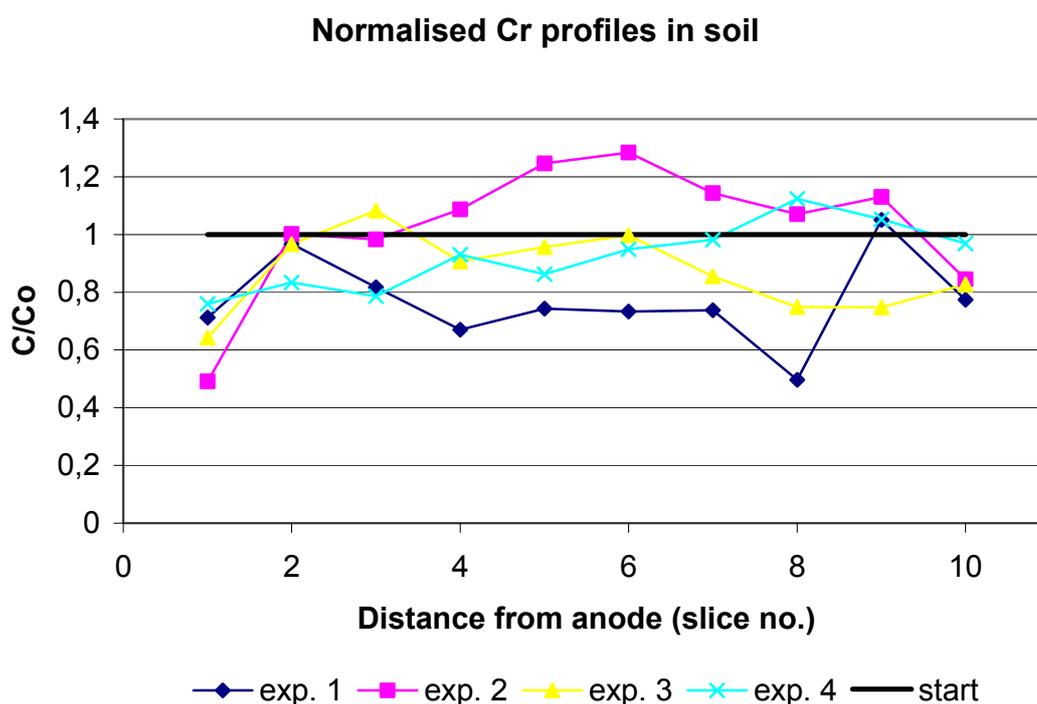


Figure 66: Normalised chromium concentration profiles in the soil for experiment 1, 2, 3 and 4

The normalised concentration profiles for experiment 4, 5 and 6 are seen in Figure 67 and the profiles have gotten a distinct shape in these experiments, than for experiment 1, 2 and 3. The concentrations are increasing over the soil from the anode towards the cathode, and an accumulation of chromium is seen in the slices closest to the cationexchange membrane. The remediation for chromium is better in experiment 5 and 6 compared to experiment 4, and the accumulation of chromium is not as pronounced in experiment 4 as in experiment 5 and 6. Chromium is mainly removed to the anode side in these experiments, see Table 28, but the concentration profiles clearly show that a transport of positively charged species towards the cathode has taken place and these can probably not pass the cationexchange membrane. When dividing the soil into slices after experiment 5 and 6, it was noticed that the slices closest to the cationexchange membrane had a strong smell of ammonia. The chromium-ammonia complexes are big, with 4, 5 or even 6 ammonia groups and the ions are monovalent, divalent and trivalent, see Appendix 3. This means that the complexes are large and will most likely be unable to enter the membrane. The concentration of ammonium citrate is high in the soil, which means that there is excess ammonium, that together with the copper tetratamin complexes are migrating towards the cathode. Thus, there will be competition for entering the cationexchange membrane between these ions. Since the chromium complexes are the largest ions and have the lowest mobility in the membrane they will not be able to penetrate the membrane (Jonsson, 2001). The ammonia smell in the soil is therefore most likely due to a combination of accumulation of chromium-ammonia complexes and the ammonia that is transported towards the cathode.

