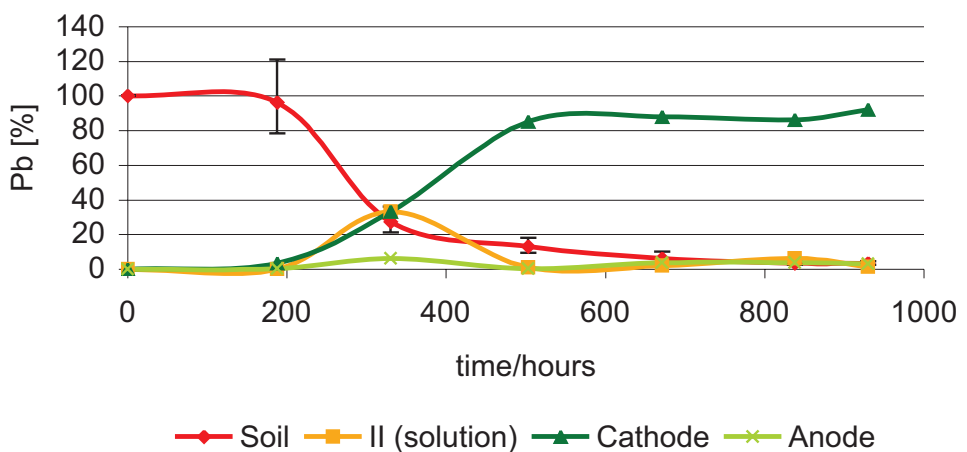


Pernille Erland Jensen

# Application of Microbial Products to Promote Electrodialytic Remediation of Heavy Metal Contaminated Soil



# **Application of Microbial Products to Promote Electrodialytic Remediation of Heavy Metal Contaminated Soil**

**PhD-thesis**



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## Preface

This PhD thesis is submitted in completion of the requirements for the PhD degree at the Technical University of Denmark (DTU). The work was made in the group of Electrochemistry in Civil Engineering at the Department of Civil Engineering (BYG-DTU). Principal supervisor was associate professor Lisbeth M. Ottosen (BYG-DTU). Co-supervisor was professor Birgitte K. Ahring (BioCentrum-DTU).

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## Abstract

In urban areas of Denmark, Pb is the most frequently observed soil-contaminant together with PAHs. Comprehensive legislation has been imposed to reduce Pb-exposure in the Danish society. The major use of Pb is at present in accumulators, which are being collected and reused. Since the use of Pb in gasoline ceased in the late 1980'es, the main human exposure derives from dust and soil. In order to eliminate the risk of children being affected by Pb-poisoning, with IQ-reduction and childhood hyperactivity as documented effects, treatment of the Pb-contaminated urban soil is a necessity. At present, Pb-contaminated soil is excavated from sites primarily due to construction activities. Such activities nevertheless lead to the handling of several million tons of Pb-contaminated soil every year. Currently this soil is being deposited, temporarily or permanently.

This study aimed at development of the electrodialytic remediation (EDR) method for efficient treatment of Pb-contaminated soil by application of microbial products.

Mobilization of Pb in soil by complexation with exopolymers and whole or disintegrated cells was investigated in column studies. Although exopolymers were previously shown to mobilize Pb in soil, the application in EDR was rejected after documentation of their negative effect on Pb-mobility in an electric current field.

In parallel with the research on the effects of exopolymers, a secondary objective was to elucidate the importance of original Pb-speciation versus soil-characteristics to mobility and distribution of Pb in industrially polluted soils. It was shown that the primary factors determining the speciation of Pb in soil are: (1) the stability of the original contamination and (2) the contamination level, while soil characteristics are of secondary importance.

The influence of Pb-speciation and soil characteristics on traditional (stationary), unenhanced EDR of Pb-contaminated soil was subsequently investigated. Results indicated that Pb-speciation is of primary importance. Specifically, organic matter and dominance of stable Pb-compounds, impedes and possibly even precludes soil remediation, while carbonate influences the remediation-time negatively. EDR remediation of fine grained, inorganic soils was documented to be feasible when the Pb is not associated with extremely stable compounds.

The potential of treating other fine-grained materials in a suspended version of EDR had at this time been demonstrated by other researchers in the group. Therefore the possibility of treating the fine fraction of Pb-contaminated soils by suspended EDR was investigated. This technology was intended for combination with conventional soil washing, in which the lack of a treatment method for the

remaining soil-fines has been the main limiting factor.

First, the influence of current strength and liquid-to-solid-ratio (L/S) was examined. It was found that during the treatment, Pb was easily dissolved by the acidification resulting from water splitting at the anion-exchange membrane. When higher currents and/or higher L/S ratios were applied, water splitting also took place at the cation-exchange membrane, resulting in a slow-down of the acidification and in decreased remediation efficiency. The optimal current strength depended linearly on the L/S of the soil slurry. Complete remediation of the soil-fines from the initial 1170mg/kg Pb to reach the accepted level for sensitive land-uses set by the Danish government (40 mg/kg Pb) was shown to be possible, with the majority of the Pb being transported into the catholyte and precipitated at the cathode. Based on the results it is recommended that EDR should be implemented using a number of reactors in series, where the initial reactor works at the highest possible removal rate, and the final reactor works at the target Pb-concentration.

Application of microbially produced siderophores, autotrophic leaching, heterotrophic leaching and biosurfactants were identified as potential methods for promotion of EDR of Pb contaminated soil. By these methods mobilization of Pb would occur due to complexation with much smaller substances than the previously examined and rejected exopolymers, why they were considered more efficient for mobilization of Pb in an electric current field.

Siderophores, which are iron-chelating compounds produced by microorganisms under iron deficiency were investigated for their Pb-mobilizing ability. After having shown that a commercially available siderophore indeed was able to extract

Pb from contaminated soil-fines, application of siderophores was however also rejected, primarily due to the insufficient concentrations produced by microorganisms in general and the unrealistic high costs of industrially produced siderophores in relation to the low value of the product to be treated. Furthermore no detection of siderophore production was possible during suspended EDR of soil-fines after incubation with a *Pseudomonas fluorescens* sp., which, in the absence of soil and current, had been shown to produce high levels of siderophores. Although a study into the mechanisms behind this observation would have been of great academic interest, it was omitted because of the lack of relevance to treatment of Pb-contaminated soil.

Autotrophic leaching, which is leaching by acidophilic, autotrophic microorganisms obtaining energy by oxidation of elemental sulfur, was shown to induce acidification of soil-fines in suspension, but removal of Pb from the treated soil-fines by suspended EDR was reduced considerably (from 94% without preceding heterotrophic leaching to less than 68% with preceding leaching) due to precipitation of Pb as lead-sulfate.

The potential of heterotrophic leaching by heterotrophic and acid producing microorganisms was tested by batch extraction of Pb from contaminated soil-fines with 11 organic acids at pH-values between 2 and 7, where acid-producing fungi grow. Five of the acids (citric acid, DL-malic acid, gluconic acid, tartaric acid and fumaric acid) showed ability to extract Pb from the soil fines at neutral and slightly acidic pH in excess of the effect caused by pure pH-changes. Addition of organic acids, however, severely impeded EDR, thus promotion of EDR of Pb from soil-

finer by combination with heterotrophic leaching was also rejected. In contrast, enhancement of EDR with nitric acid showed promising results at current densities beyond what is optimal with distilled water as solvent. Consequently addition of nitric acid is recommended in cases where the removal rate is considered important, while suspension in pure water is recommended in situations where the energy expenditure and the chemical costs are limiting factors.

Considering the results of the screening of siderophores, autotrophic leaching and heterotrophic leaching for promotion of EDR of soil-fines in suspension, it was decided to focus on the seemingly more promising unenhanced remediation. An investigation of the removal rates of Pb and common soil cations from soil-fines during EDR in suspension was initiated. The Pb-removal could be divided into four phases (1) a "lag-phase", where removal was substantially absent, (2) a period with a high removal rate involving dissolution of Pb in the soil-solution, (3) a period with a low removal-rate, where the dissolved Pb was removed from the solution, and (4) a period with no further Pb-removal as the treatment proceeded. The maximum removal rate for Pb obtained during phase 2 was 4mg/kg-hour. During phase 3, the high conductivity and low voltage suggested that removal might be accelerated by increasing the current density. During phase 1, dissolution of carbonates was the prevailing process. This dissolution resulted in a corresponding loss of soil-mass. The removal-order among the investigated soil cations was:  $\text{Ca} > \text{Pb} > \text{Mn} > \text{Mg} > \text{K} > (\text{Al and Fe})$ . Na was found to enter the soil from the electrolytes and a careful choice of electrolytes in order to meet any requirements by

subsequent receivers of the soil-fines is recommended. It is also recommended to limit the dissolution of Fe- and Al-minerals by terminating remediation as soon as Pb-extraction ceases.

The final work in this thesis provided evidence for feasible removal of a number of other toxic elements (As, Cd, Cu, Ni, Pb and Zn) by the method apart from demonstrating repeatability of experimental results. Also Cr was amenable to remediation, although removal from most of the investigated soils was slow compared to the other elements. In general therefore, conditioning of Cr-contaminated soil by addition of an oxidizing or a complexing agent is recommended. Hg was unsusceptible to EDR in suspension with 100% remaining in the soil after termination of the experiments. Some changes in the Hg-speciation towards mobilization were however established. Like for Cr-contaminated soil conditioning of Hg-contaminated soil with oxidizing or complexing agents is recommended. The maximum removals obtained after 10 days was 79% for As, 92% for Cd, 55% for Cr, 96% for Cu, 0% for Hg, 52% for Ni, 53% for Pb and 88% for Zn.





## Resumé

### Anvendelse af mikrobiologiske produkter til fremme af elektrodialytisk rensning af tungmetalforurenet jord

Sammen med PAH er bly (Pb) det oftest forekommende forurenende stof i danske byområder. Omfattende lovgivning er blevet indført for at reducere eksponeringen overfor Pb i det danske samfund. Det eksisterende forbrug af bly er primært til akkumulatorer, som indsamles og genanvendes. Siden anvendelsen af Pb i benzin blev udfaset i slutningen af 1980'erne, stammer den primære humane eksponering fra støv og jord. For at eliminere risikoen for at børn udsættes for blyforgiftning, med reduceret IQ og hyperaktivitet som dokumenterede effekter, er det nødvendigt at behandle den blyforurenet jord i byområderne. I øjeblikket bortgraves blyforurenet jord primært i forbindelse med byggeprojekter. Ikke desto mindre leder den type aktiviteter til håndtering af adskillige millioner tons blyforurenet jord hvert år. I øjeblikket deponeres denne jord enten midlertidigt eller permanent.

Dette projekt var rettet mod udvikling af den elektrodialytiske rensnings metode (EDR) til effektiv behandling af blyforurenet jord. Heriblandt undersøgelse af mulighederne for anvendelse af mikrobiologiske produkter til fremme af rensningen.

Mobilisering af Pb i jord ved hjælp af kompleksdannelse med ekstracellulære polymerer, samt hele

eller disintegrerede celler, blev undersøgt i kolonneeksperimenter. Selv om det er blevet vist, at ekstracellulære polymerer kan mobilisere bly i jord, blev anvendelsen i kombination med EDR afvist efter påvisning af deres negative effekt på blys mobilitet i et strøm-felt.

Parallelt med undersøgelsen af effekten af ekstracellulære polymerer, blev der indledningsvis sat fokus på betydningen af den originale speciering af blyforurening i forhold til jordkarakteristika for mobiliteten og fordelingen af Pb i forurenet jord. Det blev vist, at de afgørende faktorer, for specieringen af bly i jord er: (1) stabiliteten af den forurenende komponent og (2) forureningsniveauet, mens jordens karakteristika er af sekundær betydning.

Indflydelsen af blys speciering og jordkarakteristika på traditionel (stationær) EDR af blyforurenet jord blev derefter undersøgt. Resultaterne indikerede at blys speciering er af yderste vigtighed for rensningens resultat. I særdeleshed begrænser eller udelukker organisk stof samt uopløselige blyforbindelser rensning, mens karbonater påvirker rensningshastigheden negativt. EDR af finkornede, uorganiske jorder vist at være mulig, når ikke Pb er associeret i ekstremt stabile forbindelser.

Potentialet for rensning af andre finkornede materialer i en suspenderet

version af EDR var på dette tidspunkt blevet påvist. Derfor indledtes forskning i muligheden for at behandle finfraktionen af blyforurenet jord ved hjælp af suspenderet EDR. Denne teknologi var påtænkt til kombination med jordvaske processen, i hvilken mangelen på en behandlingsmetode til den overskydende finfraktion har været en begrænsende faktor.

I det første studie af suspenderet EDR undersøgtes indflydelsen af væske/faststof forholdet (L/S) og strømtætheden på rensningen. Det blev observeret at bly nemt blev opløst under processen af den syre, som blev dannet ved vandsplitning på overfladen af anionbytermembranen. Når højere strømdensitet eller L/S blev anvendt, forekom der også vandsplitning på overfladen af kationbytermembranen, hvilket resulterede i forsinkelse af forsuringen og nedsat rensningseffektivitet. Den optimale strømtæthed viste sig at afhænge lineært af L/S i jordopslæmningen. Fuldstændig rensning af finfraktionen fra startværdien på 1170mg/kg til en værdi, hvor følsom anvendelse tillades af de danske myndigheder (40mg/kg) viste sig at være mulig. Hovedparten af blyet blev transporteret ind i katolytten, hvor det udfældede på katoden. Baseret på de opnåede resultater anbefales det, at suspenderet EDR implementeres som et antal reaktorer i serie, hvor den første køres ved højest mulig rensningshastighed og den sidste ved den ønskede blykoncentration i slutproduktet.

Anvendelse af sideroforer, autotrof ekstrahering, heterotrof ekstrahering og biologisk producerede overfladeaktive stoffer blev identificeret som alternativer til de afviste ekstracellulære polymerer som potentielle metoder til fremme af EDR. Ved disse metoder vil den potentielle mobilisering af Pb fremkomme gennem kompleksering med stoffer,

som fysisk er langt mindre end de afviste ekstracellulære polymerer, hvorfor deres potentielle anvendelighed til mobilisering af bly i et elektrisk felt blev vurderet højere.

Efter at have vist at en kommercielt tilgængelig siderofortype er i stand til at ekstrahere bly fra finfraktionen af forurenet jord, blev disses anvendelse imidlertid også afvist, primært på grund af de meget lave koncentrationer, som mikroorganismer generelt er i stand til at producere, og de høje omkostninger ved opkoncentrering af sideroforer set i relation til den lave værdi af produktet som behandles. Desuden blev der i et forsøg med inkubation med en siderofore-producerende *Pseudomonas fluorescens* art og tilsætning af glukose under EDR i suspension, ikke observeret siderofore-produktion på trods af, at denne art producerede store mængder sideroforer med glukose som næringsstof i fravær af jord og strøm. Et studie af mekanismerne bag denne observation ville have været interessant, men blev ikke udført pga. den manglende relevans for rensning af blyforurenet jord.

Autotrof ekstrahering af iblevende mikroorganismer fremprovokeret ved tilsætning af svovl og vækstmedie viste sig at fremkalde et fald i pH i suspenderet finfraktion af jord. Fjernelse af bly fra den autotroft behandlede finfraktion blev imidlertid mindsket signifikant (fra 94 % uden forudgående autotrof ekstraktion til mindre end 68 % med forudgående ekstraktion) på grund af udfældning af Pb som blyulfat.

Potentialet af heterotrof ekstraktion blev testet i en indledende undersøgelse af ekstraktionen af Pb fra forurenet jord med 11 organiske syrer mellem pH 2 og 7, hvor syreproducerende svampe gror. Fem af syrerne (citronsyre, æblesyre, glykonsyre, vinsyre og fumarsyre) var

i stand til at ekstrahere Pb fra finfraktionen ved neutral og let sur pH, udover den ekstraktion, der forekom ved pH-ændringen alene. Derimod forringede tilsætningen af organiske syrer EDR alvorligt, og forbedret EDR af blyforurennet finfraktion i suspension ved kombination med heterotrof ekstraktion blev afvist som en mulighed. Derimod forbedrede tilsætning af salpetersyre rensningsresultatet ved strømtætheder over dem, som er optimale med destilleret vand som suspensionsvæske. Tilsætning af salpetersyre kan derfor anbefales i tilfælde, hvor rensningstempoet vurderes at være vigtigst, hvorimod destilleret vand anbefales i tilfælde, hvor energiforbruget og/eller kemikalieomkostninger er begrænsende faktorer.

Efter at have behandlet resultaterne af screeningen af sideroforer, autotrof ekstraktion og heterotrof ekstraktion som metoder til at fremme EDR af finfraktioner fra blyforurennet jord, blev det besluttet at fokusere på den tilsyneladende mere lovende rensning uden fremmede reagent.

I stedet indledtes en undersøgelse af rensningshastigheden for bly og almindelige kationer i jord under EDR i suspension. Rensningen kunne opdeles i fire faser: (1) en nøle-fase, hvor der stort set ikke skete nogen rensning, (2) en periode med en høj rensnings-hastighed, hvor bly bragtes i opløsning i suspensions-væsken, (3) en periode med en lav rensningshastighed, hvor det opløste bly blev fjernet fra suspensions-væsken, og (4) en periode, hvor rensningen af bly var ophørt. Den højeste rensnings-hastighed opnået i fase 2 var 4mg/kg·time. I fase 3 sås en stigende ledningsevne og en faldende spænding mellem elektroderne, hvorfor en forøget rensningshastighed i denne fase muligvis kan opnås ved at øge strømtætheden. I løbet af fase (1)

var den dominerende proces opløsning af jordens karbonatindhold. Denne opløsning resulterede i en tilsvarende massereduktion af jorden. Fjernelsen af de undersøgte kationer forløb i følgende rækkefølge:  $\text{Ca} > \text{Pb} > \text{Mn} > \text{Mg} > \text{K} > (\text{Al} \text{ og } \text{Fe})$ . Introduktion af Na fra elektrolytterne blev observeret, hvorfor et velovervejende valg af elektrolyt i overensstemmelse med eventuelle krav fra aftagere af finfraktionen efter rensning anbefales. Det anbefales også at begrænse opløsningen af Fe- og Al-mineraler ved at afslutte rensningen så snart den ønskede blykoncentration er opnået.

Ud over at demonstrere repeterbarhed af de eksperimentelle resultater, påviser det sidste arbejde i afhandlingen muligheden for at fjerne en hel række giftige elementer (As, Cd, Cu, Ni, Pb og Zn) fra finfraktionen af jord ved hjælp af EDR i suspension. Cr kunne også fjernes, selvom rensningen af dette element fra de fleste jorder forløb langsommere end de øvrige elementer. Kviksølv lod sig - med 100 % tilbage i jorden efter afslutning af rensningsforsøg - ikke fjerne. En vis ændring i kviksølvs speciering mod øget mobilitet blev dog observeret. I tilfælde af kviksølv- eller kromforurennet jord anbefales det at tilsætte et oxiderende/komplekserende stof ved rensning. Den maksimale rensning opnået efter 10 dage var: 79 % for As, 92 % for Cd, 55 % for Cr, 96 % for Cu, 0 % for Hg, 52 % for Ni, 53 % for Pb og 88 % for Zn.



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# 1. Introduction

*Pernille E. Jensen*

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Denmark, 2800 Lyngby, Denmark.*

The objective of this PhD-study is indicated by the title, namely to investigate possible applications of microbial products to promote electrodialytic remediation of heavy metal polluted soil.

The idea was born during the work of my master-thesis, where I showed how Pb can be extremely recalcitrant towards electrodialytic remediation (Jensen, 2000). Therefore enhancement options should be investigated. Application of microbial products was chosen as my field of study for three reasons: 1) A number of papers had come out at that time suggesting microbial products as mobilizers of heavy metals in soil e.g.: (Gourdon and Funtowicz, 1995; Chen *et al.*, 1995; Bosecker, 1997; Krebs *et al.*, 1997; White *et al.*, 1997; Czajka *et al.*, 1997; Jackman *et al.*, 1999; Maini *et al.*, 2000; Xiang *et al.*, 2000), 2) The idea of using pure chemicals for remediation of a low-value product such as soil seemed unrealistic, and 3) The topic aroused my curiosity. Pb was to be the contaminant of main focus; however a study of the applicability of any developed method for remediation of other heavy-metals from soil was an additional objective.

The outcome of the work is primarily a series of papers which have been submitted for publication to various journals. These papers constitute the major part of this thesis (chapters 4 through 9). The titles and contents of the papers are however not an obvious result of the project-definition. The purpose of chapter 3 is therefore to give a picture of the additional work which has been made, how conclusions were drawn and how ideas developed during the progress of the project.

The theoretical background of the thesis has been incorporated into the papers themselves as much as possible. In the first paper: "Speciation of Pb in Industrially Polluted Soils", an introduction to the behavior of Pb in soil is given. In the second paper: "The Effect of Soil Type on the Electrodialytic Remediation of Lead-Contaminated Soil", results on electrokinetic and electrodialytic remediation of Pb-contaminated soil are reviewed. In the third paper: "Electrodialytic Remediation of Soil Fines (< 63 $\mu$ m) in Suspension", an insight into water-splitting in electrodialysis is given. In the fourth paper: "Organic Acid Enhanced Electrodialytic Extraction of Pb from Soil-Fines", application of enhancing reagents for electrokinetic and electrodialytic remediation is reviewed. In the fifth paper: "Kinetics of Electrodialytic Extraction of Pb and Soil Cations from Contaminated Soil Fines in Suspension", the influence of electrodialysis on soil-constituents is treated, as well as potential applications of the remediated soil fines are touched upon. In the sixth paper: "Electrodialytic Remediation of Soil-fines (< 63 $\mu$ m) Polluted with As, Cd, Cr, Cu,



Hg, Ni, Pb and Zn in Suspension”, important behavioral characteristics of the treated elements are summarized.

During my PhD-work I also had the chance to contribute to two additional papers and a book chapter as second/third author, and to visit five international conferences with oral/poster presentations and publication of abstracts in proceedings.

As an appropriate beginning of the thesis I, however, believe that it is necessary to answer the question: Why? The answer to this question I hope the reader will find in chapter two: “Pb in the Environment: Extent, Effects and Precautions”.

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## 2. Pb in the Environment: Extent, Effects and Precautions

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In this chapter, the motivation of research on remediation of Pb-contaminated soil is given. The main focus is set on the Danish situation; however some international information is available as well. The extent and distribution of Pb-contamination is examined in section 1. Pb-sources and consumption-development are summarized in section 2. Effects of Pb-contamination are described in section 3. Precautions against lead-poisoning in the Danish society are summarized in section 4, and finally, in section 5 fate and treatment of Pb-contaminated soil in Denmark is described.

### 1 Extent Of Pb Contamination

The amount of Pb in Danish county-side soils (agricultural, natural, and forest soils) was investigated nationwide (except Bornholm and Greenland) by measurement of 433 samples (Jensen *et al.*, 1996). This investigation showed that Pb is evenly distributed throughout the nation with 0-20mg/kg except from the southern part of Funen and an area south of the Liim Fiord where the concentrations were between 20 and 40ppm (Jensen *et al.*, 1996). The average value measured was 11.3mg/kg. The Pb concentrations measured in Denmark were comparable to those found in Southern Sweden and North Germany in similar investigations (Reimann *et al.*, 2000). Compared to the average composition of the earths crust, Pb occurred in rather elevated concentrations already in the late 1970'es (Tjell and Hovmand, 1978). In both Denmark and Norway, the deposition rate has however reduced significantly over the last decades (Jensen *et al.*, 1996; Steinnes, 2001). The conclusion of the Danish study was that Pb-concentrations in country-side soils are only slightly elevated, and that contamination is not an urgent environmental problem outside the urban areas at present (Jensen *et al.*, 1996). In contrast, a Norwegian study is concerned with Pb in the southern part of Norway reaching levels as high as 150-200mg/kg (Steinnes, 2001).

In comparison, the extent of diffuse Pb-contamination in urban areas is considerably more comprehensive. Four investigations made of topsoil in Copenhagen, which was not expected to be contaminated, showed that Pb is the most problematic heavy metal in the city with an average concentration of 123mg/kg (Fabricius *et al.*, 2002). An investigation made of topsoil in the Valby neighborhood of Copenhagen showed that 90% of the samples taken in a net of sampling points in both residential and industrial

areas exceeded the soil quality criteria (SQC) set by the Danish EPA for Pb in soil (40 mg/kg) (Miljøkontrollen, 1997), and a similar investigation from Århus showed that more than half of the samples taken in the city-center were contaminated (Embedslæge institutionen *et al.*, 1999). A recent investigation of diffuse contamination made by the Danish EPA comprising 10 residential areas in Copenhagen and the provincial town Ringsted showed, how diffuse Pb-contamination is closely related to the age of the residential areas, with significantly higher contamination levels in areas with longer development history. Only areas which had not been previously built-on or used for industry were included in the investigation. The main-results of this investigation are shown in table I. Pb-contamination is generally lower in Ringsted than in Copenhagen, where the SQC for lead was frequently exceeded in the top-soil (0-0.3m depth), and in the old residential areas even the Soil Cut off Criteria (SCC) (400mg/kg) was repeatedly exceeded (Falkenberg *et al.*, 2004).

TABLE I

Pb concentration (interval) in top-soil of residential areas in Copenhagen (C) and Ringsted (R) (Falkenberg *et al.*, 2004), N = number of samples taken.

Area	Establishment	Pb [mg/kg] (N)
Nyboder (C)	1600's and 1700's	23-2700 (51)
Kartoffelrækkerne (C)	late 1800's	55-770 (39)
Østre anlæg (C)	Reference: recreational area (late 1800's)	56-105 (5)
Guldbergs plads (C)	From 1900	46-250 (14)
Banefløjen (C)	1950's	15-370 (54)
Tingbjerg (C)	1960's	22-50 (25)
Sct. Knudsgade (R)	late 1800's	20-150 (15)
Bøllingsvej (R)	1910's	26-170 (25)
Sorøvej (R)	1940's	14-78 (27)
Søndervang (R)	1950's	15-40 (40)
Bjergbakken (R)	1980's	12-22 (32)

In addition to the urban areas affected by diffuse contamination, 11% of the city-surface of Copenhagen (approximately 10km<sup>2</sup>) consists of waste used as filling-materials, of which the main part is highly contaminated with Pb (Fabricius *et al.*, 2002). This contamination-type is primarily found close to the shore, where harbor-areas were filled up and developed between 1750 and 1900. Another important example of widespread contamination exists in the suburb Glostrup, where an old metal-winning industry was placed from 1938 to 1985. The site itself is 5.5km<sup>2</sup> and consists of 150,000 tons of contaminated material with Pb-concentrations above 800mg/kg. The affected area, however, is covering several residential areas and a total area of approximately 100km<sup>2</sup> (Allermand, 2000). By the end of 2004 almost 11,000 point-source contaminations had been mapped by the Danish authorities. Of those 16% were registered to be contaminated with Pb (Bernhard Brackhahn, 2005). Particularly in the large cities, Pb-contamination is widespread, and in Copenhagen 31% of the 353 registered contaminated sites are contaminated with Pb (Varman, 2005). Worldwide there is no reason to believe that the extent of Pb-contamination is smaller than in Denmark. The fact that Pb-contamination is connected to the mining-industry speaks for itself, and e.g. in the USA, Pb is present at approximately 25% of

the 1700 National Priority sites documented by the US-EPA Superfund program (Hoy *et al.*, 1996).

## 2 Sources Of Pb-Contamination

The sources of Pb-contamination are closely related to present and historical uses of lead. The historical uses of lead are extensive and varied. Already in early history lead was exploited for a number of purposes including coins, roofing, ornaments and warfare. As far back as 4000BC lead was used for pottery glazing by Egyptians, and it was used as a stimulant by the Emperor of China prior to 300BC. In the Roman Empire lead was used extensively e.g. for coating of aqueducts. Lead was even used as a sweetener in the kitchen of the Romans (Nriagu *et al.*, 1978).

Although lead was later recognized as a toxic element, the uses of lead increased continuously due to its low price and ready availability. The use of lead in the industrialized world has largely been connected with the use of leaded gasoline.

TABLE II  
Consumption development of Pb in Denmark

<i>Pb</i>	<i>Year</i>	1985 <sup>a</sup>	1994 <sup>b</sup>	2000 <sup>c</sup>
<b>Total consumption (in 1000 tons)</b>		<b>21-25</b>	<b>16-20</b>	<b>15-19</b>
<b>Imported (in 1000 tons)</b>		<b>34-40</b>	<b>20-22</b>	<b>18-23</b>
<b>Exported products (in 1000 tons)</b>		<b>13-15</b>	<b>3-5</b>	<b>3-4</b>
<b>Exported scrap and waste (in 1000 tons)</b>		<b>10-12</b>	<b>10-12</b>	<b>12-15</b>
<b>Reuse (in 1000 tons)</b>		<b>0.5</b>	<b>0.5</b>	<b>0.5</b>
Accumulators (%)		51	48	52
Flashings + roofs (%)		14	18	23
Cable sheathings (%)		10	12	2
Ammunition (%)		4	3	1
Boat keels (%)		4	< 1	3
Fishing equipment (%)		2	4	4
PbSn alloys* (incl. solder) (%)		?	2	2
Gasoline additive (%)		1	< 0.1	0
Pigments (%)		2	0.4	0.3
Glass incl. tubes* (%)		?	5	5
Stabilizers in PVC (%)		< 1	2	3
Side component in coal (%)		1	0.5	0.3

\*Not included in 1985, <sup>a</sup> (Hansen and Busch, 1989)

<sup>b</sup> (Lassen and Hansen, 1996), <sup>c</sup>(Lassen *et al.*, 2003)

In the 1970's when the emission of lead from gasoline was at its highest in Denmark, it reached almost 1000tons/year. During the following decades, the use of leaded gasoline declined to 190 tons emitted in 1985, 10tons in 1994 and almost completely ceased from 1996. A thorough mapping of the uses of Pb in Denmark between 1985 and 2000 was given by the Danish EPA in three succeeding reports, which are summarized in table II. The table shows, how the consumption of Pb decreased from 1985 to 1994, while it remained stable in the period between 1994 and 2000. The consumption, however, represents neither the manufacturing nor the accumulation of Pb in Denmark, which are affected by a considerable import and export of products and waste-materials containing Pb. The amount of exported products decreased

drastically between 1985 and 1994 due to substitution with other materials, while the amount of exported scraps and wastes increased slightly between 1994 and 2000. The reuse has remained stable and insignificant. The most dominating uses are in accumulators, as roof flashings and as cable sheathings. The amount used as cable sheathings decreased significantly between 1994 and 2000. On a world scale the uses of lead resemble the uses in Denmark with the important differences that leaded gasoline is still used in many third-world countries, especially in Africa (Fewtrell *et al.*, 2003). The consumption in the OECD-countries increased from 3 million tons in 1970 to 5.6 million tons in 2000. The world consumption increased from 4.5million tons to 6.5million tons during the same period. The lead mining activity, however, decreased slightly from 3.4 million tons in 1970 to 3.1million tons in 2000 (Lassen *et al.*, 2003). Historically, the main sources of diffuse contamination in the country-side in Denmark were leaded gasoline, combustion of municipal solid waste and lead shots. In addition, long-range contamination from sources in other parts of Europe is made likely by a Norwegian study, showing how the southern part of Norway has been subjected to such contamination (Steinnes, 2001). Although Pb from fireworks has probably been emitted throughout the period, it was not included in the mass-flow-analysis until 2000, where it showed to be the major source of Pb-emission into air followed by waste-incineration, foundry activities, and the production of iron and steel (Lassen *et al.*, 2003). Diffuse contamination of urban areas is connected to the city-development, where municipal and industrial wastes were previously deposited on site, as were construction-materials after demolition or fires. Other important diffuse sources in city-areas are connected to the infrastructure such as roads and railroads, and smoke emission from the heating of houses and industrial activity (Falkenberg and Riis, 2002).

TABLE III  
Emission of Pb to the environment in Denmark (tons),  
with the emission to soil specified.

<i>Pb</i>	<i>Year</i>	1985 <sup>a</sup>	1994 <sup>b</sup>	2000 <sup>c</sup>
<b>To air</b>		<b>250-300</b>	<b>11-33</b>	<b>3-17</b>
<b>To water</b>		<b>400-950</b>	<b>160-590</b>	<b>170-600</b>
<b>To soil</b>		<b>1300-3900</b>	<b>630-2400</b>	<b>470-2200</b>
<b>Deposited</b>		<b>1800-4300</b>	<b>1800-3600</b>	<b>1300-2300</b>
Scrapping etc.		500-2500	7-26	6-30
Ammunition		720	195-270	43-68
Discarded cable sheathings		< 430	400-2000	400-2000
Flashings + roofs		55-90	3-12	3-25
Paint and other chemicals		30-55	10-34	6-19
Fertilizer etc.		28-180	7-15	4-11
Wastewater sludge		8-27	8.3	4-5
Biological waste treatment		?	0.3	6-9
Red lead		5-15	1-5	1-3
Accumulators		?	?	1-11

<sup>a</sup> (Hansen and Busch, 1989) <sup>b</sup> (Lassen and Hansen, 1996) <sup>c</sup> (Lassen *et al.*, 2003)

The three mass-flow analyses in addition give estimates of the flows of Pb into soil, air, and water, which are summarized in table III. It is likely that Pb emitted into air and water will eventually end up in soil or sediment which serves as sinks for Pb.

Deposited Pb includes land filled Pb as well as slag/ash used for road-construction. The emissions of Pb to soil are subject to some uncertainty, due to the lack of information on contaminating activities. The only clear trend is that the flow of Pb to soil from ammunition has decreased since 1985 as has the emission of Pb to air from leaded gasoline. The list of sources in table III includes the amount of Pb discharged to soil as paints and chemicals, which may include some industrial point-source contaminations; however the variety of sources for point-source contamination with Pb is much wider, illustrated by the sources given in a list of contaminated sites registered in the county of Copenhagen between 1995 and 1997: production of brass-products, production of cables, production of batteries, a gasworks, metal extraction, galvanization, chromium-plating, ceramics production, accumulator production, engine works, reparation of drums for oil and paint, and foundry activity (Københavns Amt, 1996). The amount of Pb emitted to soil from accumulators was omitted in the first two reports, but another report estimated that 600-2400tons of Pb has been discharged to soil from lead accumulators per year until 1985 (Miljøstyrelsen, 1988b). Perspective is given to the values in table IV when it is kept in mind, that 1 ton of Pb can contaminate 2500 tons of soil above the SCC set by the Danish EPA. Deposition of 2000tons Pb/year for 10 years can produce 50 million tons of contaminated soil.

### 3 Effects Of Pb-Contaminated Soils

A person's exposure to Pb is reflected in the person's blood-Pb-level (PbB). The most recent investigations document effects at children even at very low PbBs ( $< 10\mu\text{g Pb/dl}$ ). A no-effect concentration has not been established (Fabricius *et al.*, 2002), and the observed effects at low concentrations include a number of effects on the nervous system including learning disabilities and behavioral problems (childhood-hyperactivity), which are often undiagnosed. One of the first convincing studies in the area (Pihl and Parkes, 1977), showed significantly higher Pb-concentrations in the hair of learning disabled children compared to a control group. The more recent works primarily covered the relation between PbB and intelligence (Lanphear *et al.*, 2005). There is a close connection between the concentration of Pb in the blood of children and their IQ: an increase in the PbB with  $10\mu\text{g/dL}$  results in an IQ decrease of 2.6 (Fabricius *et al.*, 2002). At high concentrations (PbBs above  $70\mu\text{g Pb/dl}$ ) severe neurological problems like seizure, coma, and death arise (Meyer *et al.*, 2003). WHO has specified a PTWI (Provisional Tolerable Weekly Intake) of  $25\mu\text{g/kg}$  body weight. This limit is just below the intake where effects have been documented.

Mainly leaded gasoline, glazed household ceramics, and lead-containing paints have been related to severe Pb-poisonings. These sources are presently decreasing and the effect is visible although not as pronounced as hoped (Meyer *et al.*, 2003). Any further decrease in lead exposure is difficult to obtain due to the Pb-sources in the living environment. In Denmark (Fabricius *et al.*, 2002) stated that after the reduction of Pb in the atmosphere due to phasing out of leaded gasoline, soil/dust is main responsible for the Pb-intake by children. The Danish EPA estimated that an average 9 month old child living in an area with  $40\text{mg Pb/kg}$  will take up  $6\mu\text{g/kg}$  body weight a day, while a child living in an area with  $200\text{mg Pb/kg}$  will take up  $30\mu\text{g/kg}$  body weight (Miljøstyrelsen, 1995). A recent study showed a well correlated relation between Pb in soil of residential areas, and average Pb in the blood of children  $\leq 6$  years (Mielke *et al.*, 1999):

$$\text{PbB } [\mu\text{g/dL}]$$

$$= 3.06 + 0.33(\text{Pb in soil [mg/kg]})^{0.5}$$

The correlation gives a mean blood concentration of 10µg/dl for a child exposed to a soil concentration of 400mg Pb/kg (the Danish SCC). It is important to recognize that the correlation is based upon median values, and many children will have PbBs higher than the calculated. Therefore a safe soil concentration should be below 400mg/kg. Even at 80mg/kg some sensitive children with occasionally high pica behavior will be affected (Mielke *et al.*, 1999). A Danish investigation did, however, show that children of families owning allotments contaminated with 500mg Pb/kg had average PbBs around 4.0µg/dL (Fabricius *et al.*, 2002). A likely reason for the decreased exposure is the fact that most families only stay in allotments during a minor part of the year. A report published by the Danish EPA estimated that for children 53% of the daily maximum intake of Pb comes from other sources than soil (food, toys etc.). If the maximum daily intake set by WHO is not to be exceeded, maximum 47% must come from soil, which requires a limit for Pb in soil of 20mg/kg for the most sensitive children (Miljøstyrelsen, 1996b).

## 4 Precautions Against Pb In The Danish Society

### 4.1 LEADED GASOLINE

From the beginning of the 1970'es attention was paid towards the expose of humans to Pb. The Danish EPA contributed with a number of reports, the first in 1976 (Miljøstyrelsen, 1976). At that time Pb from gasoline was considered to be the most serious threat, because airborne Pb was subjected to the highest uptake, and 90-98% of the airborne Pb originated from leaded gasoline. Particular concern was paid towards those living and cultivating in the vicinity of heavily trafficked roads and gas-stations, or working in exposed environment. Possible solutions mentioned were reduction of Pb in gasoline or separation of heavily trafficked roads from residential areas. Succeeding reports evaluated the environmental, practical and economical implications of an eventual reduction of Pb in gasoline in Denmark (Miljøstyrelsen, 1978; Miljøstyrelsen, 1979). In 1984 the Danish government made the decision that unleaded gasoline should be available at the Danish market as soon as possible and at the latest by the end of 1986 (Miljøstyrelsen, 1985). The maximum content of Pb in gasoline was set to 0.15g/L and taxes on unleaded gasoline were reduced compared to leaded gasoline. Presently, leaded gasoline is still legal and available, but the use is very limited (Miljøministeriet, 1997).