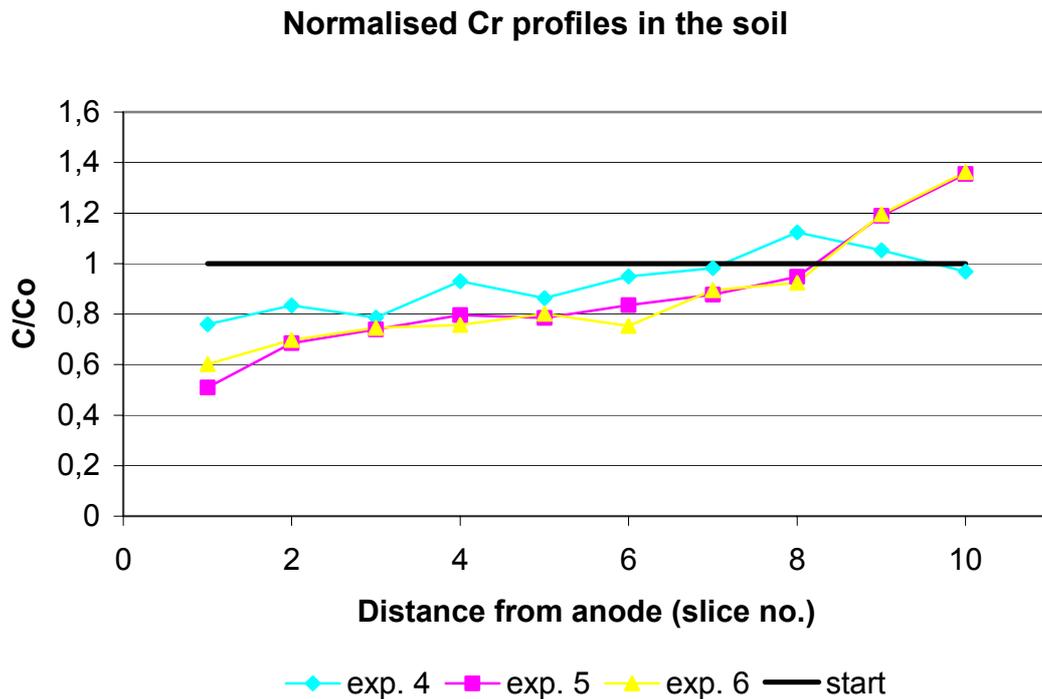


Figure 67: Normalised chromium concentrations in the soil for experiment 4, 5 and 6

It is seen that the chromium concentration profiles are not reaching the stage where the accumulated chromium near the cationexchange membrane is changing charge as is expected in the predicted profiles, because there is still an accumulation in the slices in experiment 4, 5 and 6. It is impossible to say when this change starts, but the remediation of chromium is clearly dependent on the time when this starts to happen. Comparing the profiles in Figure 66 and Figure 67, with the predicted profiles, the concentration profiles corresponds to the predicted profiles at time 1 (experiment 1, 2 and 3), time 2 (experiment 4) and time 3 (experiment 5 and 6).

Chromium shows a different behaviour in the soil solution than copper, see Figure 68. The concentration in the soil solution in experiment 1, 4, 5 and 6, is increasing during the experiments. For experiment 2 and 3 the start concentration is much lower than for the other experiments, even if there are only small differences in the start concentration in the soil, but the difference is due to the lower ammonium citrate concentration. The chromium concentration is also increasing in experiment 2 and 3, and in experiment 2 the concentration reaches the same level as for the experiments with 1 M ammonium citrate. These results are in agreement with the results for the extraction experiments, see Figure 22, which shows that the extraction of chromium to the soil solution is highly dependent on the concentration of ammonium citrate, even more than copper. This could indicate that chromium would either not be removed from the soil or that desorption is slower, with a low concentration of ammonium citrate. Clearly, the removal is lower for the experiments 2 and 3.

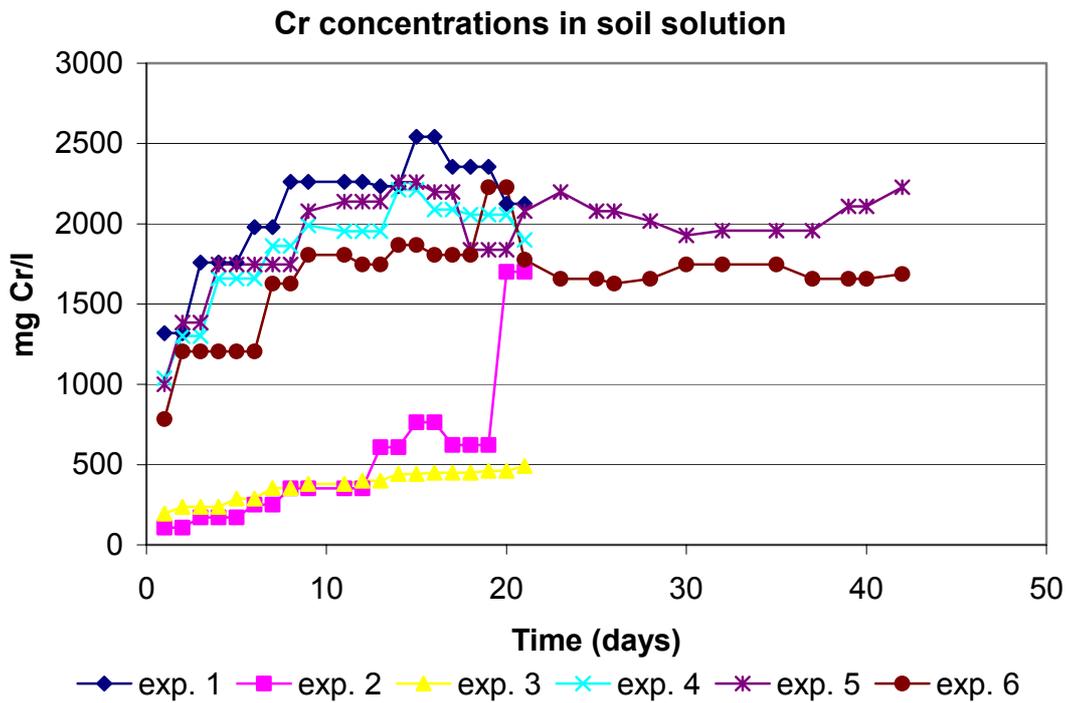


Figure 68: Chromium concentrations in soil solution for all experiments

The normalised chromium profiles in the soil solution are shown in Figure 69, and the concentrations are normalised against the start concentration. The general pattern is that the start concentrations are lower than the concentrations during the experiments. The concentrations are not decreasing to a level, which implies that the soil is remediated for chromium, and the release to the soil solution from the soil is slow. The normalised profile for experiment 2, with the lowest concentration of ammonium citrate is increasing the most during the experiment. The high final concentration can indicate that chromium is starting to be released from the soil, but since there are not more samples from this experiment, conclusions cannot be made.