### 4.2 OTHER PB-USES

During the 1970'es, 80'es and 90'es a number of specific Pb-uses attracted attention. For Pb in glazing of ceramic household utensils legislation had come into effect from 1973, and the acts in force prescribe that ceramics for household utensils may contain maximum 0.1% Pb (Miljøministeriet, 1997). In 1982 focus was set on lead shots (Hartmann, 1982), and the suitability of steel shots as replacement of lead shots was evaluated. The report was positive towards the substitution, and it became forbidden to use lead shots in bird-territories of international importance in 1985 (Miljøministeriet, 1985), and in 1986 the content of Pb in Pb shots was in general restricted to 28.5g pr. shot (Miljøministeriet, 1986). Unfortunately steel shots became problematic to the wood-industry, and the legislation was changed, so that lead-shots could be used in forests larger than 3ha. Succeedingly, the consequences of introduction of steel shots to the wood-industry were evaluated in detail (Petersen and



Kofod, 1987). Here it was verified that steel shots severely damage wood-processing machinery, while another report on the environmental consequences of lead shots again recommended to stop trap shooting with lead shots as immediate as possible (Miljøstyrelsen, 1989). An investigation into alternative shot-materials was conducted (Keller, 1991), with the disappointing conclusion, that no realistic alternatives to lead shots existed at that time. Since then a number of alternative shot materials were developed and approved, and from 1996 lead shots were completely banned (Miljøministeriet, 1994). In 1984 the Pb-level in toys was investigated with the intention to legislate in the area (Miljøstyrelsen, 1984), and current legislation limits the bioavailability of Pb in toys to maximum  $0.7\mu\text{g}$  a day by normal use (Sikkerhedsstyrelsen, 2003). In 1985 the Danish metal-winning industry Paul Bergsøe, which had for many years been collecting and recovering lead-accumulators in Denmark, closed. This created a waste problem, and as a consequence the Danish EPA investigated the possible start-up of a new facility to recover and reuse lead-accumulators (Sønnichsen, 1987). The investigation concluded that the project was possible but unprofitable. Later, pledges on new accumulators were suggested, to solve the economical impediment of collection (Miljøstyrelsen, 1988b), as was export of Danish accumulators to an existing recovery facility in Sweden (Miljøstyrelsen, 1988a). Since 1993 the organization ReturBat has been organizing collection and reuse of lead accumulators in Denmark with success: Approximately 17,000tons are collected every year. It was made obligatory to label accumulators containing more than 0.4% Pb (w/w) with reference to individual collection and reuse (Miljøministeriet, 1999). In 1984 regulation of the Pb-content in wastewater sludge applied as agricultural fertilizers was introduced. The limiting value was set to 400mg Pb/kg dry matter (Miljøministeriet, 1984). This limiting value was later changed to 120 mg/kg or 10,000 mg/kg total phosphate, which is still valid (Miljøministeriet, 2000c). Additives (stabilizers and pigments) in PVC were among the few expanding uses of Pb since 1985 (table II), and in 1992 substitution of Pb with other additives were discussed (Hoffmann, 1992). The conclusion was that substitution was possible, and from Marts 2001 import and sale of PVC, pigments, stabilizers containing more than 100mg Pb/kg was prohibited (Miljøstyrelsen, 2000a). Also substitution of Pb in paint and enamel was concluded to be possible investigated (Hoffmann, 1992), and paint containing lead-carbonates and lead-sulphates were banned in 1997 (Miljøministeriet, 1997), while all paints containing more than 100mg Pb/kg were prohibited from Marts 2001 (Miljøstyrelsen, 2000a). Substitution of lead in solder was evaluated to be partly possible with health, economy, solder temperature, and technical aspects as the reducing factors (Hoffmann, 1992). From December 2002 Pb-containing solder was banned with a few exceptions for high temperature soldering etc. (Miljøstyrelsen, 2000a). Possible modes of substituting Pb in the building sector (flashings, roofs, plumbing etc.) were also investigated. Most uses could be substituted although economy and manufacturability were reducing factors, and for leads of windows no substitution was available (Hoffmann, 1992). In 1997 economical consequences of introduction of environmental tax on the use of lead for flashings were evaluated (Hansen and Sørensen, 1997). However, such taxes were never introduced. Instead, the possibility of prohibiting Pb flashings completely was investigated (Maag *et al.*, 2001), and from March 2001 import and sale of Pb-roofs was prohibited, while from December 2002 also Pb-flashings were covered by the prohibition (Miljøstyrelsen, 2000a). The substitution of Pb for flashings was facilitated by development of PEM-flashings (named after the inventor Poul Erik Meier) between 1999 and 2002 (Meier, 2002). Pb in cable sheathings on land could be



substituted with durability as limiting factor, while no substitution possibilities were found for sheaths at sea (Hoffmann, 1992). Later the economical consequences of an eventual introduction of environmental tax on the use of lead for cable sheaths on land were evaluated (Hansen and Sørensen, 1997), while from December 2002 use of Pb-containing land based cable sheathings was prohibited (Miljøministeriet, 2000a). Similarly the economical consequences of introduction of environmental tax on the use of lead for ship keels and fishing tools were evaluated (Hansen and Sørensen, 1997), but from December 2002 use of Pb-containing fishing tools was prohibited (Miljøministeriet, 2000a). A new EU-directive in 1998 set focus on the content of heavy metals including Pb given off by water-pipes for drinking water. A report showed that commonly used materials often released Pb exceeding the criteria for drinking water quality and the Pb-release from some materials increased with increasing hardness of the water (Nielsen, 2001). Currently, the only measure taken against this Pb-source is that Pb in solders for plumbing was banned from December 2002. Finally, import and sale of electronic equipment containing Pb (with quite a few exceptions) will be banned from July 2006 (Miljøministeriet, 2004). Apart from regulating the mentioned areas, the comprehensive Danish lead-regulation, which was formulated in 2000 (Miljøstyrelsen, 2000a) in general prohibits import and sale of products containing more than 100 mg Pb/kg in homogeneous individual parts. This includes e.g. fireworks and products for hobby/ornamental purposes. It is still allowed to import and manufacture Pb-containing material for export purposes. Economic consequences of the comprehensive lead-regulation were analyzed (Gudum, 2002), and it was estimated that it costs the Danish society approximately 40million DKr. a year to substitute the 2000tons Pb used for roofs/flashings, fishing tools, cable sheathings and stabilizers in PVC, which constituted 90% of the Pb comprised by the regulation. The report pointed at the positive side effect for the Danish industry, of being ahead when other countries introduce regulation on lead in the future. One example is the development of PEM-flashings due to the expected prohibition of Pb-flashings (Meier, 2002). However, unexpected environmental consequences may arise from the substitution with metals having unknown environmental and toxicological effects (Kjølholt *et al.*, 2003). E.g. in soldering Pb is widely substituted with silver, which is less toxic for humans but considerably more toxic towards aquatic organisms (Juul *et al.*, 2003).

### 4.3 PB-CONTAMINATED SOIL

In 1995 the Danish EPA published a report in which Soil Quality Criteria (SQC) were recommended for a number of inorganic contaminants in surface soil. (Scott-Fordsmand and Pedersen, 1995). SQC were defined as the highest concentration in the soil environment where no ecological effects were predicted (Predicted No-Effect Concentration – PNEC), and it was stressed that these SQC's dealt only with the effect on structure and function of the soil environment itself, while it did not deal with the question on how to use the area, and therefore can not be used solely for the assessment of needs for soil cleaning. The SQC for Pb was set to 50mg/kg. Based on the known toxicological effects towards humans, a health-based SQC of 40mg Pb/kg was recommended (Nielsen *et al.*, 1995), while in 1996 a report on SQC in sub-soil meaning soil from 80cm below surface to the water table recommended 100 mg/kg Pb as a safe SQC (Miljøstyrelsen, 1996c). The health-based SQC of 40mg Pb/kg is still used by the Danish authorities, although it was attempted to increase the value several times in order to decrease the number and extend of contaminated sites. In 1996 a report evaluated the human uptake of Pb at sites with various uses. This report

recommended: 1) a maximum Pb-concentration where a site could be used freely, 2) an interval of Pb-concentrations where advising of the user on precautions against lead-uptake should be given, and 3) a concentration where the use of the site should be cut off (Soil Cut-off Criteria - SCC). The report advised that the use of Day-care-centers should be cut off at Pb-concentrations as low as 2-20mg/kg. The advises given for other utilizations are shown in table IV (Miljøstyrelsen, 1996a). The report lacks some reliability due to the fact that recommended cut off values for parks were lower than for residential areas. This result was obtained because a higher level of skin-contact was assumed for children in a park than in a garden. Nevertheless it is striking that free use for all scenarios is recommended only at values that are lower than background level.

TABLE IV  
Utilization based SQC and SCC values recommended in (Miljøstyrelsen, 1996a)

	Park	Residential area with no cultivation of food	Residential with kitchen garden
<b>Free use (SQC)</b>	< 2.2	< 8	< 1
<b>Advisory interval</b>	2.2-25	8-800	1-150
<b>SCC</b>	> 25	> 800	> 150

Advice given on Pb in soil (mg/kg) (Miljøstyrelsen, 1996a)

In another report from 1996, the Danish EPA again evaluated different scenarios for use of contaminated sites. In this report the maximum acceptable Pb-level in Day care centers was calculated to 20mg/kg. For kitchen gardens it was 6mg/kg, with the note that if root vegetables were not cultivated, it could be increased to 20. In flower-gardens 120mg/kg Pb was accepted and in parks 20mg/kg Pb (based on the same assumption of a higher level of skin-contact for children in a park than in a garden). In contrast to the previous report, also limiting values for consolidated areas were given, and here 100,000mg/kg Pb was estimated to be acceptable (Miljøstyrelsen, 1996b). Again in 1998 the idea of accepting higher concentrations than the SQC at certain sites was evaluated (Miljøstyrelsen, 1998), but exact limits were not suggested. Instead it was recommended that speciation and bioavailability of Pb should be evaluated for each specific site. Until this point all reports assumed that all Pb inhaled/digested with soil/dust is taken up, while in the next report, the human bio-accessibility of Pb in soil was evaluated (Grøn and Andersen, 2003). This report recommended evaluation of human bio-accessibility before remediation of sites contaminated with Pb, with the expectation that considerably higher concentrations than the SQC could be acceptable at individual sites. The acceptance of higher concentrations than the SQC based on decreased bioavailability of the present Pb-compounds implies that dissolution is a prerequisite for uptake, which is supported by comprehensive investigations e.g. (Davis *et al.*, 1993), although some uncertainty on the assumption exist because e.g. poorly soluble Mn was shown to be taken up by rats through inhalation when bound to particles < 1.3µm (Fechter *et al.*, 2002). Since it seemed impossible to argue for a general health-based increase of the soil-quality criteria except at consolidated areas, and the number of sites contaminated above the SQC greatly surpassed the treatment-capacity, an advisory interval was introduced including soils with Pb-concentrations between the SQC and a pragmatic decided SCC of 400mg Pb/kg. This SCC was set on the expectation that interventions and

advises could reduce the Pb-exposure of children approximately 10 times (Larsen, 1998). Exposure of children to contaminated soil in the advisory interval was, and continues to be, reduced through physically alteration of play-grounds in day-care-centers and public parks and advising of employees. Advising of families living in areas contaminated with Pb in the advisory interval on preventive behavior was also recommended (Miljøstyrelsen, 2000b). Among the recommended advises were deprecation from cultivation of own vegetables. Not so much because of the content of Pb in the vegetables themselves but rather because of the increased soil-contact and uptake of Pb through dust during cultivation. Advice was given to: wash hands, keep nails short, not to wear outdoor shoes indoor, keep floors clean etc. (Miljøstyrelsen, 2000b). Another report from the same year accordingly showed that the uptake of Pb in fruits and vegetables is low. Only in root crops an uptake was seen, however the concentration was generally lower than in the soil, and the Pb was concentrated in the surface of the vegetables why it was peeled of with the peel. The importance of avoidance of intake of soil with the cultivated crops was emphasized (Samsø-Pedersen *et al.*, 2000). An investigation was made on the effects of the activated interventions (Nielsen and Kristiansen, 2003). This investigation concluded that the physical interventions reduced exposure of children to Pb in day-care centers within the advisory interval to be almost equal to the reference exposure in a day-care-centre with < 40mg Pb/kg. Between the children, however, very uneven exposure was observed, probably due to different playing-behavior. Another report evaluated the knowledge, response, and behavior of families in connection with use of sites with Pb in the advisory interval (Nielsen and Elverdam, 2003). This report concluded that neither in public nor in private situations were the conditions for success fulfilled. Half of the families did not behave as prescribed, and the effect of the given information was unsatisfactory. The report concluded that the advising authorities should either reconsider the concept of the advisory interval or the character of the information. Finally in 2004 the latest attempt in increasing the SQC was made. A special evaluation of soil contaminated with Pb and PAH was initiated in order to update the toxicological information on the two substances and thereby the SQC. The initiative was motivated by the fact that: “these substances are of particular importance to the dimensions of the effort against soil contamination” (Miljøstyrelsen, 2004). The result of the special evaluation was that a health-based soil quality criterion for Pb should be 5mg/kg, which is below background-level, why it was argued that the existing soil-quality-criteria of 40mg/kg should be kept. Without questioning the reasonability of this decision, the irony of the result is obvious. Maybe it is about time to stop the attempts in increasing target values and instead find reasonable solutions for the contaminated soil?

## 5 Treatment Of Pb-Contaminated Soil

No efficient remediation method for Pb-contaminated soil exists at present. Apart from electrokinetic remediation, which was reviewed in 1994 (Ottosen, 1994), and is treated in detail in this thesis, phytoremediation, stabilization, soil wash and extraction were evaluated in (Andersen, 1998) with the purpose to decide if any of the methods qualified for further testing by the Danish EPA. The report mentioned three qualifications which are of prime importance for the relevance of heavy-metal remediation technologies in Denmark: They should be able to 1) remediate moderate concentrations of several heavy metals in mixture, 2) remediate Pb-contaminated soil, and 3) handle relatively clayey soils. The report concluded that phytoremediation and electrokinetic remediation have the highest potential. Soil washing was mentioned as

a potential method on the condition that the remaining soil-fines can be treated by electrokinetics. Extraction was only thought to be relevant if more environmentally friendly extractants were developed, and stabilization was thought to be of relevance primarily towards specific single contaminants which cannot be treated with any other methods (Andersen, 1998). Later electrokinetic remediation and soil wash were again recommended for future aims at remediating mixed contaminations of heavy metals and organics (Lindskov *et al.*, 1999). In 2000 a report on phytoremediation of heavy metals was published (Andersen *et al.*, 2000). Pb was unfortunately shown to be the least concentrated metal in the selected plants, and although elevated concentrations in roots were observed, less than 0.1% of the Pb was taken up during the three months of the experiment. This is in accordance with results of international investigations. Experiments with soil washing showed some success, although the lack of a density-separation process impaired the results for Pb-contaminated soils (Lindskov and Oemig, 2001). The potential of remediating Pb-contaminated soil by electrokinetic methods has not been investigated by the Danish authorities; but a report on electrokinetic remediation of Cu, Cr and As from wood impregnation showed that the method has potential for such contaminations (Ottosen and Villumsen, 2001).

The strategy of the Danish effort against contaminated sites has given high priority to remediation of ground-water threatening contaminations. This strategy is a logical consequence of the dependency of the Danish water-supply on ground-water resources. Since Pb-contaminations are rarely included in this category, they have been given low priority. Only sites with sensitive use (i.e. day-care centers) and > 400mg Pb/kg are explicitly remediated, however due to construction activities in the cities, Pb-contaminated soil still finds its way to remediation- and disposal-sites around the country. In 1998 it was estimated that around ¼ million tons of heavy metal contaminated soil was handled every year in Denmark, of which the main part was contaminated with Pb (Andersen, 1998). Current law prescribes that soil with <40mg Pb/kg can be reused for building and construction purposes without any special permission. Soil with >40 mg Pb/kg can be reused with permission if the area is to be consolidated, however if the leachate from the soil contains more than 10µg Pb/l, the use is further restricted. A consolidated area is understood as an area covered by asphalt, concrete, flagstones or minimum 1m of soil with < 40mg Pb/kg (Miljøministeriet, 2000b). Less soil is reused than desired, why an investigation of the barriers against reuse of contaminated, remediated and clean soil was made (Nejrup *et al.*, 2002). The barriers identified were: reuse is not “rewarded”; no tax on deposition of contaminated soil; only negligible tax on raw materials; lack of sites for separation, identification and interim storage of soil; insufficient knowledge of reuse options; no demand for reuse; resentment against spreading of contaminated soil to new areas; the soil is not technically suitable; there is no reliance on the soil quality; prolonged administrative procedures; unnecessary large amounts of contaminated soil are produced due to inadequate separation at source; it is not possible to receive the soil at the right moment. Due to these reasons, the majority of the Pb-contaminated soil is still deposited of at landfills. In fact there is tax on deposition of contaminated soil, but obviously all users are not aware (Hansen, 2006). The flow of contaminated soil in Denmark in 2001 was made up to 2.7 million m<sup>3</sup> (Mortensen *et al.*, 2004) of which approximately 50% was sent for remediation (soil contaminated with organics), and the rest for storage, deposition, or reuse. 92% of the remediated soil was subsequently deposited off as lightly contaminated primarily due to their content of heavy metals, which were not remediated.

## 6 Conclusions

The Pb-concentration in country-side soils in Denmark is only slightly elevated and contamination of such soils is not an urgent problem. In urban areas Pb is the most frequently observed contaminant in Denmark together with PAH. Particularly in Copenhagen the diffuse contamination of surface-soil is widespread, and at national scale, 16% of the almost 11,000 mapped point source contaminations include Pb. The major use of Pb at present is in accumulators. Extensive legislation on Pb-containing-products has limited the dissipation from leaded gasoline, lead shots, municipal solid waste, and fireworks as well as the consumption of Pb for flashings and roofs, cable sheathings and many other minor uses. Pb is toxic primarily towards children. There is a close relationship between PbB and intelligence, and even at low PbB learning disabilities and childhood hyperactivity is observed. After the reduction of Pb in gasoline, soil is the main source for Pb-uptake by children. A close relationship between the concentration of Pb in soil and PbB has been reported. No efficient method for remediation of Pb-contaminated soil exists, but the ability to remediate Pb was emphasized as an important quality of any potential remediation method. Although treatment of Pb-contaminated sites has been given low priority due to the low risk of groundwater contamination, construction activities lead to the handling of several million tons of Pb-contaminated soils every year.

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### 3. Application of Microbial Products - Recapitulation

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Microorganisms interact with metals in a number of ways, which could be explored for applicability in promotion of electro-dialytic remediation (EDR) of heavy metal polluted soil. The purpose of this work was to identify and investigate such possibilities with focus on remediation of Pb-contaminated soil. In the present chapter, the various ideas are identified and discussed. After an introduction of the main interactions between microorganisms and heavy metals and the principles of EDR, the chapter contains results of experimental work, currently not considered for publication elsewhere. Results submitted for publication in international journals are referred to the original papers, which constitute the succeeding chapters of this thesis.

#### 1 Interactions Between Microorganisms and Heavy Metals

Microorganisms need certain metal ions to subsist. The basic supplement of metal ions takes place through an unspecific, energy efficient uptake system, which relies upon chemical osmotic or electrical potential gradients over the cell-wall, and does not distinguish between essential and toxic metals. In the case of metal-deficiency, specific, but energy consuming, pathways may in addition be expressed for uptake of most essential metals (Nies, 1999). Because Pb has no known biological function, it is primarily taken up accidentally through the unspecific pathways.

Among microbial responses to toxic metals such as Pb, differentiation between tolerance and resistance is made. Tolerance defines the ability of a microorganism to tolerate increased metal-concentrations without changing functions: A population may e.g. develop heavy metal tolerance by selection of organisms with a weak expression of the genes for unspecific metal-uptake. In contrast, metal resistance is understood as specific metal-induced mechanisms that act against toxicity (Gadd, 1992). These mechanisms include: efflux systems; metal-precipitation; metal-complexation; and, for certain metals, volatilization or redox-reactions to less toxic redox-states (Silver, 1983; Sterritt and Lester, 1986; Barton *et al.*, 1992; Barton *et al.*, 1994).

Genes for resistance are frequently carried by plasmids (Silver and Phung, 1996), and may therefore be shared among microorganisms in a contaminated environment. Evidence exists that such resistance is based predominantly on efflux mechanisms (Nies, 1999). Some microorganisms, however, have chromosomal determinants of toxic metal resistance (Silver and Phung, 1996), which allows them to be categorized

as extremophiles due to their adapted preference for heavy metal contaminated environments (Nies, 2000).

In a study of microbial communities in soils contaminated with Pb, it was shown that the fraction of microorganisms with Pb-resistance was almost identical in uncontaminated and severely contaminated soil samples. The microbial community in highly contaminated soil, however, diverged much in composition from the community in uncontaminated soils, and the number of colony-forming units (CFU) in a highly contaminated soil was only 1/3 of that in uncontaminated samples (Konopka *et al.*, 1999). DNA-sequencing of the microbial community in contaminated and uncontaminated soils showed a dramatic decrease in the bacterial diversity due to Pb-contamination from 16,000 bacterial genomes/g soil in an uncontaminated soil to 6,400 genomes/g in a slightly contaminated soil and 2,000 genomes/g in a severely contaminated soil. Also shifts among the populations of larger phylogenetic groups due to the presence of heavy Pb-contamination were established (Sandaa *et al.*, 1999).

All together microbial processes may lead to dissolution, complexation, adsorption, precipitation or transformation of toxic metals. Biological treatment of Pb-contaminated soil may focus on either stabilization to reduce bioavailability or mobilization with removal as the final target. In this study only the last issue is considered with the perspective to use EDR for succeeding or simultaneous contaminant removal. Among the mentioned processes, mobilization of Pb may be obtained through either complexation with mobile substances or dissolution. Complexation may occur with: (1) extracellular polymers and cell-constituents; (2) metallophores such as siderophores; (3) organic ligands of acids produced by certain fungi and bacteria (heterotrophic leaching); or (4) biosurfactants. Dissolution may occur due to (1) acidification; or (2) a second alternative relevant only to organically bound Pb: degradation of organic compounds. In addition, mobilization of Pb could be thought to occur by microbially mediated transformation into volatile methyl-lead compounds (Thayer, 1995). While the opposite reaction, namely metabolic degradation of trimethyl-lead by certain fungi and bacteria was documented (Macaskie and Dean, 1990), occurrence of microbially mediated Pb-methylation remains to be established.