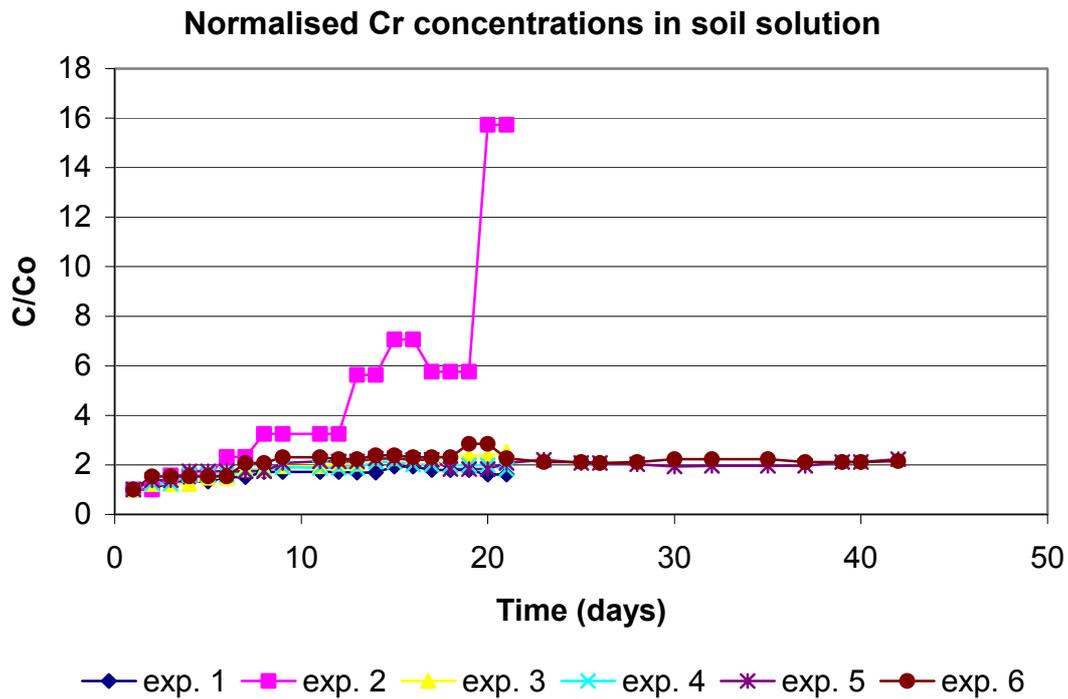


Figure 69: Normalised chromium concentration profiles in soil solution for all experiments

Chromium in the soil solution also follows the predicted profiles, but again as for copper, the remediation has not progressed enough to see the sudden drop in the concentrations.

10.2.5 Electrical conductivity of the soil solution

The electrical conductivity of the soil solution in all the experiments are shown in Figure 70. The concentration of ammonium citrate is clearly determining the magnitude of the electrical conductivity, the higher the concentration the higher is the magnitude. The copper concentration profiles for the experiments 1, 4, 5 and 6 see Figure 64, are following the decreasing profile of the electrical conductivity in Figure 70. The chromium profile does not follow the profile of the electrical conductivity, since the chromium concentration is increasing in the soil solution. An increase in the electrical conductivity for experiment 2 follows the increasing copper and chromium concentrations for this experiment, see Figure 64 and Figure 68. For experiment 3, there are not any distinct changes in the electrical conductivity, even though the concentrations in the soil solution are increasing, see Figure 64 and Figure 68. The electrical conductivity is high for all the experiments, but the concentration of copper and chromium is also high in the soil solution. The high electrical conductivity is probably why copper and chromium are not being removed from the soil solution, because the composition of the soil solution is dominated by ammonium and citrate. The concentrations of ammonium and citrate in the soil solution have not been measured.