## 2 Electrodialytic Soil Remediation

Electrodialytic remediation (EDR) is a variation of electrokinetic remediation (EKR), in which ion-exchange membranes are applied as barriers between soil and electrolyte solutions. Under the influence of a direct current (DC) electric field, transport of free ions, soil solution and small charged particles is induced into the soil. This transport may be utilized for removal of contaminants. The fundamental principles of the transport processes are described below in order to establish an understanding of the remediation process prior to the discussion of potential applications of microbial products.

### 2.1 ELECTROMIGRATION

Electromigration refers to the movement of individual ions within the soil solution driven by the electrical potential gradient. The flux of an ionic specie caused by electromigration is described by equation (1) (Acar and Alshawabkeh, 1993):

$$J_j^m = -u_j^* c_j \nabla U \quad (1)$$

In this equation  $c_j$  is the concentration of specie  $j$ ,  $\nabla U$  is the gradient of the electrical potential, and  $u_j^*$  is the effective ionic mobility.  $u_j^*$  is related to the ionic mobility in free solution according to equation (2):

$$u_j^* = \frac{u_j}{x_e} \quad (2)$$

$x_e$ , the tortuosity, accounts for the longer traveling distance in soil compared to free solution. The ionic mobility can be related to the diffusion coefficient through the Einstein relation (Atkins, 1994):

$$u_j = \frac{D_j z_j F}{RT} \quad (3)$$

Here  $D_j$  is the diffusion coefficient in free solution, and  $z_j$  the valence of the ion.  $D_j$  can be calculated according to the Stokes-Einstein equation:

$$D_j = \frac{kT}{6\pi\eta a_j} \quad (4)$$

$\eta$  is the viscosity of the fluid, and  $a_j$  is the radius of the particle in question. It is important to notice that for ions,  $a_j$  is the hydrated ionic radius as opposed to the free ionic radius. Bringing together (3) and (4), equation (5) is obtained:

$$u_j = \frac{z_j e}{6\pi\eta a_j} \quad (5)$$

It appears that the electromigration of a specific ion relies upon the ion-concentration and -valence, as well as the size of the hydrated ion, the viscosity of the fluid and the electric potential.

Because diffusion coefficients for hydrated ions are more readily available than their hydrated radius itself, equation (3) is more useful for practical calculation of the ionic mobility. The order of  $u_j$  [ $10^{-8} \text{ m}^2/(\text{V}\cdot\text{s})$ ] for chosen ions is given below (Lide, 1997).

$$\begin{array}{cccccccccccc} \text{H}^+ & > & \text{OH}^- & > & \text{Pb}^{2+} & = & \text{Cd}^{2+} & > & \text{Fe}^{3+} & > & \text{Cr}^{2+} & > & \text{Al}^{3+} & > & \text{Ca}^{2+} & > & \text{Cu}^{2+} & = & \text{Fe}^{2+} & > & \text{Zn}^{2+} & > & \text{Na}^+ \\ 36.2 & & 20.6 & & 7.36 & & 7.36 & & 7.06 & & 6.94 & & 6.32 & & 6.17 & & 5.6 & & 5.6 & & 5.47 & & 5.19 \end{array}$$

The ionic mobility of most ions is found within a quite narrow range. Exceptions are hydrogen and hydroxide ions, which are 3 to 5 times more mobile than other ions, with the hydrogen ion being the more mobile of the two. This fact is important for the chemistry in the remediation zone.

## 2.2 ELECTROOSMOSIS

In addition to electromigration of ions, the electrical potential causes water to flow. The flow-direction will in most cases be towards the cathode because cations in the electrical double layer around the soil particles exert more momentum to the pore

fluid than do the fewer mobile anions (Yeung and Datla, 1995). At low pH-values, however, charge reversal of the soil may occur, and cause the electroosmotic flow to change direction. The electroosmotic flux can be described by the following equation (Acar and Alshawabkeh, 1993):

$$J_j^e = -k_e \frac{c_j}{c_w} \nabla U, \quad (6)$$

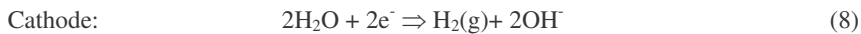
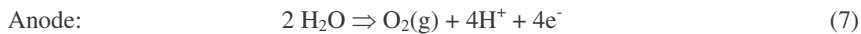
where  $k_e$  is the electroosmotic permeability and  $c_w$  the concentration of water ( $\approx 1$ ). Because the electroosmotic flow does not depend on the hydraulic conductivity, it may contribute significantly to the fluid flow in soils with low hydraulic conductivity. The electroosmotic mobility is usually in the order of  $5 \cdot 10^{-9} \text{ m}^2/\text{V}\cdot\text{s}$  (Lageman *et al.*, 1989). For dissolved ionic elements moving with the water, this is an order of magnitude smaller than the ionic mobility, thus electroosmosis is important mainly for transport of large ions and neutral species. In EDR the electroosmotic transport is reduced significantly by the application of membranes, making EDR suitable for selective transport of small, charged species.

### 2.3 ELECTROPHORESIS

Electrophoresis refers to the movement of charged particles in water in an applied electric field (Lageman *et al.*, 1989). The electrophoretic mobility varies between  $0.1 \cdot 10^{-9}$  and  $3 \cdot 10^{-9} \text{ m}^2/(\text{V}\cdot\text{s})$  (Lageman *et al.*, 1989). For ionic elements, this is more than one order of magnitude smaller than the electrokinetic mobility, and the process is rarely encountered in EKR/EDR.

### 2.4 ELECTRODE REACTIONS

As the current passes and various substances are removed from the soil, the chemical equilibrium among the soil-phases is shifted and physico-chemical reactions such as adsorption/desorption and dissolution/precipitation become important. The chemical equilibrium is in particular affected by the dominating electrode reactions: Application of a DC electric field to inert electrodes immersed in water induces water-splitting reactions and vaporization of gases according to equations (7) and (8).



At the anode, reaction (7) results in production of hydrogen-ions, while at the cathode (8) hydroxide-ions are produced. In EKR, these ions enter the soil and result in the development of an acidic front evolving from the anode towards the cathode, and an alkaline front evolving from the cathode towards the anode. In EKR intrusion of the alkaline front into the soil is most often hindered by neutralization of the catholyte with acid. In EDR an anion-exchange membrane between soil and anolyte, and a cation-exchange membrane between soil and catholyte hinders the intrusion of the electrolyte-products into the soil as illustrated in figure 2.1. Despite the introduction of these membranes, an acidic front is still developing within the soil specimen due to water-splitting at the surface of the anion-exchange membrane. This process is described in further detail in chapter 6 of this thesis. Depending on the present metals

and the electrode potential, electrodeposition of metals may in addition occur at the cathode:

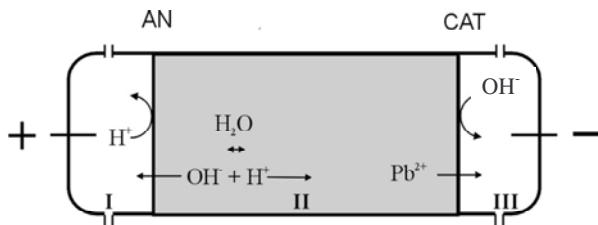


Figure 2.1: Principles of Electrodialytic Soil Remediation.

The nature of the described processes, imply that application of microbial products preferentially should result in formation of small, charged Pb-species, which are soluble under neutral/acidic conditions to make electromigrative transport out of the soil as efficient as possible.

### 3 Aims and Progress of the Work

The initial focus of this study was on mobilization of Pb in soil through complexation with microbial products such as extracellular polymers, whole cells and disintegrated cell-material, on which experimental results are summarized in section 3.1, this chapter. In parallel, reference experiments on EDR of Pb-contaminated soil were made to elucidate the influence of soil-type and Pb-speciation on remediation. This work expanded, and resulted in submission of two papers, found as chapters 4 and 5 of this thesis. The next focus was set on Pb-mobilization by complexation with siderophores, on which results and considerations are given in section 3.2 of this chapter. As this topic was addressed, the advantage of remediating fine-grained material by EDR in suspension had become evident from work with other contaminated materials such as fly ashes, sludge and sediment (Pedersen, 2002; Pedersen, 2003a; Jakobsen *et al.*, 2004; Pedersen *et al.*, 2004; Ferreira *et al.*, 2005; Nystroem *et al.*, 2005). Because application of microbial products seemed more practical in the suspended situation, EDR of soil fines in suspension was subjected to an investigation, which gave the encouraging results reported in chapter 6. The third microbiologically related topic addressed was autotrophic leaching in combination with EDR in suspension, on which results and considerations are given in section 3.3, this chapter. Finally heterotrophic leaching, likewise combined with suspended EDR, was addressed. The first screening of this option seemed promising enough to initiate a full series of experiments, of which results are reported in chapter 7 of this thesis. At this point it became clear that the unenhanced version of EDR in suspension was the most promising and interesting outcome of the present work. Therefore, the last phase of the research was dedicated to explore this method concerning the kinetics of Pb-removal and dissolution of soil-constituents (chapter 8), and the feasibility of treating soil-fines contaminated by other common toxic elements than Pb (chapter 9).

### 3.1 BIOSORPTION

The first focus of this study was on the option of using microbial products such as bacterial extracellular polymers to mobilize Pb in soil. Preliminary experiments were made with the yeast *Saccharomyces cerevisiae* (bakers yeast), which as a waste product from industrial processes is cheap and easily obtainable in large amounts. Lead adsorption to commercially available *S. cerevisiae* cells was studied, and the effect of addition of disintegrated cells of *S. cerevisiae* to soil prior to EDR was investigated. Column studies made by MSc-student Kirstine Bondo Pedersen under my co-supervision also contributed to elucidation of the feasibility of this technology by investigating the effect of whole and disintegrated cells of two other organisms: *Zoogloea ramigera* and *Pseudomonas fluorescens*, on the mobility of Pb in contaminated soil subjected to a DC field.

#### 3.1.1 Introduction

The number of studies on microbial biosorption of Pb for treatment of industrial wastewaters is overwhelming (e.g. Veglio and Beolchini, 1997; Volesky, 2001). Most studies concluded that treatment of metal-bearing wastewaters by adsorption to microbial matter has great potential, and that Pb is one of the metals with the highest affection for adsorption to microbial biomass (e.g. Bailey *et al.*, 1999). In most cases it made little difference whether the adsorbing cells were dead or alive, whole or disintegrated (e.g. Kapoor and Viraraghavan, 1995), although some species were shown to take up Pb actively during growth (e.g. Vesper *et al.*, 1996).

Microbial biosorption is also thought to be of major importance to speciation and mobility of heavy metals in soils (Ledin, 2000), where sorption to immobile cell- and biofilm-material may decrease mobility, while sorption to mobile extracellular material may increase mobility. The potential of extracellular polymers to enhance mobility of the metals in contaminated soil was established (Chen *et al.*, 1995a), and extracellular polymers significantly enhanced Cd mobility in soil compared to electrolyte solutions (Chen *et al.*, 1995b). Also, a general reduction in Pb-adsorption to sand was demonstrated in the presence of extracellular polymers (Chen *et al.*, 1995b). It was shown that the retardation factor for the studied extracellular polymer in aquifer sand was < 21, while it was 19,000 for Pb. In other words Pb bound to the extracellular polymer could be expected to travel almost 1,000 times faster through the sand (Czajka *et al.*, 1997).

#### 3.1.2 Materials and Methods

*S. cerevisiae* was obtained as bakers yeast in a supermarket. *Pb-analysis* were made by AAS. In *adsorption experiments* 1g of bakers yeast was added to plastic bottles with solutions consisting of: 25ml, 20ml, 15ml, 10ml, 5ml, 2.5ml, 1ml, 0.25ml, and 0.05ml respectively of 1000mg Pb/L solutions at pH 2.0 and pH 7.0, filled up to 25ml. The samples were shaken for 1 hour at 200 rpm. pH was measured and adjusted with HNO<sub>3</sub> to 2.0 or 7.0. This procedure was continued until pH remained constant at 2 or 7. The adsorption was allowed to equilibrate for 1 week while shaken at 200rpm. The samples were filtered through a 0.45µm filter, and the lead content in the filtrate was analyzed by AAS. The yeast was rinsed with 25 ml distilled water, and the lead content of the rinsing water was analyzed by AAS. The yeast was dried over night at 50°C, weighed, and digested according to the Danish standard procedure DS259. The Pb content was measured by AAS. *Electrodialysis experiments* were made with two soils (soils 8 and 9 as characterized in chapter 4) in plexiglass® cells with three compartments (Figure 2.1). The center compartment contained the soil specimen

which was 10 cm long and 8 cm in diameter. The anolyte and the catholyte were separated from the soil specimen by anion- and cation-exchange membranes (Ionics®, AR204SZRA and CR67 HVY HMR427, respectively). Electrolytes were circulated between electrolyte chambers and glass reservoirs by a mechanical pump (Masterflex® model 7553-76). Platinum-coated electrodes (Permascand) were used as working electrodes. The electrolytes initially consisted of 500mL 0.01 M  $\text{NaNO}_3$  adjusted to pH 2 with  $\text{HNO}_3$ . Prior to the beginning of each experiment, soil specimens were mixed with deionized water to a moist but unsaturated consistency. A constant current of  $0.2\text{mA}/\text{cm}^2$  was maintained in all experiments. pH in the electrolytes, current and voltage were observed approximately once every 24 hours. The experiments ran for 8 weeks each. After each experiment, the soil specimen was divided into five sections perpendicular to the current-direction. Pb, pH and water content were measured in each slice. Membranes were cleaned overnight in 1M  $\text{HNO}_3$  and electrodes were cleaned overnight in 5M  $\text{HNO}_3$ . Volumes of the cleaning acids as well as the electrolytes were measured followed by analysis of the Pb-concentration by AAS. Two experiments were made with each soil: one with addition of 36 g dw disintegrated (autoclaved) *S. cerevisiae* cells/1000 g soil prior to remediation and one reference experiment with no additions.

### 3.1.3 Results

The adsorption study showed (figures 3.1-3.2) that Pb does adsorb to *S. cerevisiae*, and that adsorption is higher at neutral pH than in acid, which is in accordance with the literature. The adsorption coefficients were however much higher than those reported in the literature, and unsatisfactory mass-balances suggest that these results be applied with care. Despite these insecurities and the high variance on results obtained at neutral pH (figure 3.2) the tendency reported in the literature, that microbial matter including *S. cerevisiae* may adsorb Pb in amounts that constitute a significant fraction of their own weight is supported by these results. This gives reason to believe that whole or disintegrated cells of *S. cerevisiae* could affect the mobility of Pb in soil. Because disintegrated cell constituents are more amenable to electromigrative transport due to their small size, the effect of disintegrated cells of *S. cerevisiae* on the mobility of Pb in soil during EDR was subsequently investigated.

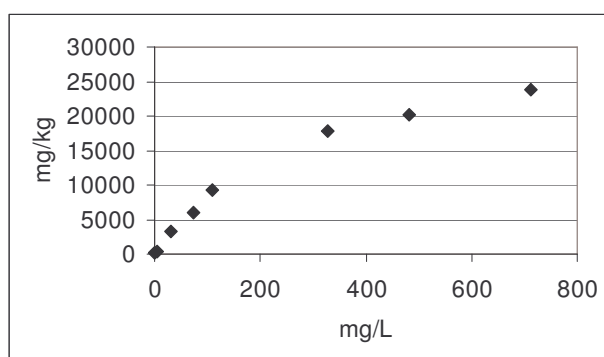


Figure 3.1: Adsorption of Pb to *S. cerevisiae* at pH 2.  $K_d = 39.4$ .



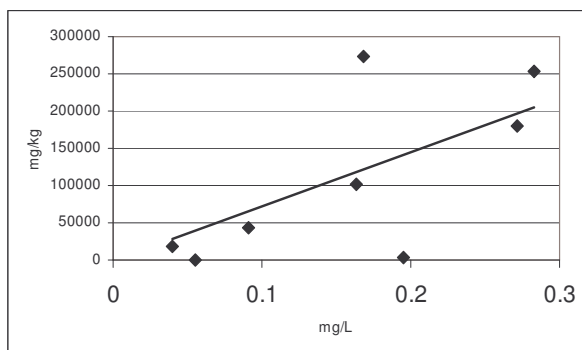


Figure 3.2: Adsorption of Pb to *S. cerevisiae* at pH 7,  $K_d = 726531$ .

Results of the electrodialysis experiments are given as the normalized Pb-concentrations in the soil-specimens as a function of the distance to the anode (figures 3.3-3.4). Only insignificant amounts of Pb had been removed from the soil in all four experiments. Nevertheless, the results indicated that Pb-transfer towards the anode dominated in the experiments where disintegrated *S. cerevisiae* cells had been applied (the center of mass of Pb moved towards the anode), in contrast to the reference experiments where transfer towards the cathode was dominating (the center of mass moved towards the cathode). The results thereby suggested that the mobile fraction of Pb had been shifted from being predominantly positively charged to being negatively charged by addition of disintegrated *S. cerevisiae* cells, which could be a sign of Pb-adsorption to mobile constituents of the disintegrated *S. cerevisiae* cells. The profiles obtained after addition of disintegrated *S. cerevisiae* cells much resemble those of soil containing a large organic fraction as discussed in chapter 5.

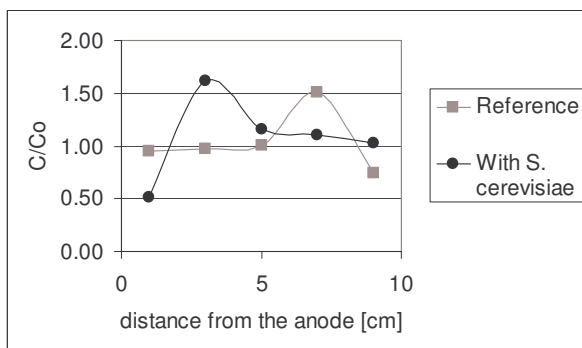


Figure 3.3: Pb-profiles after 8 weeks of EDR of soil 9 with and without *S. cerevisiae*.

Kirstine Bondo Pedersen investigated the effect of living and disintegrated cells of *Zoogloea ramigera* (a bacteria known for its ability to produce extracellular polymers and adsorb heavy metals in wastewater treatment systems) and *Pseudomonas fluorescens* (a common soil bacteria) on mobility of Pb in contaminated soil with and without application of current (Pedersen, 2003b). She found that application of these microorganisms and their products, whether living or disintegrated resulted in the accumulation of Pb in the columns regardless of whether current was applied or not;

the effect of the microorganisms, however, more distinct in the current columns. These results together with the simultaneously obtained results referred in chapter 5 on the negative effect of organic matter on EDR of Pb-contaminated soil led me to seek other means of mobilizing Pb during EDR of contaminated soil.

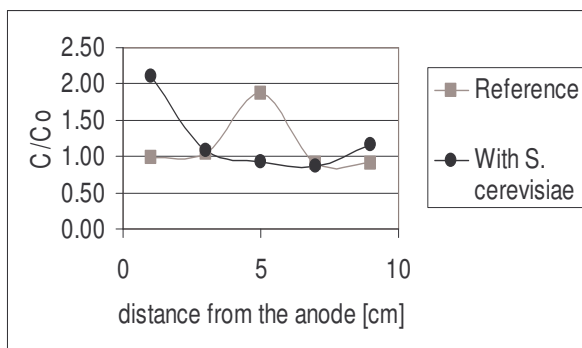


Figure 3.4: Pb-profiles after 8 weeks of EDR of soil 8 with and without *S. cerevisiae*.

### 3.2 SIDEROPHORE MOBILIZATION

The feasibility of application of siderophore-producing microorganisms for mobilization of Pb during EDR of soil-fines in suspension was studied. The study included: (1) investigation of the influence of growth-media on yield and siderophore-production of a *Pseudomonas fluorescens* sp.; (2) extraction of Pb from industrially contaminated soil-fines by a commercially available siderophore; and (3) detection of siderophore production during EDR of soil fines in suspension.

#### 3.2.1 Introduction

In aerobic environments iron exists almost exclusively as insoluble Fe(III). Therefore, in order to supply themselves with adequate amounts of iron, microorganisms developed a specific uptake system, which involves exclusion of chelating agents with iron-binding constants as high as  $10^{52}$  (Hersman *et al.*, 1993). Such compounds are named siderophores. Due to their powerful iron-mobilizing ability, siderophores have been suspected to impact the behavior of other metals than iron, including toxic and radioactive elements in the environment.

Most numerous are the studies on the effect of siderophores on actinides such as uranium and plutonium, for which siderophore-mediated dissolution and leaching was documented (e.g. Hersman *et al.*, 1993; Kalinowski *et al.*, 2004; Yoshida *et al.*, 2004). A few studies elucidate the effect of siderophores on Pb in soil. In one of them the first stability constant for complexation between Pb and the most frequently studied siderophore desferrioxamine B (DFO-B) was determined to be  $10^{10.0}$ , which recognizes DFO-B's Pb-chelating ability to lie between those of EDTA and citrate (Hernlem *et al.*, 1996). Adsorption of Pb to goethite was investigated in the presence of an actinide-specific catecholate derivative of DFO-B, DFOMTA. At pH 7.8 the adsorption was decreased from 100% to approximately 5% in the presence of DFOMTA, while below pH 5, Pb-adsorption to goethite was increased by DFOMTA (Kraemer *et al.*, 2002). For other heavy metals (Cu, Cd and Zn) the same effect was seen with DFO-B on goethite (Neubauer *et al.*, 2002), and Kaolinite (Neubauer *et al.*,

2000), while with montmorillonite DFO-B only reduced adsorption at pH higher than 8.5 (Neubauer *et al.*, 2000). Furthermore it was observed that the effect of DFO-B on heavy metal adsorption to goethite disappeared as a response to addition of soluble Fe(III) (Neubauer *et al.*, 2002). Other studies reported on siderophore-mediated absorption of heavy metals in bacteria. E.g. a remediation method suitable for sandy soils was developed on the basis of the ability of the bacteria *Ralstonia metallidurans* CH34 to exclude siderophores and absorb heavy metals. A density-separation method could be applied for separation of the heavy metal loaded biomass and the clean sand, because the biomass-density was lower than that of sandy soil. With this method Pb-concentrations were reduced from 459mg/kg to 74mg/kg in industrially contaminated soil (Diels *et al.*, 1999). Another study detected increased absorption of aluminum in *Bacillus megaterium* in the presence of siderophores (Hu and Boyer, 1996).

### 3.2.2 Materials and Methods

DS178, a siderophore producing strain of *P. fluorescens* isolated from a heavy metal contaminated site in Belgium was obtained from Dr. L. Diels, VITO, Belgium. *Detection of siderophores* was made by the Chrome Azurol S (CAS) assay as described by (Schwyn and Neilands, 1987): 6.0 ml 10 mM hexadecyltrimethylammonium bromide was added to a 100 ml volumetric flask and diluted to approximately 25 ml. 1.5 ml iron(III) solution (1 mM  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 10 mM HCL) and 7.5 ml 2 mM CAS-solution were mixed, and rinsed slowly into the 100 ml volumetric flask under stirring. 4.307 g anhydrous piperazine was dissolved in water and 6.25 ml 12 M HCl was added carefully to make a buffer solution at pH 5.6. The buffer solution was rinsed into the volumetric flask, which was filled to the mark by distilled water. CAS-assay solution without iron was made and used as 0-reference. Both solutions were stored in darkness in polyethylene flasks. Siderophore-production was assessed by spectrophotometer: The dark-blue CAS-assay solution changed color over grey to orange and yellow as a function of the siderophore-concentration, thereby giving a rise to a negative correlation between the absorbance and the concentration of siderophores as observed by (e.g. Schwyn and Neilands, 1987; Alexander and Zuberer, 1991). The effect of centrifugation and filtration on the absorbance was determined to be negligible (results not shown); likewise the absorption was observed to be constant from 1 to at least 630hours after mixing of the CAS-assay solution and the siderophore-containing solution (results not shown). In *growth experiments*, 3 ml culture was taken out approximately once pr. hour for the first 14 hours followed by less frequent sampling. The cell-density was assessed by spectrophotometer. A 1 ml sub-sample was taken out and centrifuged at 10 000 rpm for 10 min. The supernatant (0.7 ml) was transferred to a micro-cuvette, and 0.7 ml CAS solution was added. The color-change was observed after one hour and the absorbance measure. Siderophore production was determined as a function of growth in two complex growth-media, and three chemically defined growth-media: *LB-medium* containing 5.0 g yeast extract, 10.0 g trypton and 10.0 g NaCl pr 1000 ml; *PK-medium* containing 5.0 g peptone and 3.0 g meat extract pr 1000 ml. *M9C-medium* containing 200 ml modified M9 salt-dissolution (6 g  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , 2 g  $\text{KH}_2\text{PO}_4$ , 2.5 g NaCl, 5.0 g  $\text{NH}_4\text{Cl}$ , and 4.0 g pipes to 1000 ml), 775 ml buffer-solution (2.5 g pipes, 1 g  $\text{Na}_2\text{HPO}_4$ , and 0.5 g  $\text{KH}_2\text{PO}_4$  to 800 ml), 2 ml 1M  $\text{MgSO}_4$ , 0.1 ml 1M  $\text{CaCl}_2$ , and 25 ml citrate-solution (5 g  $\text{NaH}_2\text{-citrat}$  to 25 ml). *M9G-medium* containing the same ingredients as the M9C-medium apart from the citrate solution, which was exchanged for a glucose-solution containing 5 g glucose to 25 ml. *M9GC-medium* containing the same ingredients as the M9C-medium apart from the citrate solution, which was exchanged for a solution

containing 2 g casaminoacids and 5 g glucose to 25 ml. An industrially contaminated Danish *soil* of unknown origin (referred to as soil 10 in chapters 4 and 5), obtained from a pile after excavation, was used as experimental soil. The soil fines were obtained by simple wet-sieving of the original soil with distilled water through a 0.063 mm sieve. Concentrated slurry of fines was obtained by centrifugation at 3000 rpm for 10 min. and decantation of the supernatant. The soil fines were kept in slurry and stored at 5°C in access of oxygen. The Pb-content of the soil-fines was 1300 mg/kg. *Extraction of Pb* from industrially contaminated soil-fines by the commercially available siderophore deferroxamine M (DFO-M) obtained from NOVARTIS was made by allowing 5.00 g soil fines to equilibrate with 25 ml 0.2 M DFO-M at room temperature for 7 days while shaken at 180 rpm. The metal content was measured in the liquid phase by AAS. An *Electrodialysis experiment* was made in a cylindrical Plexiglas-cell with three compartments. Figure 2.1 illustrates the electrodialytic cell. Compartment II, which contained the soil-slurry was 10 cm long and 8 cm in inner diameter. The slurry was kept in suspension by constant stirring with plastic-flaps attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). The anolyte was separated from the soil specimen by an anion-exchange membrane, and the catholyte was separated from the soil specimen by a cation-exchange membrane. Both membranes were obtained from Ionics® (types AR204SZRA and CR67 HVY HMR427). Electrolytes were circulated by mechanical pumps (Totton Pumps Class E BS5000 Pt 11) between electrolyte chambers and glass bottles. Platinum coated, rod-shaped electrodes from Permascand® were used as working electrodes and the power supply was a Hewlett Packard® E3612A. The electrolytes initially consisted of each 500mL 0.01 M NaNO<sub>3</sub> adjusted to pH 2 with HNO<sub>3</sub>. Conductivity in chamber II, pH in all chambers, and voltage between the working electrodes were observed approximately once every 24 hours. pH in the electrolytes was accordingly kept between 1 and 2 by manual addition of HNO<sub>3</sub>/NaOH. pH in chamber II was kept between 6 and 7 by manual addition of NaOH. The experiment lasted 22 days and had a liquid-to-solid-ratation (L/S) of 3.5. 1.8 g glucose was added initially to obtain the same concentration as in the M9G and M9GC media. 1.8 g glucose was added ever 4.th day. Siderophore-detection by the CAS-assay and glucose detection with strips was performed daily in chambers I, II and III. 5 ml of *P. fluorescens* DS178 culture adapted to growth on M9G-media was added initially. The current was applied after 48 hours.



Figure 3.5: Photograph of electrodialytic cell.

### 3.2.3 Results and Discussion

It was previously observed that rich media, like LB, should be avoided when applying the CAS-assay, because they interfere with the assay in an irreversible manner (Schwyn and Neilands, 1987). Therefore the interference of the complex substrates used in this study was examined. The results in figure 3.6 show how the LB-media decreases the absorbance of the CAS-assay solution by 15%, thereby indicating the presence of iron-complexing substances in this complex media. No interference was observed by the PK-media.

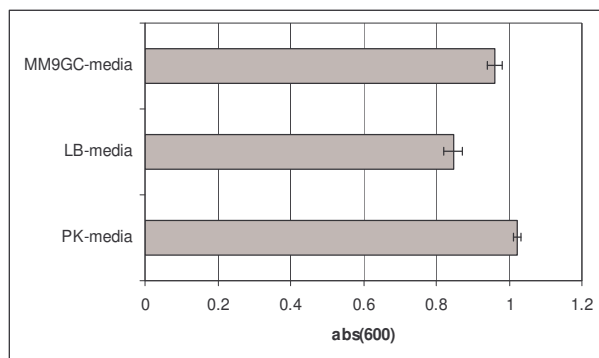


Figure 3.6 Interference of media with absorbance in the CAS-assay. Abs(600) was measured one hour after mixing 0.7 ml pure media with 0.7 ml CAS-assay solution.

Figures 3.7 to 3.9 illustrate growth and siderophore-production of *P. fluorescens* DS178 in the five different media. With PK-media (figure 3.7) only a slight reduction in the absorbance of the CAS-assay solution was observed during growth, indicating that the PK-media is supplying the culture with sufficient amounts of iron to either suppress siderophore-production or to saturate the produced siderophores, rendering them undetectable by the CAS-assay. By growth on the M9GC-media (figure 3.8), iron-deficiency and siderophore-production was clearly indicated by the observed absorbance reduction of the CAS-assay solution. Despite iron-deficiency, growth seemed to be stimulated by the defined M9GC-media compared to the complex PK-broth. In contrast figure 3.9 illustrates significant growth reduction on the defined M9G and M9C-media compared to the complex LB-broth. By applying the CAS-assay solution, significant and immediate absorbance reduction was demonstrated in the M9C-media. By testing with the pure M9C media, the same reduction was observed, and the effect was therefore attributed to iron-complexation by citrate and not siderophore production. Growth on the M9G-media resulted in a developing siderophore-production like that observed on the M9GC-media. Siderophore-production was not detected when grown on the LB-media, suggesting that both complex media supplies sufficient amounts of iron.

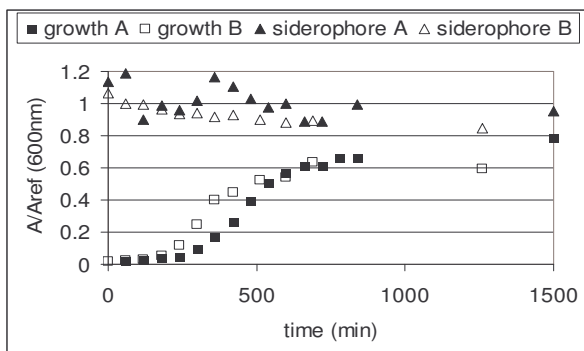


Figure 3.7: Growth and siderophore-production of *P. fluorescens* DS178 in PK-media (A and B are repeated experiments).

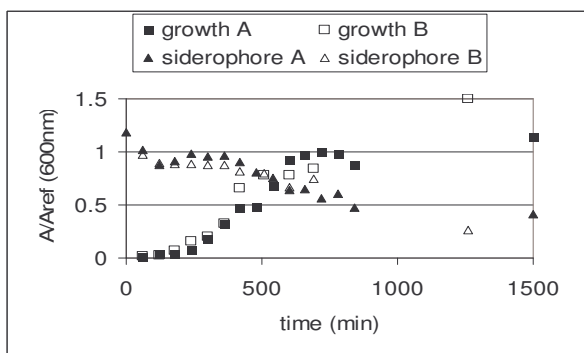


Figure 3.8: Growth and siderophore production of *P. fluorescens* DS178 in M9GC-media (A and B are repeated experiments).

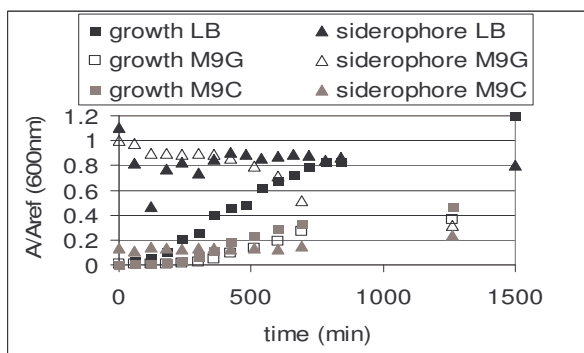


Figure 3.9: Growth and siderophore production of *P. fluorescens* DS178 in LB-, M9G- and M9C-media.

Extraction of Pb by the commercially available siderophore DFO-M (0.2 M) from industrially contaminated soil reached as much as 23% at pH 6.4. This extraction was encouraging, and identical to that of citrate (0.2 M) from the same soil (chapter 7). The siderophore concentration used was, however, 1000 times higher than that

commonly obtained by bacterial growth in iron-deficient substrates (Schwyn and Neilands, 1987; Alexander and Zuberer, 1991). Combined with the fact that the Pb-concentrations applied in the studies documenting siderophore-enhanced dissolution of Pb from soil-minerals was several size-orders below that in contaminated soils (Neubauer *et al.*, 2000; Kraemer *et al.*, 2002; Neubauer *et al.*, 2002), this fact made a doubt rise on the applicability of siderophores for promotion of EDR of Pb-contaminated soil.

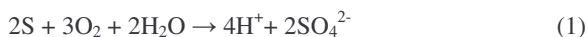
In order to exclude any unaccounted positive effects, the track was, however, followed a little further by making a laboratory-scale EDR experiment, where the ability of *P. fluorescens* DS178 to produce siderophores and enhance Pb-remediation was tested. Glucose consumption was documented by the negative detection after less than 24 hours after addition. Siderophore-production could not be detected at any point of time. After termination of the experiment < 1% of the Pb had been remediated. Consequently no further research in this topic was completed, and the reasons behind the glucose depletion and lacking siderophore production were therefore not elucidated. Possible reasons could be: inherent soil-microorganisms oust *P. fluorescens* DS178; sufficient iron is released from the soil to make siderophore production unfeasible; growth is impeded in the electric field and glucose is oxidized at the anode.

### 3.3 AUTOTROPHIC LEACHING

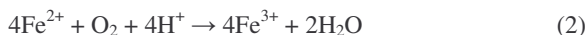
The feasibility of sulfur amendment for stimulation of autotrophic leaching prior to or simultaneous with EDR of soil-fines in suspension was studied. Batch extractions of Pb from soil-fines with sulfuric acid were made to evaluate the resulting Pb-mobilization. Subsequently, EDR-experiments made by MSc-student Gry Pedersen under my co-supervision made it possible to draw final conclusions on the feasibility.

#### 3.3.1 Introduction

Leaching of metal-sulfides from solid material (e.g. low-grade ore) by the strictly aerobic, autotrophic bacteria *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* is traditionally referred to as autotrophic leaching or bioleaching. In this process, carbon requirements are fulfilled by CO<sub>2</sub> from the atmosphere, and the energy required for fixation of CO<sub>2</sub> is derived from the oxidation of sulfur and/or reduced sulfur compounds to sulfate:



*A. thiooxidans* oxidizes elemental sulfur more efficiently than *A. ferrooxidans*, which in addition is able to oxidize ferrous iron to ferric iron:



Both *A. thiooxidans* and *A. ferrooxidans* are extremely acidophilic, and grow exclusively at pH-values below 4.0 while decreasing pH of the substrate to values between 1 and 2. Above this pH-interval, less acidophilic species dominate the aerobic oxidation of sulfur. These include: *Thiomonas intermedia* (decreases pH to 2.0-2.8); *Halothiobacillus neapolitanus*, *Thiomonas perometabolis*, and *Thiobacillus delicatus* (decrease pH to 2.8-3.5); *Thiobacillus thioparus* (decreases pH to 3.5-4.5), *Thiobacillus denitrificans*, *Starkeya novella*, *Thermithiobacillus tepidarius* (decrease pH to 4.5-5.5); and *Paracoccus versutus* (decreases pH to 5.5-6.8) (Blais *et al.*, 1993).



Complete acidification of neutral material may therefore be obtained by successive growth of less acidophilic and extremely acidophilic sulfur-oxidizing bacteria.

Because it was shown early that *A. ferrooxidans* and *A. thiooxidans* are sensitive to even low concentrations of a wide variety of organic substances often present in soils (Tuttle and Dugan, 1976), the efforts on application of this technique to decontamination of soil was low until it was later shown that some strains are tolerant to organic substances (Blais *et al.*, 1993; Zagury *et al.*, 1994). Since, a number of studies on bioleaching of heavy metals from contaminated soils and sediments were made, however being ambiguous in their results on the leachability of Pb: Leaching of Pb by incubation with elemental sulfur and in some cases specific species was successfully obtained from storm water detention pond sediments (Anderson *et al.*, 1997; Anderson *et al.*, 1998); wastewater sludge (Du *et al.*, 1995; Shanableh and Omar, 2003); sewage sludge (Ravishankar *et al.*, 1994) and anaerobically digested sludge (Xiang *et al.*, 2000; Wong *et al.*, 2004). In many works, however, dissolution of Pb by sulfur-oxidizing bacteria was excluded due to precipitation of leadsulfate, which has a very low solubility compared to other metal-sulfates ( $K_{sp} = 1.6 \times 10^{-8}$ ). Bioleaching experiments with various industrially contaminated soils successfully dissolved most of the heavy metals present, but not Pb (Gourdon and Funtowicz, 1995; White *et al.*, 1998; Gomez and Bosecker, 1999), and in a highly contaminated river sediment Zn, Cd, Mn, Co, Cu and Ni were leachable, while Pb and Cr were nearly immobile (Seidel *et al.*, 2004).

The referred results suggest that bioleaching of Pb from sediments in general is more feasible than from soils. This hypothesis was supported by a study, where 96% of the Pb was leached from contaminated wastewater sludge while from a mixture of contaminated soil and wastewater sludge only 10-33% of the Pb was leached (Shanableh and Omar, 2003). In other words: the low solubility of lead-sulfate may not be the only limiting factor. The different compositions of soil and sediments also seem to play an important role.

Indigenous presence of sulfur-oxidizing species was documented in several soil and sediment samples: In sewage sludge it was shown that *T. thioparus* and *A. thiooxidans* dominated the acidification amendment with sulfur (Blais *et al.*, 1993). *A. ferrooxidans* was found indigenous in stormwater detention pond sediment, while *A. thiooxidans* and the less acidophilic species were not (Anderson *et al.*, 1997). In two contaminated soils and a river sediment both *A. thiooxidans* and *A. ferrooxidans* were found to be indigenous, while in a rainwater-collection basin sludge only *A. thiooxidans* was identified (Gomez and Bosecker, 1999).

Direct current was found to be detrimental to low cell densities of the bacteria *A. ferrooxidans* and an *Acidiphilium* sp. in liquid culture. In contrast, bacterial metabolism was stimulated by the current in soil slurries (Jackman *et al.*, 1999), which support the feasibility of enhanced remediation by simultaneous bioleaching and EDR of contaminated soil. One work showed how energy consumption by EKR of copper from soil was reduced by an integrated method incorporating sulfur-oxidizing bacteria (Maini *et al.*, 2000).