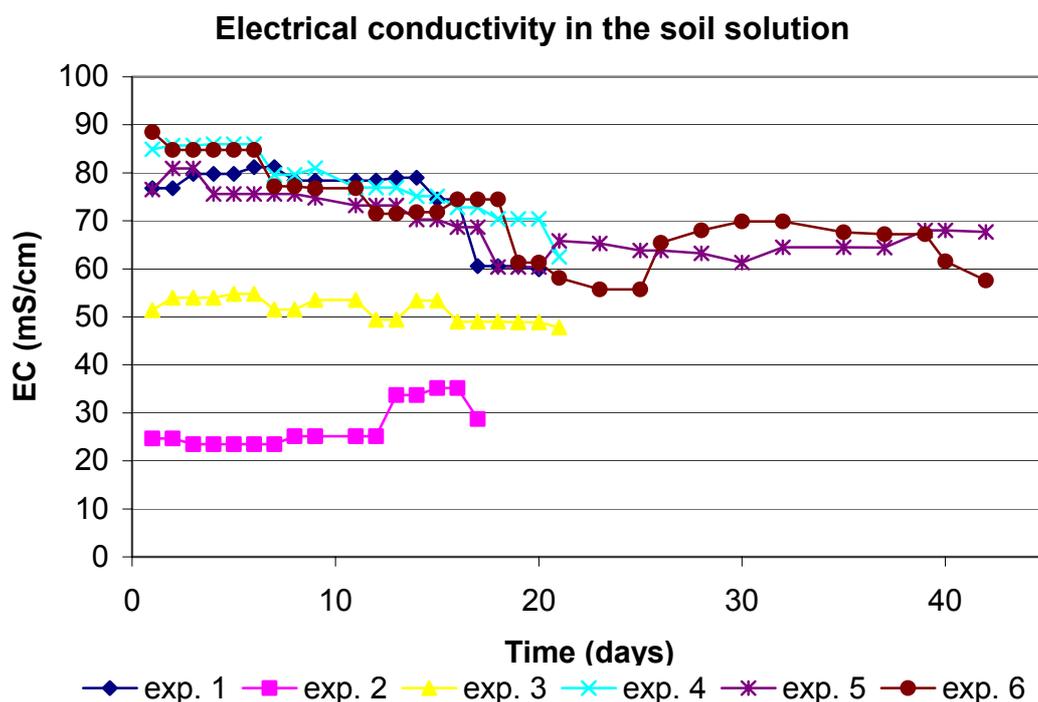


Figure 70: Electrical conductivity in the soil solution for all experiments

In Table 29, the percentage of the current that is used to remove copper and chromium from the soil in the experiments are shown, calculations are presented in Appendix 14. From Table 29 it is seen that the percentages are low, especially for chromium, which means that the current is mainly used to transport other ions out of the soil, which must be citrate and ammonium, since they are the dominant ions in the soil. Compared to the estimated K_{Cu} (30 – 90 %) and K_{Cr} (1-9 %), from Table 20, the percentages in the actual experiments are much lower, especially for copper. Thus, it seems that the K_{Me} is overestimated. This could be due to that K_{Me} is calculated based on the free metal and not complexes and is only exact for diluted solutions. Even though the K_{Me} is used as an estimate for the soil solution, it is in this case highly overestimated. The variations in the K_{Me} show that the exact speciation of the metals charge is crucial for determining the value. Since K_{Cu} is considerably higher than K_{Cr} , it should be expected that the copper concentration would influence the electrical conductivity more than chromium does, and this is also implied from the soil solution concentrations in the experiments, see Figure 64 and Figure 68.

From Table 29 it is seen that the current efficiency is highest in the experiments with the lowest current density (experiment 1 – 3). When the current density increases (experiment 4) the current efficiency is decreasing and is decreasing even more if the remediation is longer (experiments 5 and 6).

Experiment	I_{Cu} (%)		I_{Cr} (%)	
	Anode	Cathode	Anode	Cathode
1	3.4	1.9	0.8	0.1
2	0.7	1.3	0.5	0.1
3	11.4	2.2	0.8	0.05
4	2.2	1.1	0.3	0.05
5	0.4	0.4	0.2	0
6	0.3	0.3	0.1	0

Table 29: Percentages of the total current that has been used to remove copper and chromium towards the anode and the cathode

10.3 Comparison of soil and soil solution concentrations

The concentrations in the soil solution are high during the experiments, even though the concentration in the soil is decreasing. This is especially seen in experiments 5 and 6, where the concentration in the soil at the sampling point is getting lower, but the concentration in the soil solution is not equally lower. This is due to migration of the heavy metals through the soil, but could also be due to the earlier mentioned redistribution of heavy metals towards the more available phases after electrodiolytic remediation, see chapter 7.2 Physical and chemical soil parameters. A continuous redistribution towards the available phases during the experiment implies the high concentration in the soil solution, due to the continuous release of heavy metal to the soil solution. This can explain why the chromium concentration is increasing in the soil solution during the experiment, see Figure 68. The amount of available chromium is limited in the beginning of the experiment, see Figure 13 and the pool of available chromium will increase during the experiment. Copper is distributed more in the available phases from the beginning of the experiment, see Figure 13, which results in the copper concentration being much more stable in the soil solution and is also decreasing. When the copper concentration starts to decrease, it means that there is not more available copper to be desorbed from the soil. In addition, a further decrease in the concentration will follow until the soil is remediated.

Even though the concentrations of copper and chromium in the soil solution are high during the whole experiment, the soil is not remediated. This could be expected, but is not happening probably because of the high electrical conductivity. The high electrical conductivity means that the current, apart from transporting copper and chromium through the soil, also transports ammonium and citrate and these ions are present in much higher concentrations than the heavy metals, because all the ammonium citrate is not being used for forming complexes. The concentration of copper in the soil solution is much higher than the chromium concentration, which indicates that copper is much more available for complex formation with ammonium citrate, than chromium is.