### 3.3.2 Materials and Methods

An industrially contaminated Danish *soil* of unknown origin (referred to as soil 10 in chapters 4 and 5), obtained from a pile after excavation, was used as experimental soil. The soil fines were obtained by simple wet-sieving of the original soil with distilled water through a 0.063 mm sieve. Concentrated slurry of fines was obtained by centrifugation at 3000 rpm for 10 min. and decantation of the supernatant. The soil



finer were kept in slurry and stored at 5°C in access of oxygen. The Pb-content of the soil-fines was 1300 mg/kg. *Acid-enhanced extraction* of Pb from the soil was investigated by extraction of 5.00g dry, crushed soil with 25.00ml reagent at 200rpm for 7 days. The reagents were as follows: 1.0M NaOH, 0.5M NaOH, 0.1M NaOH, 0.05M NaOH, 0.01M NaOH, distilled water, 0.01M HNO<sub>3</sub>, 0.05M HNO<sub>3</sub>, 0.1M HNO<sub>3</sub>, 0.5M HNO<sub>3</sub>, 1.0M HNO<sub>3</sub>, 0.01M H<sub>2</sub>SO<sub>4</sub>, 0.05M H<sub>2</sub>SO<sub>4</sub>, 0.1M H<sub>2</sub>SO<sub>4</sub>, 0.5M H<sub>2</sub>SO<sub>4</sub>, 1.0M H<sub>2</sub>SO<sub>4</sub>. pH was measured after 10min settling, after which the liquid was filtered through a 0.45µm filter for subsequent Pb-analysis AAS. Non acidic samples were preserved with one part of conc. HNO<sub>3</sub> to four parts of liquid in autoclave at 200 kPa and 120°C for 30 minutes prior to AAS measurement

### 3.3.3 Results and discussion

In figure 3.10 and 3.11 the acid-enhanced desorption of Pb from soil-fines is illustrated. Extraction with nitric acid was efficient below pH 2, and some extraction was seen by sodium-hydroxide above pH 13. Extraction with sulfuric acid was very limited. Only 3% of the Pb was extracted even at pH below 1 (figure 3.11). In figure 3.12 the speciation of Pb in the presence of sulfate is illustrated. According to these equilibrium calculations, the majority of the Pb will precipitated as crystalline lead-sulfate. The limited extraction of Pb with sulfuric acid is therefore likely to be due to precipitation of lead-sulfate. Under influence of a DC current field, the equilibrium would however be shifted by constantly removing soluble species. Therefore enhancement of EDR by sulfur-induced heterotrophic leaching can not be excluded on basis of these batch-extraction results.

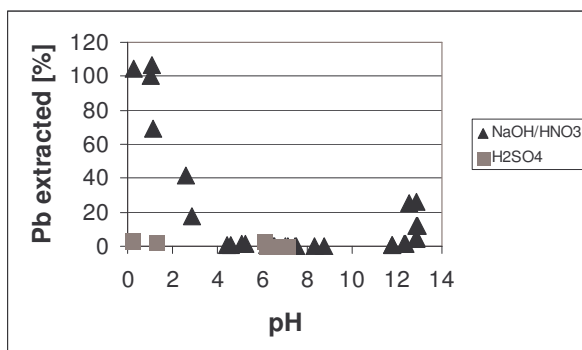


Figure 3.10: Acid-enhanced extraction of Pb from contaminated soil-fines.

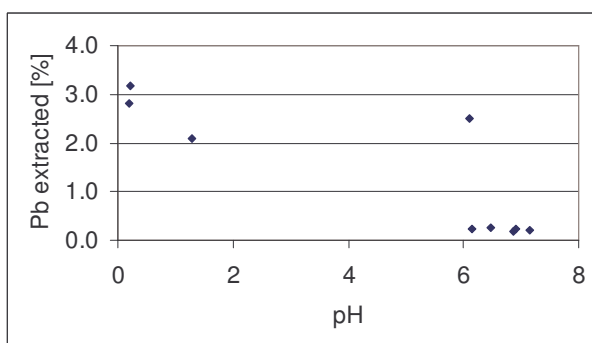


Figure 3.11: Extraction of Pb from contaminated soil-fines with sulfuric acid.

Gry Pedersen investigated the possibility of enhancing EDR of Pb-contaminated soil-fines by sulfur-amendment (Pedersen, 2005). She found that indigenous bacteria were able to acidify the soil-fines slightly upon sulfur-amendment, however no acidification below pH 4 was obtained, indicating that only the least acidophilic sulfur oxidizers like *Paracoccus versutus* were indigenous. In experiments where pH was adjusted manually to pH 4, the lack of further acidification upon sulfur-amendment indicated that extremely acidophilic sulfur-oxidizing species were not present in the soil. Identical EDR-experiments with contaminated soil-fines left 32% of the Pb in the soil subjected to acidification by sulfur-amendment and only 6% after remediation without sulfur-amendment. Direct addition of sulfuric acid gave even worse results with 98% of the Pb left in the soil-fines after experimental remediation. Apart from Pb, the soil was contaminated with Zn, and in order to evaluate the feasibility of autotrophic leaching for toxic metals, which do not precipitate easily as a sulphate, the removal of Zn was monitored in the same experiments. In that case addition of sulfuric acid and sulfur-amendment gave significantly better results: 18 and 23% of the Zn was left in the soil after remediation with sulfuric acid and sulfur-amendment respectively. In comparison, an average of 37% of the Zn was left in the soil after remediation in the reference experiments. The results suggest that precipitation of crystalline lead-sulfate impedes EDR of Pb-contaminated soil-fines significantly, and that heterotrophic leaching in combination with EDR of Pb-contaminated soil-fines in suspension is not a viable technology, while it may be for toxic metals which do not precipitate as sulphates.

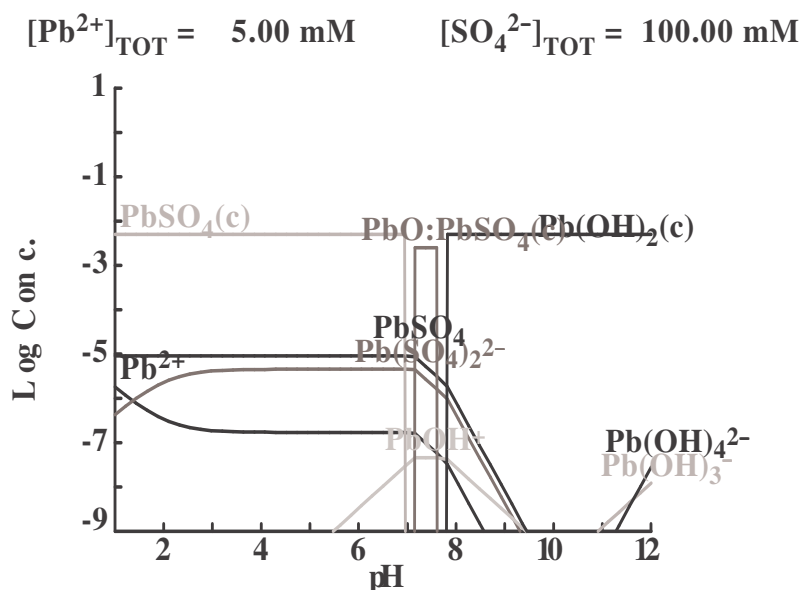


Figure 3.12: Speciation of Pb (Puigdomenech, 2002) in the presence of sulfate (Puigdomenech, 2002).

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## 4. Speciation of Pb in Industrially Polluted Soils

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### Abstract

This study was aimed at elucidating the importance of original Pb-speciation versus soil-characteristics to mobility and distribution of Pb in industrially polluted soils. Ten industrially polluted Danish surface soils were characterized and Pb speciation was evaluated through SEM-EDX studies, examination of pH-dependent desorption, distribution in grain-size fractions and sequential extraction. Our results show that the first factors determining the speciation of Pb in soil are: (1) the stability of the original speciation and (2) the contamination level, while soil characteristics are of secondary importance. In nine of ten soils Pb was concentrated strongly in the soil fines (< 0.063mm). In all soils, particles with a highly concentrated Pb-content were observed during SEM-EDX. In eight of the soils, the particles contained various Pb-species with aluminum/iron, phosphate, sulfate and various metals (in solder and other alloys) as important associates. In the one soil, where Pb was not concentrated in the soil fines, Pb was precipitated solely as  $\text{PbCrO}_4$ , while pure (metallic) Pb was repeatedly observed in the last soil. Pb was bound strongly to the soils with > 50% extracted in step III (oxidizing) and IV (residual) of sequential extraction for all soils but one. A significant amount of exchangeable Pb existed only in severely contaminated soils, where the bonding capacity of organic matter and oxides was exceeded. Among soil constituents, Pb was observed to adsorb preferentially to feldspars and organic matter while presence of phosphate increased the strength of the Pb-bonding in phosphate-rich soils.

**Keywords:** Pb, pollution, soil, SEM-EDX, sequential extraction, speciation, XRD.

### 1 Introduction

Soil is a sink for anthropogenic Pb, which accumulate in surface soil due to its low solubility and high affinity for adsorption. Knowledge on the adsorption capacity of single soil components for Pb has been established by addition of soluble Pb-salts to uncontaminated soils and soil constituents with more or less well defined characteristics. When considering industrially polluted soils where Pb-species such as



metallic Pb and insoluble organics or inorganics often constitute the original contamination, less is known about the distribution and fate of Pb, although such knowledge is essential to perform realistic risk-assessment and evaluation of remediation possibilities. In this work, a short review of the existing knowledge on speciation of Pb in soil is given, followed by examination of ten industrially Pb-polluted soils concerning soil characteristics, Pb association as evaluated by SEM-EDX and strength of Pb-bonding through extraction with acid/base and sequential extraction. SEM-EDX studies give a qualitative impression of the Pb-speciation which is useful in the study of urban Pb-contaminated soils where Pb from various and often unknown sources result in the presence of a number of chemical forms, crystalline as well as amorphous, for which identification is a challenge as discussed by (Manceau *et al.*, 1996). The speciation of Pb in each soil is discussed with respect to mobility and stability, and the relative importance of soil constituents is evaluated through correlation between soil constituents and the speciation as revealed by sequential extraction.

## 2 Background

The chemistry of Pb in soils is affected by: (1) specific adsorption or exchange adsorption to the mineral matrix; (2) precipitation of sparingly soluble compounds; (3) formation of complexes with organic matter (Adriano, 1986). In this section current knowledge on the three types of bonding is summarized. Already in 1975 it was stated that the affinity for Pb among soil constituents is in the order: humus > clay minerals > Fe hydroxides (Hildebrand and Blum, 1975), and it was observed that soil affinity for lead is high compared to other metals. Later it was suggested that the selectivity of mineral and organic soils towards heavy metals correspond to the order of increasing  $pK$ 's of the first hydrolysis product of the various metals (e.g.  $PbOH^+$ ):  $Pb > Cu > Zn > Ni > Cd$  (Elliott *et al.*, 1986), an observation which is confirmed in several investigations (Aualiitia and Pickering, 1987; Puls *et al.*, 1991; Yong and Phadungchewit, 1993b; Papini *et al.*, 2004; Pinskii and Zolotareva, 2004). Through modeling of Pb adsorption onto a sandy loam it was indeed shown that  $PbOH^+$  and  $Pb(OH)_2^0$  species are favorably adsorbed onto soil compared to the  $Pb^{2+}$  ion (Weng, 2004). It should be noted that this adsorption mechanism only prevail at pH values above 4 or 5. At lower pH-values, the order is changed, although Pb is still preferentially adsorbed (Yong and Phadungchewit, 1993a).

### 2.1 ADSORPTION TO THE MINERAL MATRIX

In a study of Pb uptake by 14 different minerals and soil materials, Pb-uptake was found to takes place at pH values well below that of hydroxide precipitation. Among the pure clay-minerals, smectite and bentonite (montmorillonites) had a higher adsorption capacity than illite and kaolinite (Arnfolk *et al.*, 1996). Another study, involving adsorption of trace levels of Pb to several inorganic particulates, the following uptake-sequence was found:  $Mn(IV)$  oxides >  $Fe(III)$  oxides >  $Al(OH)_3$  > illite > montmorillonite >> kaolin (Aualiitia and Pickering, 1987). The contrasting results concerning illite and montmorillonite are explained by a difference in the experimental procedure, where the latter study used 1M sodium-acetate as background solution, resulting in decreased adsorption to particularly montmorillonites due to ion-exchange, as observed by (Farrah and Pickering, 1978), who investigated the strength of Pb bonding to clay-minerals by subjecting pre-contaminated clays to different chemical solutions. Pb-bonding was found to be more

firm with kaolin and illite clays compared to montmorillonite, from which a solution of excess cations (Na and Ca) displaced > 50% of the adsorbed Pb, and suggesting that adsorption to this clay type occurs primarily by an ion exchange process. Desorption from kaolin and illite was found to be sensitive towards pH, which suggests that hydroxyl bridging to clay sites may be a significant step in the sorption mechanism to these clays.

A higher affinity of the Mn-oxide phase for Pb compared to the Fe-oxide phase was observed (Aualiitia and Pickering, 1987; Zachmann and Block, 1994). However the Mn-oxide phase commonly constitute less than 1% of the Fe-oxide phase in soils and sediments, leading to a decreased importance of this mineral phase as adsorbent. In addition, pH, CEC, organic matter, clay and carbonate were found to correlate better with Pb adsorption than both Fe and Mn-oxides in complex soils (Hooda and Alloway, 1998).

## 2.2 PRECIPITATION OF SPARINGLY SOLUBLE COMPOUNDS

Precipitation of Pb-compounds influences the speciation of Pb in soil. Figures 2.1 to 2.3, made by the chemical-equilibrium-diagram-tool Hydra/Medusa (Puigdomenech, 2002), illustrates how Pb-precipitation may occur due to pH-changes and presence of common ions. Considering only pH effects,  $\text{Pb}^{2+}$  is dominant at low pH, while precipitation of  $\text{Pb}(\text{OH})_2$  dominates at neutral-alkaline pH. Pb is amphoteric, and at extremely alkaline conditions the negatively charged ion  $\text{Pb}(\text{OH})_4^{2-}$  is dominating (figure 2.1a). In equilibrium with the atmosphere precipitation of  $\text{PbCO}_3$  at neutral pH and dissolution of Pb as  $\text{Pb}(\text{CO}_3)_2^{2-}$  at alkaline pH becomes important (figure 2.1b).

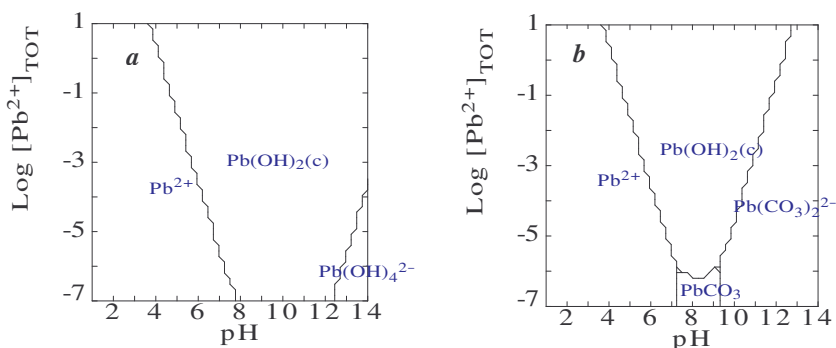


Figure 2.1: **a)** Predominance diagram of Pb in solution considering only pH effects; **b)** Predominance diagram of Pb in the presence of carbonate ( $\log P_{\text{CO}_2(\text{g})} = -3.5$ ) (Puigdomenech, 2002) [ $\text{Pb}^{2+}$ ] in M.

Precipitation of lead-phosphates and lead-sulphate (figure 2.2 and 2.3) plays an important role in soils containing significant amounts of these substances. The interaction between lead and phosphorus is considered to be an important buffer-mechanism controlling the migration and fixation of lead in the environment. On the basis of thermodynamic data it was concluded that stability of pyromorphites  $[\text{Pb}_5(\text{PO}_4)_3\text{X}]$ ,  $\text{X} = \text{OH}/\text{Cl}/\text{Br}/\text{F}$  and plumbogummite  $[\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}]$  dominate that of other secondary lead-minerals under the geochemical conditions prevailing in the surface environment (Nriagu, 1974). Phosphate minerals were shown to bind Pb tightly in several studies on stabilization of Pb in soil (Ma *et al.*, 1994; Cotter-Howells, 1996; Laperche *et al.*, 1996; Chen *et al.*, 1997). The studies

consistently showed how apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH}/\text{F}/\text{Cl})$ ) dissolved and precipitation of Pb and phosphate as pyromorphite occurred. As pictured in figure 2.2a and b neither sulphate, nor phosphates influence the solubility of Pb at high pH, however they markedly decrease the solubility at low pH. In figure 2.3a and b the predominance of pyromorphite and plumbogummite is illustrated.

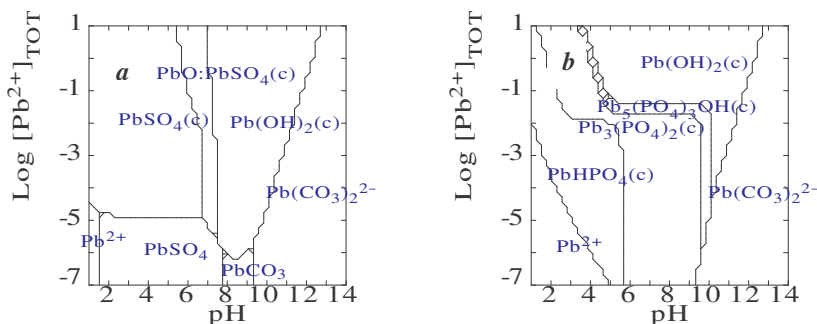


Figure 2.2: Predominance diagram of Pb in soil solution with carbonate ( $\log P_{\text{CO}_2(\text{g})} = -3.5$ ) and **a**) sulphate ( $[\text{SO}_4^{2-}]_{\text{TOT}} = 10 \text{ mM}$ ); **b**) phosphate ( $[\text{PO}_4^{3-}]_{\text{TOT}} = 10 \text{ mM}$ ) (Puigdomenech, 2002)  $[\text{Pb}^{2+}]$  in M.

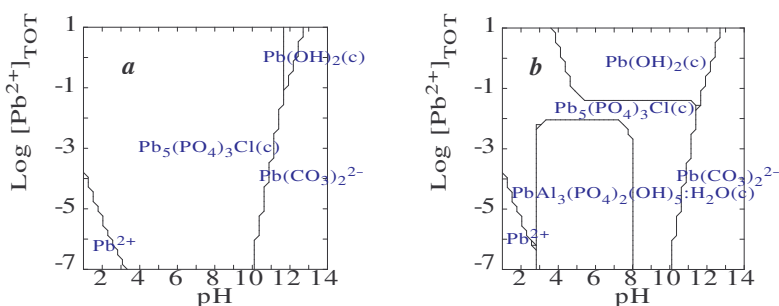


Figure 2.3: Predominance diagram of Pb in soil solution with **a**) carbonate ( $\log P_{\text{CO}_2(\text{g})} = -3.5$ ), phosphate ( $[\text{PO}_4^{3-}]_{\text{TOT}} = 10 \text{ mM}$ ), chloride ( $[\text{Cl}^-]_{\text{TOT}} = 10 \text{ mM}$ ); **b**): the same species but in the presence of aluminum ( $[\text{Al}^{3+}]_{\text{TOT}} = 10 \text{ mM}$ ) (Puigdomenech, 2002)  $[\text{Pb}^{2+}]$  in M.

Altogether figures 2.1 through 2.3 show, how dissolved Pb-compounds are likely to re-precipitate with ions present in soil-solution in consistence with the low mobility of Pb generally observed.

## 2.3 FORMATION OF COMPLEXES WITH ORGANIC MATTER

In a study involving 17 different soils, it was shown that fixation of Pb in soil primarily involved insoluble organic matter, while precipitation as carbonates and sorption by hydrous oxides appeared to be of secondary importance (Zimdahl and Skogerboe, 1977). Soon after other researchers showed that among major soil groups, organic soils adsorbed three times as much Pb as other groups (Nriagu *et al.*, 1978), a tendency confirmed by (Morin *et al.*, 2001). Studies of lead uptake in complex soils conclude that lead uptake capacity is best correlated with soil pH and organic matter

(Cline and Reed, 1995a; Cline and Reed, 1995b; Arnfalk *et al.*, 1996; Gao *et al.*, 1997; Hooda and Alloway, 1998), and in a study on the kinetics of Pb sorption and desorption, it was revealed that soil organic matter increase the adsorption and impeded the desorption of Pb from soil (Strawn and Sparks, 2000). When studying adsorption of heavy metals by 60 organic samples of forest soil, the sorption affinity of the organic soils was found to be up to 30 times higher than that of mineral soils when accounting for the pH-difference, although the influence of dissolved organic matter in many cases counteracted the effect (Sauve *et al.*, 2003).

The importance of Pb-complexation by soluble organic matter has been established as well. A recent study showed that the activity of Pb in soil solution at contaminated sites was low in general, and that most of the soluble lead was complexed to soluble fulvic acids (> 80% at pH 5.5-8) (Ge *et al.*, 2005). Another study concluded that humic acids have an even higher affinity for Pb binding than fulvic acids, and it was found that Pb mobility increased by a factor of 4-8 in the presence of dissolved organic matter in an otherwise sandy soil (Jordan *et al.*, 1997). Consistently, most of the Pb in solution in polluted soil from railway yards was shown to exist as organic complexes (Ge *et al.*, 2000), just as 60-80% of the dissolved lead was found present as organo-Pb complexes in a study of 84 polluted and non-polluted soils, resulting in a markedly increased Pb solubility (Sauve *et al.*, 1997). This was even the case in soils amended with phosphate minerals for stabilization of Pb (Sauve *et al.*, 1998).