The higher current density in experiment 4 compared to experiment 1, gave higher removal for copper, but not for chromium, although, the soil concentration profile for copper in experiment 4 was more distinct than in experiment 1, which means that the remediation is dependent on the current density. If experiment 4 is compared to experiment 5 and 6, it is seen that a longer remediation time clearly changes the remediation profile for copper and more copper is removed from the soil. The

chromium profile show that a higher accumulation will take place in the longer lasting experiments, but the shape of the profile is still the same. All in all, a high concentration of ammonium citrate and a high current density will give the best remediation for both copper and chromium.

The copper and chromium concentrations in the soil solution are highly dependent on the concentration of the ammonium citrate. For copper, 0.5 M and 1.0 M ammonium citrate give the highest concentrations in the soil solution, as seen in experiment 1, 3, 4, 5 and 6. A high chromium concentration in the soil solution is only obtained with 1.0 M ammonium citrate, as observed in experiment 1, 4, 5 and 6. Obviously, the highest concentration of ammonium citrate is the most effective for desorbing both copper and chromium, to high concentrations in the soil solution. Different current densities and remediation times are not, to a large extent, reflected in changes in the soil solution concentrations.

When comparing the found soil concentration profiles for copper (Figure 62 and Figure 63) and chromium (Figure 66 and Figure 67) with the predicted soil concentration profiles, it is seen that the remediation for both metals has reached the same stage, stage 3. It would be expected that copper will be removed from the soil first, followed by chromium, but how long it will take to reach time 5 for copper and time 8 for chromium, as presented in the predicted profiles, is not known.

10.4 Comparison with other experiments

The experiments presented in Appendix 2, show similar results as for the experiments made in this thesis. Most importantly is the observation that chromium is not found in the cathode side of the cell, when the experimental set – up was the same as for the experiments in this thesis. However, if an extra compartment was placed in the cell at the cathode side, which separated the soil with a passive membrane instead of a cationexchange membrane, chromium was found in the electrolyte in this extra compartment in high concentrations, but not in the catholyte. This implies again that chromium is forming positively charged complexes with ammonia and that these chromium complexes cannot pass the cationexchange membrane. For the experiments where a cationexchange membrane was separating the soil from the catholyte, there was not seen any accumulation of chromium in the slices closest to the membrane, but the slices were remediated. This indicates that when chromium is not transported through the cationexchange membrane, which was observed in the experiments in this thesis. However, chromium will after some time, change charge, due to the equilibrium with citric acid and thus chromium can migrate towards the anode. This is likely to happen due to the high concentration of ammonium citrate in the soil.

10.5 Optimisation

The results show that the remediation is slow and if the use of a soil solution sampler should be used to evaluate when the soil is remediated, the sampling frequency could be much lower than used in this thesis. There will most likely be a sudden drop in the soil solution concentrations when the soil is almost remediated, but when this will happen is unknown. A passive membrane, which would let the negatively charged chromium complexes be removed from the soil, should replace the cationexchange membrane.

This would also shorten the removal time for chromium, because chromium would be removed to the cathode side and not have to change charge and be transported back through the soil.

11 Conclusion

In this project, soil solution sampling, with a porous cup as soil solution sampler, from six electro-dialytic soil remediation experiments, has been successful. It is possible to collect soil solution from the electro-dialytic experiments by making an adjustment in the experimental set-up. Normally, ionexchange membranes are separating the soil from the electrolytes. Dewatering of the soil closest to the anode will happen, because the electroosmosis will transport the water in the direction of the cathode, and the water transport through the ionexchange membranes is very limited. If the soil gets undersaturated, soil solution samples cannot be collected. To keep the humidity in the soil, an extra compartment was introduced in the cell, which was separated from the soil by a passive membrane, which will let both ions and water pass. Thus, the soil was kept saturated during the experiments and the soil solution could be sampled during the experiments, without great difficulty. The soil solution sampler was placed in the middle of the soil and when the sample was collected, vacuum was applied by using a 20 ml syringe. 2-5 ml of sample was collected and the sampling took between 10 – 120 minutes and the sampling was harder in the end of the experiments. The sample radius is less than three cm from the soil solution sampler.