## 2.4 TRANSFORMATION OF ORIGINAL CONTAMINATION

Several XRD techniques were applied for identification of Pb-minerals in contaminated soil e.g. X-Ray Powder Diffraction (Ettler *et al.*, 2005), X-Ray Absorption Fine Structure (Ostergren *et al.*, 1999) and more (Jorgensen and Willems, 1987; Manceau *et al.*, 1996; Ostergren *et al.*, 1999; Vantelon *et al.*, 2005). Transformation of metallic Pb into hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), cerussite ( $\text{PbCO}_3$ ) and (less commonly) anglesite ( $\text{PbSO}_4$ ) in shotgun pellets was observed in several studies (Jorgensen and Willems, 1987; Lin *et al.*, 1995; Vantelon *et al.*, 2005). The transition sequence was suggested to be litharge ( $\alpha\text{-PbO}$ )  $\rightarrow$  hydrocercucite  $\rightarrow$  cerucite (Vantelon *et al.*, 2005). Complete transformation was estimated to occur in 100-300 years, but could be as little as 15-20 years in organic soils (Jorgensen and Willems, 1987; Lin *et al.*, 1995). One soil contaminated by a lead smelter, contained Pb bound as insoluble lead-oxide and in phosphates (Hrsak *et al.*, 2000), while in another soil contaminated by lead metallurgy anglesite was confirmed (Ettler *et al.*, 2005). In some mining wastes, Pb was shown to weather to anglesite and pyromorphite, which drastically reduced its bioaccessibility (Davis *et al.*, 1993), while in other, jarosite ( $\text{PbFe}_6(\text{SO}_4)(\text{OH})_{12}$ ) and Pb adsorbed to soil-constituents was observed (Ostergren *et al.*, 1999). In soil contaminated by alkyl-tetravalent lead compounds, Pb was found to be complexed to organic matter; while in soil contaminated by battery reclamation anglesite and silica-bound lead were predominant forms (Manceau *et al.*, 1996). In the vicinity of a lead smelter, the number of chemical forms was too high to allow for individual identification (Manceau *et al.*, 1996).

Three studies supplied XRD by SEM-EDX which allows for identification of amorphous Pb-compounds in addition to crystalline although in contrast to XRD-studies the results remain qualitative of nature. Formation of pyromorphite as a weathering product in diffusely contaminated urban soils was demonstrate by SEM-EDX (Cotter-Howells, 1996). The presence of pyromorphite could not be verified by

XRD due to its impure and possibly also its poorly crystalline nature. In a study of soils contaminated by copper-mining, Pb was found to exist as magnetoplumbite ( $\text{Pb}(\text{Fe}/\text{Mn})_{12}\text{O}_{19}$ ) and plumferrite ( $\text{PbFe}_4\text{O}_7$ ), which are likely to be untransformed slag from the smelting wastes; and in soils originating from the vicinity of a battery factory  $\text{PbCO}_3$ ,  $\text{PbSO}_4$ ,  $\text{PbO}$  and  $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$  were identified. These results were confirmed by SEM-EDX studies which in addition showed that most Pb was found in discrete particles of lead-compounds (Welter *et al.*, 1999). Transformation of metallic Pb in a sub-surface lead-pipe into litharge, hydrocerussite and cerussite was observed by XDR and confirmed by SEM-EDX in the crust of the pipe as well as in the surrounding soil (Essington *et al.*, 2004). Formation of stable phosphates could not be verified although SEM-EDX proved presence of apatite, possibly for the same reasons as those given by (Cotter-Howells, 1996).

Sequential extractions showed that bonding of Pb at background levels ( $\leq 20\text{mg/kg}$ ) mainly occur in the reducible and the residual fraction i.e. bound to oxides and the mineral matrix. In soils diffusely contaminated by industrial emissions however, the fractions of oxide bound, carbonate bound and organically bound lead, are increasing at the expense of residual lead. Generally only little exchangeable lead was found compared to other metals with the exception of acidic soils ( $\text{pH} < 5$ ) (Chlopecka *et al.*, 1996). Consistently, Pb was found to bind preferentially to organic matter in another diffusely contaminated soil (Miller and Mcfee, 1983) and in several other industrially polluted soils Pb was found to bind preferentially to oxides, carbonates and organics (Yarlagadda *et al.*, 1995; Ma and Rao, 1997). Interpretation of sequential extractions of industrially contaminated soils should however be made with care, because sequential extraction procedures are based on the assumption that Pb interacts primarily with common soil constituents. In industrially contaminated soils other contaminating substances might play a key role. This was taken into consideration in a study of soil contaminated by mining and ore-processing, where a sequential extraction procedure was designed especially for extraction of the Pb-species expected to appear in such contamination, Pb was found preferentially in the residual fraction assumed to consist of sulfide (Cordos *et al.*, 1995). This approach should however also be applied with care, because it might lead to wrong interpretations if the actual speciation differ from the expected.

### 3 Materials and Methods

#### 3.1 SOILS

Ten samples of industrially polluted surface soil from Danish sites were collected in 1999. Their most probable contamination sources are given in table I.

#### 3.2 SOIL CHARACTERIZATION

All soils were analyzed concerning grain-size distribution; pH; carbonate-content; organic matter content; CEC; concentrations of Fe and Cl; conductivity; phosphate; mineralogy and the heavy metals: Pb, Ni, Cu, Cd, Zn, Sn, Cr. All results are given as the mean result of at least three analyzed samples, except grain size distribution for which only one sample was analyzed, and phosphorus, which was analyzed in double. *Metal analysis* (Fe, Pb, Ni, Cu, Cd, Zn, Fe, Sn, Cr) were made according to the Danish standard method DS259 (Dansk Standardiseringsråd, 1991), which includes acid digestion of 1g soil with 20.00mL of half concentrated  $\text{HNO}_3$  in autoclave at 200kPa and 120°C for 30 minutes. The metal-content in solution was measured by

AAS (graphite-furnace for Sn) after filtration through a 0.45µm filter. AAS analyses were for all metals validated through analysis of reference samples.

TABLE I  
Pb contaminated soils.

<i>Soil</i>	<i>Activity and probable Pb-source</i>	<i>Activity period</i>
1	Ancient, burned down, church with Pb-roof	1627
2	Extraction of metals from scrap and ore and recycling of lead-acid accumulators. Smelter waste products deposited on site.	1938-1985
3	Car painting (lead based paints).	1900's
4	Harbor area, filled up with waste from porcelain production and a gasworks. Breaking up and scrapping of locomotives.	1880-1988
5	Former waste-dump with mixed industrial waste and household waste. Covered with sewage sludge, ash and mould.	1913-1937
6	Former waste-dump with mixed industrial waste and household waste. Covered with sewage sludge, ash and mould.	1913-1920
7	Gravel pit used as waste dump. Source unknown.	1900's
8	Metal foundry	1921-1976
9	Harbor area filled up with harbor sludge and surface soil from central Copenhagen between 1780 and 1820. Site laid out as army ammunition site with chemical storage.	After 1780
10	Soil collected by contractor north of Copenhagen. Source unknown.	Unknown

*Grain-size* distribution was determined by wet-sieving approximately 100g natural wet soil with 0.002M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> through a 0.063mm sieve followed by separation by dry sieving of the larger fractions (>0.063 mm) and sedimentation velocity measured by XRD of the smaller fractions (<0.063 mm) on Micromeritics® SEDIGRAPH 5100. *pH* was measured by electrode MeterLab® CDM220 after shaking of 5.0g dry soil with 12.5mL 1M KCl constantly for 1 hour, followed by settling for 10min. *Carbonate* content was determined volumetrically by the Scheibler-method when reacting 3g of soil with 20mL of 10% HCl. The amount was calculated assuming that all carbonate was present as calciumcarbonate. *Organic matter* was determined by loss of ignition in a heating furnace at 550°C for 1 hour. *CEC* was determined after ion exchange of 10g dry soil with NH<sub>4</sub><sup>+</sup>, followed by exchange of NH<sub>4</sub><sup>+</sup> for Na<sup>+</sup>. The ammonium concentration of the supernatant was measured by spectrophotometer via flow-injection. *Conductivity* was measured by electrode MeterLab® CDM210 in solution prepared by constantly mixing of 10g soil and 25ml distilled water for 30min, followed by settling for 20min. *Phosphate* was measured after digestion of 0.2-0.5g sample at 550°C followed by boiling with HCl, reaction with ammonium molybdate to form yellow phosphor-molybden acid, and reduction by ascorbic acid in the presence of antimony. The strong blue color was measured by spectrophotometer Shimadzu UV-1601. *XRD analysis*: All soils were subjected to XRD-analysis to reveal the mineral composition of the bulk soil as well as the clay fraction. The bulk-minerals were quantified on basis of peak-height while the clay-minerals were

quantified on basis of peak-area after ethylene-glycolation and heating to first 350°C and then 550°C.

### 3.3 SPECIATION ANALYSIS

*Pb distribution in soil fractions* was determined upon analysis of the grain size distribution. Samples of each fraction were crushed, and the Pb concentration in each fraction was measured by AAS. The < 2µm fraction, which was separated out for XRD-analysis of clay minerals was additionally analyzed for Pb. For *SEM-EDX* analysis carbon coated, polished pucks were analyzed by a JEOL scanning electron microscope, JSM 5900. EDX results were treated by the software: Oxford Instruments INCA version 4.02. One specimen of each soil was analyzed (two specimens of soils 2 and 3), looking for bright spots (back-scatter-mode), which might contain Pb. When such a spot was found, it was analyzed for total elements, and in case it contained Pb, the relative amounts (atomic %) of all elements (except C, O and H, which could not be determined due to the sample preparation) in the spot were determined. *Mobilization of Pb due to pH changes* was quantified after extraction of 5.00g dry, crushed soil with 25.00ml reagent at 200rpm for 7 days. The reagents were as follows: 1.0M NaOH, 0.5M NaOH, 0.1M NaOH, 0.05M NaOH, 0.01M NaOH, distilled water, 0.01M HNO<sub>3</sub>, 0.05M HNO<sub>3</sub>, 0.1M HNO<sub>3</sub>, 0.5M HNO<sub>3</sub>, 1.0M HNO<sub>3</sub>. pH was measured after 10min settling, after which the liquid was filtered through a 0.45µm filter for subsequent measurement on AAS. Non acidic samples were preserved with one part of conc. HNO<sub>3</sub> to four parts of liquid in autoclave at 200 kPa and 120°C for 30 minutes prior to AAS measurement. *Sequential extraction* was performed according to the method from the Standards, Measurements and Testing Program of the European Union (former BCR) (Mester *et al.*, 1998). 0.5g of dry, crushed soil was treated in four steps as follows: I) Extraction with 20.0ml 0.11M acetic acid pH 3 for 16 hours. II) Extraction with 20.0 ml 0.1M NH<sub>2</sub>OH·HCl pH2 for 16 hours. III) Extraction with 5.0ml 8.8M H<sub>2</sub>O<sub>2</sub> for one hour and heating to 85°C for one hour with lid followed by evaporation of the liquid phase at 85°C until it had reduced to < 1ml by removal of the lid. The addition of 5.0 ml 8.8M H<sub>2</sub>O<sub>2</sub> was repeated followed by resumed heating to 85°C for one hour and removal of the lid for evaporation until almost dryness. After cooling down the sample, 25.0 ml 1M NH<sub>4</sub>OOCCH<sub>3</sub> pH 2 was added, and extraction took place for 16 hours. IV) Digestion according to DS 259. Between each step the sample was centrifuged at 3000rpm for 15min, and the supernatant was decanted and stored for AAS. Before addition of the new reagent the sample was washed with 10.0ml distilled water for 15min, centrifuged at 3000rpm for 15min and the supernatant was decanted. All extractions were performed at room temperature and shaking at 100rpm unless otherwise mentioned. *Sequential extraction of pure phases* was made in order to study the extraction of common contaminating Pb-species, and facilitate interpretation of extraction results. Metallic Pb and Pb bound in solder were obtained commercially. Lead-sulphate and lead-chromate were both precipitated in the lab by mixing a concentrated lead-nitrate solution with sulfuric acid and potassium dichromate respectively followed by filtration through a 0.45µm filter and three times washing with distilled water.



## 4 Results

### 4.1 SOIL CHARACTERISTICS

Characteristics of the 10 soils are listed in table II. The soils are all typical surface soils with mixed grain size and a significant content of organic matter although both clayey and sandy soils are represented.

TABLE II  
Characteristics of the 10 soils +/- (Std.dev.).

Soil	1	2	3	4	5	6	7	8	9	10
<i>Parameter</i>										
<b>Clay (%)<sup>a</sup></b>	5	35	8	8	6	11	20	13	14	10
<b>pH</b>	6.9	6.1	7.2	6.9	6.3	7.2	6.8	7.6	7.6	7.8
<b>±</b>	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.2
<b>CaCO<sub>3</sub> (%)<sup>b</sup></b>	3.7	0.5	3.7	6.7	0.9	4.9	1.0	9.1	7.7	9.2
<b>±</b>	0.3	0.1	0.3	3.1	0.1	0.9	0.1	0.7	0.7	0.5
<b>OM (%)</b>	2.6	4.1	3.5	7.4	21.3	11.7	3.6	3.4	7.0	2.8
<b>±</b>	0.1	0.1	0.4	0.6	1.1	0.8	0.2	0.1	0.6	0.2
<b>CEC (meq/100g)</b>	6.6	15.3	3.7	6.3	26.0	10.3	5.3	4.9	8.2	4.5
<b>±</b>	1.5	1.2	0.1	3.1	14.6	2.8	1.8	0.1	0.2	0.1
<b>Fe (g/kg)</b>	5.3	18.8	9.5	24.4	37.6	30.4	21.5	12.0	13.6	13.6
<b>±</b>	1.1	1.4	1.8	1.5	1.3	3.6	1.7	0.6	0.7	1.2
<b>EC (µS/cm)</b>	244	446	194	455	1820	351	281	1848	1659	637
<b>±</b>	10	28	22	6	109	4	5	134	16	39
<b>P [mg/kg]</b>	1200	745	2224	1257	2455	539	741	1036	1123	1547
<b>±</b>	1	10	63	74	54	20	11	23	43	120

<sup>a</sup> fraction < 2 µm <sup>b</sup> Assuming all carbonate is present as calcium-carbonate.

TABLE III  
Heavy metals in the soils (mg/kg).

Soil	G.L.*	1	2	3	4	5	6	7	8	9	10
<i>Metal</i>											
<b>Pb</b>	40	<b>413</b>	<b>1157</b>	<b>581</b>	<b>693</b>	<b>868</b>	<b>1317</b>	<b>8836</b>	<b>298</b>	<b>789</b>	<b>3066</b>
<b>±</b>		365	28	127	50	87	1225	4259	30	87	1892
<b>Ni</b>	30	<20	20	<20	<b>48</b>	<b>94</b>	<b>62</b>	<b>33</b>	<b>31</b>	22	23
<b>±</b>			0		3	1	5	4	1	2	5
<b>Cu</b>	500	<50	124	<50	261	<b>584</b>	<b>1800</b>	82	<b>688</b>	153	164
<b>±</b>			0		18	89	2307	5	298	15	53
<b>Cd</b>	0.5	<2	<b>10</b>	<2	<2	<b>5</b>	<b>2</b>	<2	<b>5</b>	<b>4</b>	<b>3</b>
<b>±</b>			1			0	0		1	1	0
<b>Zn</b>	500	277	382	435	<b>779</b>	200	142	<b>766</b>	<b>607</b>	485	179
<b>±</b>		20	8	45	201	13	26	34	49	49	26
<b>Sn</b>	500	<24	49	<24	33	90	66	<24	252	47	89
<b>±</b>			5		2	22	10		382	37	66
<b>Cr</b>	**500	<50	<50	104	50	358	77	<50	79	<50	<50
<b>±</b>				17	2	31	1		13		

\*Governmental assigned Limit for sensitive land-use (residences, child care centers and public playgrounds) given by the Danish EPA. \*\* Cr(VI) maximum 20 mg/kg.



In table III concentrations of seven different heavy metals are shown. The bolded values are those exceeding the governmental limits (G.L.) for sensitive land use. Apart from Pb, five soils are contaminated with Ni, three with Cu, six with Cd, three with Zn while no soils exceed the limit with respect to Sn and total Cr, although several of the soils contain those metals at elevated concentrations (background Sn =1-10mg/kg, Cr ~30mg/kg (Alloway, 1995)).

## 4.2 SOIL MINERALOGY

XRD results (table IV) show that all soils contain quartz, k-feldspar, plagioclases and calcite. An impression of the exactness of the analysis is obtained through comparison of calcite results from XRD measurements and calcite-content obtained by volumetric calcium-carbonate decision which are also given in the table. The results differ by 0-50% with XRD results generally showing slightly higher calcite content than volumetric decision. This variation may result from the fact that XRD-results are given as % of the crystalline fraction and not of the whole soil, so e.g. organic matter is not included. Considering clay-minerals, the only general result is that chlorite was absent in all samples.

TABLE IV  
Minerals identified in the soils through XRD analysis (% of the minerals).

Soil	1	2	3	4	5	6	7	8	9	10
Mineral										
Quartz	59	51	86	61	48	26	61	63	49	33
K-feldspar	11	8	2	16	10	44	19	15	19	32
Plagioclase	23	25	2	7	22	16	13	8	24	23
Calcite	4	1	7	9	1	7	1	8	6	10
CaCO <sub>3</sub> *	3.7	0.5	3.7	6.7	0.9	4.9	1.0	9.1	7.7	9.2
Hematite					12	4				
Dolomite				2	3					
Kaolinite	0.6	0.9	0.4	1.0	3.5	1.0	1.2	0.8	0.2	0.3
Illite	1.8	1.3	0.6	2.0		1.7	1.4	0.5	0.8	1.0
Smectite	1.7	2.9	0.5	1.0			1.4	1.4	0.2	0.7
EU**		10.8	2.8				2.2	4.5	0.6	1.0

\*Measured volumetric (from table III) for comparison (% of total).

\*\*EU = Expandable Undefined: Mixed elementary layers of several of the defined clay minerals.

## 4.3 pH-DEPENDENT EXTRACTION

In figure 4.1 the influence of pH on extraction of Pb from the soils is visualized. At pH values between 4 and 12.5 desorption was close to 0% for all soils. The only exceptions were soils 6, 7 and 10 for which 10% of the Pb was desorbed at pH 5.8, 4.5 and 4.7 respectively. Below pH 2 extraction of Pb was observed from all soils, but pH had to become as low as 1 before the majority of the Pb was extracted. At pH-values above 12.5 the amphoteric nature of Pb was visible. Pb appears least mobile in soils 3 and 6 under acidic conditions, while at alkaline conditions Pb in soil 3 and 7 is more mobile than average.

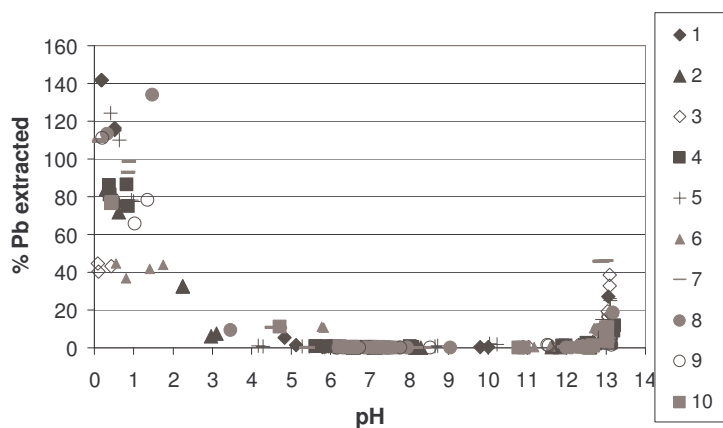


Figure 4.1: The influence of pH on desorption of Pb from the soils.

#### 4.4 LEAD DISTRIBUTION IN SOIL FRACTIONS

Figure 4.2 shows how Pb binds to the different size-fractions of the soils. There is a clear tendency of Pb to concentrate in the clay-size fraction of soil with soil 3 as the only exception.