Ammonium citrate was chosen as desorbing agent for the electro-dialytic experiments. Copper and chromium behave very differently in the soil solution when ammonium citrate is used as desorbing agent. Only 1 M ammonium citrate can be used, if a high concentration of both copper and chromium in the soil solution is desired. The equilibrium between copper in the soil and in the soil solution is faster than the equilibrium between chromium in the soil and in the soil solution. This is reflected in the concentration profiles in the soil solution for both copper and chromium. The copper concentrations in the soil solution during the experiment do not vary much from the start concentration, but the chromium concentration in the soil solution during the experiment is increasing compared to the start concentration. The copper and chromium concentration is decreasing in the soil solution during the end of the experiments, but not to a sufficient low level, whereas the soil could be remediated. The different current densities used in the experiments do not change the concentration level in the soil solution.

Copper and chromium form both negatively and positively charged complexes with ammonium citrate, which are mobile in the electric field. Even though, chromium is only removed as anions in the experiments. Accumulation of chromium in the soil closest to the cationexchange membrane is observed in two of the experiments. The positively charged chromium-ammonia complexes are too large to penetrate the cationexchange membrane and they will be found in neither the cationexchange membrane nor the catholyte. Thus, it could be falsely concluded, that chromium only forms negatively charged complexes. The experiments show that copper is removed from the soil mostly as anions, but also as cations. The soil concentration profiles indicate that copper is removed faster in the soil than chromium, since distinct changes in the concentration profiles are seen earlier for copper than for chromium. None of the six experiments were remediated for neither copper nor chromium. This means that even if the concentration of copper and chromium in the soil solution is high from the beginning of the experiment, it does not catalyse the remediation noteworthy.

Conclusion

Higher current density and longer remediation time resulted in higher removal rates for both copper and chromium, but did not imply full remediation. The soil can be fully remediated, if the remediation times are longer.

Soil solution sampling can be used to determine when the soil is remediated, but the remediation profiles in the soil must be known. Predicted soil concentration profiles for copper and chromium from the experiments, show that copper would first be removed from the middle of the cell and chromium would be removed first from the slice closest to the cathode. A sudden drop in the soil solution concentrations will thus be observed for both copper and chromium, indicating that the soil is clean. However, when this drop happens, the soil is only partly remediated, and to obtain full remediation it is crucial to continue the experiment.

12 Perspectives/future work

The method to collect soil solution samples from the soil in electro-dialytic remediation, which has been used in this thesis, can be used to determine when the soil in electro-dialytic remediation is fully remediated. Since the investigations about the use of soil solution sampling in the electro-dialytic remediation still is limited, it is difficult to predict how it should be applied. Soil is classified as clean, when the copper and chromium concentrations are under 500 mg/kg, which means that removal to concentrations less than 500 mg/kg is not necessary. The predicted soil and soil solution concentration profiles in this thesis are made on the assumption that the soil will be fully remediated.

The variation in the heavy metal concentrations in different soils can be large and thus, the concentrations in the soil solution cannot be predicted beforehand. Due to the variations in the soil concentrations, the described drop in the soil solution concentration could happen after the soil was cleaned to under the classification concentrations. It would be interesting to perform different experiments on different soils that were fully remediated for copper and chromium, to see the development of soil solution profiles.

The soil solution sampler could also be installed in the bench and pilot plant experiments, to see the development in the soil solution in these experiments. The sampler would occupy a smaller total volume in the bench and pilot plant experiments, since the cell is larger than in the laboratory experiments, and then more samplers could be placed in the soil to investigate the soil solution several places in the soil.

Copper and chromium forms both negatively and positively complexes with ammonium citrate and these complexes could not be fully identified in this thesis. It would be very interesting to specify the charge of copper and chromium in the soil solution and different methods for this do exist. The main problem is, that the volume of sample is limited and the methods will probably require more than a couple of ml.

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