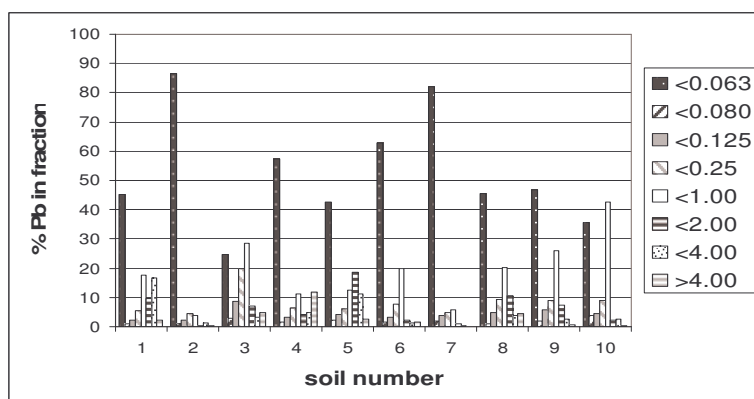


Figure 4.2: Distribution of Pb in the size-fractions (mm) of each soil.

#### 4.5 SEM-EDX

SEM-EDX results (atomic %) are listed in table V. Only Pb enriched grains are observed by the method, why the method is particularly suitable for observation of Pb which has not been transformed and redistributed in the soil. In accordance with the findings of (Welter *et al.*, 1999), all soils contained Pb in such enriched discrete particles. Leading to the conclusion that Pb in industrially contaminated soil in general is distributed inhomogeneously and not fully associated to soil constituents. In soil 3, Pb was consistently associated with Cr, while in soil 7 solely pure Pb-grains were observed. In soil 2 Pb associated with phosphate was dominating although metallic Pb-associates and Pb-sulfate were also represented. These compounds were representative of most of the compounds found in the remainder soils supplied by

Fe/Al-associates. The metallic compounds included pure metallic Pb, solder (SnPb) and metallic alloys.

TABLE V  
Results of SEM analysis of Pb-containing grains in the 10 soils

Soil	Elements observed (atomic %)	N*	Association
1	Pb(2)Sn(43)Fe(5)Ca(10)P(2) Si(28)Al(9)	2	Solder
	Pb(19)Ba(7)Zn(10)Fe(18)Ca(13)Cl(4)S(6)P(18)Al(5)	1	P
	Pb(28)Fe(2)Ca(2)K(2)Si(60)Al(7)	1	Al/Fe
2	Pb(8)Zn(1)Cu(1)Fe(27)Ti(4)Ca(4)K(1)S(6)P(4)Si(29)Al(12)Mg(2)	1	Sulfate
	Pb(21)Fe(3)Ca(6)P(12)Si(49)Al(8)	>10	P
	Pb(8)Sb(2)Sn(57)Zn(2)Fe(2)Si(20)Al(9)	1	Alloy
	Pb(35)Sb(19)Sn(17)Fe(2)Ca(6)P(2)Si(13)Al(5)	1	Alloy
	Pb(19)Fe(6)Ca(10)K(3)P(13)Si(39)Al(10)	>10	P
3	Pb(38)Cr(40)Ti(3)Ca(1)Cl(7)Si(7)Al(3)	2	Chromate
	Pb(34)Fe(12)Cr(31)Ca(2)Si(16)Al(6)	5	Chromate
4	Pb(34)Fe(8)Ca(7)Si(43)Al(8)	1	Fe/Al
	Pb(13)Fe(7)Ca(18)K(3)Cl(4)P(15)Si(30)Al(11)	1	P
	Pb(32)Fe(9)Ca(22)Cl(12)P(20)Si(4)	1	P
5	Pb(43)Sb(10)Sn(6)Fe(9)Ca(8)Si(14)Al(10)	1	Alloy
	Pb(13)Fe(2)Ca(1)K(4)Si(45)Al(34)Na(2)	1	Al/K
	Pb(4)Fe(3)Ca(2)K(8)Cl(1)Si(71)Al(1)Na(10)	1	K/Fe
6	Pb(4)Sn(57)Zn(3)Cu(25)Fe(1)Si(7)Ca(3)	1	Alloy
	Pb(9)Sn(80)Fe(1)Ca(5)Si(5)	1	Solder
	Pb(12) Ba(1)Zn(1)Fe(14)Mn(6)Ca(4)K(14)P(40)Si(2)Al(2)Mg(3)	1	P
	Pb(4)Sb(42)Sn(52)Al(2)	1	Alloy
7	Pb(92-100)	>10	None
8	Pb(48)Fe(1)S(48)Al(3)	1	Sulfate
	Pb(1)Sn(35)Ag(1)Zn(3)Cu(3)Fe(18)Ca(4)Si(23)Al(10)Mg(2)	1	Alloy
	Pb(37)S(38)Si(14)Al(7)Na(5)	1	Sulfate
9	Pb(98)Ca(2)	1	None
10	Pb(2)Cu(4)Fe(50)Ca(3)K(1)Si(26)Al(10)Mg(2)	1	Cu/Fe/Al
	Pb(22)Fe(4)Ti(4)Ca(4)K(10)Si(39)Al(16)	1	Al/K
	Pb(65)Sb(5)Fe(2)Ca(5)Si(23)	1	Alloy
	Pb(10)Sn(75)Cu(2)Cl(3)Si(11)	1	Solder
	Pb(46)Fe(1)Ca(12)Cl(29)Si(9)Al(2)	1	Chloride
	Pb(96)Si(4)	1	None

\* N = Number of times Pb was observed in a similar composition

#### 4.6 SEQUENTIAL EXTRACTION

Results of sequential extraction are illustrated in figure 4.3. Between 50 and 95% of the Pb was bound in fractions III (Organic) and IV (residual) in all soils except soil 7, illustrating strong bonding and possibly importance of bonding to organic matter. The strongest bonding was seen for soils 8 and 10, while soil 7 contained considerably more mobile Pb than the 9 other soils. There is no relation between mobility as revealed through sequential extraction and through pH-dependent extraction, which revealed Pb in soil 6 to be the least mobile. Most of the soils contain little or no Pb bound in fraction I (ionexchangeable/ carbonate bound), but from the three most polluted soils (2, 7, 10), significant amounts of Pb were extracted during this step, with >5% extracted from soils 2 and 10 and >35% extracted from the severely contaminated soil 7. In general it can however not be verified that the fractions oxide

bound, carbonate bound and organically bound Pb are increasing on the expense of residual lead in contaminated soil as found by (Chlopecka *et al.*, 1996), possibly because many of the soils in this study are contaminated by industrial sources in contrast to the diffusely contaminated soils investigated by (Chlopecka *et al.*, 1996).

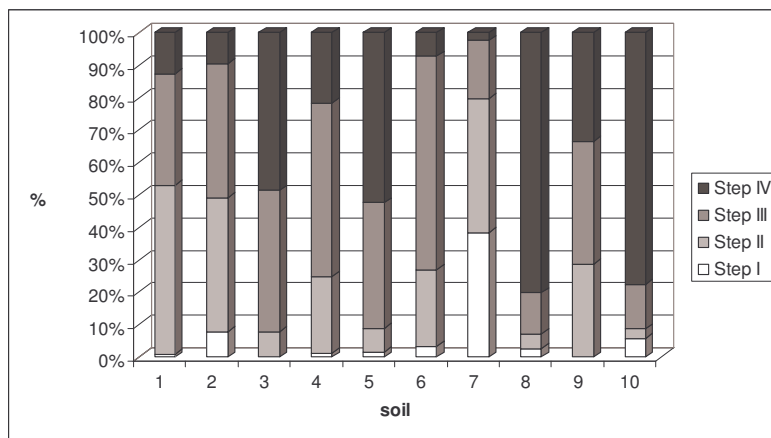


Figure 4.3: Results of sequential extraction of Pb from the 10 soils.

The large fraction of residual Pb in soils 3, 4, 9, and in particular 8 and 10 suggests presence of incompletely transformed contaminating compounds or transformation into highly stable compounds like anglesite, pyromorphite or plumbogummite rather than absorption of Pb in the lattice structure of soil minerals as is the case in uncontaminated soils. During sequential extraction of pure compounds, metallic lead was extracted almost completely in step III (36%) and IV (44%).  $\text{PbSO}_4$  was extracted partly in step III (17%) and IV (27%). Less than 4% of the  $\text{PbCrO}_4$  was extracted during the whole procedure, while solder was extracted completely in step IV (98%). In other works, the residual Pb has been observed to consist of Pb absorbed in the mineral matrix, Pb bound to phosphates (Ma and Rao, 1997) and sulfates (Lin *et al.*, 1998). The fact that metallic Pb and  $\text{PbSO}_4$  in this work was shown to be extracted over two steps, underline how sequential extraction is rather a measure of mobility than an exact quantification of Pb-speciation.

## 5 Discussion

### 5.1 INDIVIDUAL SOILS

*Soil 1* is a sandy soil relatively low in organic content, but with a considerable content of feldspars and phosphate. Pb is the only contaminant present as a consequence of the burn down of an ancient church in 1627. The soil contains increased Pb-concentrations in the  $< 0.063\text{mm}$  fraction and, to a lesser extent, in the 1-4 mm fraction. SEM-EDX results show that Pb exists in association with phosphate, as well as with aluminum and iron. Pb was also found in connection with Sn at two spots during SEM-EDX, but since the concentration of Sn in this soil is much lower than the concentration of Pb, this cannot be the general case. The presence of Pb and P in almost equivalent amounts with Cl, Al and Fe suggests a mixture of pyromorphite and plumbogummite. The residual fraction is relatively small, and SEM-results together with the age of the contamination and knowledge of transformation of metallic Pb in

soil (Jorgensen and Willems, 1987; Lin *et al.*, 1995) suggests that most of the originally metallic Pb has been transformed. Results of sequential extraction show that Pb has been primarily transformed into oxide-bound and organically bound Pb. The large fraction of organically bound Pb illustrates that even a relatively low content of organic matter dramatically influences the speciation of Pb in soil. *Soil 2* is a clayey soil contaminated with Pb and Cd by metallurgical processes and recycling of lead-acid accumulators. The large fraction of undefined expandable clay minerals and low carbonate content suggests advanced weathering of the soil, which could be related to acidic waste from accumulators. The majority of the Pb is concentrated in grains < 0.063mm although an extraordinary high concentration of Pb is observed in the 2-4mm fraction, suggesting incomplete transformation of original Pb-compounds in this soil. The small fraction of grains in this size-interval however causes this Pb to constitute an insignificant fraction of the total Pb. SEM-EDX results indicate phosphate minerals, and metal-compounds as Pb-associates. The relative atomic percentages in the phosphates indicate presence of pyromorphite which has been observed repeatedly in studies of lead-mineralogy in soil e.g. (Chen *et al.*, 1997; Ostergren *et al.*, 1999). The metals (ZnCu and SnSb) may well be representative of the original contamination with smelter waste products from metal-extraction. S was found together with Pb, Fe, Zn and Cu, likely to represent metal-sulfates originating from accumulator recycling activities as those observed by (Manceau *et al.*, 1996) or smelter emission as found by (Ettler *et al.*, 2005) possibly as jarosite. Sequential extraction results show that the soil contains a relatively large fraction of Pb bound to oxides. The organic fraction is slightly greater than that of soil 1, reflecting the larger content of organic matter. The residual fraction is relatively small reflecting a large degree of transformation as suggested by the grain-size fractionation.

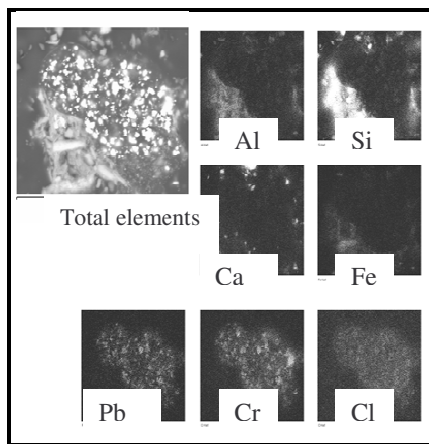


Figure 5.1: Distribution of elements in lead-polluted grain of soil 3. Pb is associated with Cr and Cl.

*Soil 3*, a sandy soil from car painting activity was found solely to contain Pb in association with Cr. The almost equivalent amounts suggest that Pb exists as lead-chromate, a yellow pigment previously used in paint. Considering the total amounts, Cr can be responsible for binding 4/5 of the Pb as lead-chromate, keeping in mind that  $\text{PbCrO}_4$  was shown to be extremely stable even during digestion, which leaves the possibility that the soil being far more contaminated by both species than revealed

open. The finding renders probable that a large fraction of the Cr exists as Cr(VI), far exceeding the governmentally assigned limit for Cr at this oxidation-state (see note table III). Figure 5.1 shows a mapping of the elements in a grain of soil 3. Apart from Cr, Cl seems to be associated with Pb and Cr, thus lead may also exist as lead-chloride. Soil 3 is the only soil in which Pb is not concentrated in the smallest size-fractions of the soil, pointing towards a small degree of transformation of the original pollution, in accordance with the consistent SEM-EDX results. Slow transformation is made likely by the extremely low solubility of lead-chromate, and although the soil contains much phosphate, Pb in association with phosphate was not seen during SEM-EDX. Indeed a considerable residual fraction is revealed, and incomplete dissolution at acidic pH is supporting the presence of insoluble Pb-species. *Soil 4* is a sandy soil, rich in organic matter, and with some feldspar. It contains Pb, Ni, Cd and Zn at contaminant level, and the Pb is primarily concentrated in the < 0.063mm fraction, but also at increased concentrations in the larger grain-sizes (> 1mm). SEM-EDX results reveal Pb in association with Fe/Al-minerals and phosphate minerals which like in soil 1 are likely to consist of a mixture of pyromorphite and plumbogummite; sequential extraction results show a dominant organic fraction, indicating that a large fraction of Pb in this soil has been transformed from the original speciation and adsorbed by soil-constituents. *Soil 5* is highly organic and has a considerable content of feldspars. Pb, Ni, Cu and Cd are found at contaminant level. SEM-EDX analysis shows Pb in a metallic alloy with Sn and Sb as well as in Fe/Al-minerals. The soil is rich in phosphate, but no association with phosphate is revealed. Sequential extraction shows a surprisingly large residual fraction and a corresponding small organic fraction relative to the large organic content. The oxide-fraction is also small. This observation led us to repeat sequential extraction, doubling the number of times which the soil was oxidized by H<sub>2</sub>O<sub>2</sub> during step III to make sure that all organic matter had been oxidized. The results resembled the original results within 2 %, why it was concluded that step III satisfactorily oxidizes all organic matter, and that Pb in this soil exists in stable compounds from which it is only slowly released to the organic matter. Increased concentrations of Pb in the larger size-fractions (1-4mm) in addition suggest the presence of stable and not yet transformed Pb-contaminants as e.g. metallic alloys. The large content of Cr (larger than soil 3) suggest a possible presence of PbCrO<sub>4</sub> in this soil as well, however this is not confirmed by SEM-EDX and a 100% dissolution under acidic conditions which was not seen for soil 3 suggest unlike speciation in soil 5, dominated by metallic alloys. *Soil 6* is another organic soil, containing the same metals as soil 5. The soil is relatively clayey and rich in feldspars while low in phosphate. Pb is concentrated in the < 0.002mm fraction of this soil, suggesting extensive disintegration of the originally contaminating species. During SEM-EDX, Pb was found as solder/alloy and in phosphate minerals (possibly plumbogummite). Sequential extraction shows that the organic fraction of Pb prevails, while oxides also exist. The low solubility of Pb from this soil at low pH could be due to the large fraction of organically bound Pb. This could explain both the relatively high solubility at pH 5.8 and the relatively low solubility at low pH, since humic acids are insoluble under acidic conditions (pH < 2) but soluble at higher pH values. *Soil 7* is a clayey soil which contains little phosphate, organic matter and carbonate and medium feldspars. In addition to Pb the soil is contaminated with Zn and Ni. Pb is extremely concentrated in the < 0.063mm fraction in this soil. During SEM-EDX almost pure Pb was found at several spots; however, sequential extraction reveals a high mobility of Pb in this soil. Apart from reflecting the clayey nature of the soil, the large exchangeable fraction also reflects the high contamination level, at which the

adsorption capacity of oxides and organic matter may be exceeded. Indeed a considerable Pb-fraction is bound to oxides, while the organic fraction is small, reflecting the small amount of organic matter. The residual fraction is small, suggesting that the pure Pb observed may not be metallic, but more soluble compounds like e.g. lead carbonates or oxides (e.g. hydrocerussite and cerussite) as observed by e.g. (Welter *et al.*, 1999; Vantelon *et al.*, 2005). The high mobility and exchange-ability is supported by extraction of 10% Pb already at pH 4.7, complete extraction at low pH and high extraction at alkaline pH. *Soil 8* is a relatively clayey soil with a high carbonate-content, while medium in phosphate, organic matter and feldspars. Apart from Pb, the soil is contaminated with Ni, Cu, Cd and Zn, and has a markedly elevated content of Sn. SEM-EDX showed Pb with sulfate (anglesite) in consistence with the findings of (Ettler *et al.*, 2005) and metallic solder/alloy. The high Sn-concentration supports the fact that Pb exists as solder/Sn-containing alloys in this soil, in consistence with its origin from a metal foundry, as does the fact that more than 80% of the Pb was released during step IV during sequential extraction. *Soil 9* is another relatively clayey soil, resembling soil 8, but high in feldspars. Only one spot with Pb was found during SEM-EDX studies, showing Pb without any association. This could be carbonates, oxides or metallic Pb. Sequential extraction shows almost even distribution of Pb between the oxides, organically bound Pb and the residual fraction. *Soil 10* is a carbonate and feldspar-rich soil. It is low in organic matter but relatively rich in phosphate. Pb is concentrated in the < 0.063mm fraction, but shows elevated concentrations in the 0.25-1.00mm fraction. SEM-EDX results reveal a mixed Pb-pool in this soil, where Pb in association with iron/aluminum-minerals, metallic alloy, solder, chloride and pure Pb is identified. Sequential extraction reveals a large residual fraction. The large residual fraction suggests that a large part of the Pb is still in its original form, supported by the observation of Pb in alloy, solder and possibly metallic.

## 5.2 GENERAL DISCUSSION

Correlations between amounts of Pb (mg/kg) (table VI) extracted in each step of sequential extraction and all quantified soil parameters were made. The best correlations are given in table VII.

TABLE VI  
Extracted amount of Pb (mg/kg) in each step of sequential extraction

Soil	1	2	3	4	5	6	7	8	9	10
Step I	2	72	9	8	9	37	1577	36	0	95
Step II	127	389	34	137	39	261	1688	62	196	49
Step III	83	390	432	311	207	731	739	169	258	228
Step IV	31	89	223	127	280	81	99	1079	229	1287
Tot	244	940	697	583	534	1109	4102	1345	683	1658

A convincing correlation is found between the amounts extracted in step I, II (and III) and the total concentration of Pb in the soil. The exactnesses of these correlations decrease with the progress of the sequential extraction. This illustrates how the amount of Pb extracted in the first steps is primarily a function of the total amount of Pb in the soil, while the extracted amounts in the residual fraction is not. No correlation is seen between the extracted amount of Pb in step I and content of  $\text{CaCO}_3/\text{CEC}$ , and no correlation is seen between the extracted amount in step II and



the content of iron, although a major part of the reducible Pb could be expected to be bound to iron-oxides. Instead an indication of a positive correlation is found between extracted amounts in steps I and II and content of feldspars, suggesting a preferential adsorption to feldspars. This is in consistence with the presence of Pb in association with Al-minerals in many soils.

TABLE VII  
Correlation coefficients ( $r^2$ ) obtained by linear correlation between soil-characteristics and amount of Pb (mg/kg) extracted during each step of sequential extraction (- indicates a negative correlation).

Step	Total Pb (mg/kg)	CaCO <sub>3</sub> (%)	OM	CEC	Fe	P	Feldspars (%)
I	0.89	-0.15	0.04	-0.04	0.01	-0.12	0.27
II	0.81	0.21	0.04	0.04	0.02	-0.23	0.33
III	0.38	0.14	0.00	0.01	0.06	-0.59	0.07
IV	0.01	0.48	0.01	0.07	0.06	0.32	0.02

A correlation between the content of organic matter and Pb extracted in step III could have been expected, as seen by (Zhang *et al.* 1997). However in this work, the organic soil 5 exhibits much lower extraction in step (III) than expected from the content of organic matter and the most contaminated soil 7 shows a much higher extraction in step (III) than expected from the content of organic matter. Within the rest of the soils a positive correlation ( $r^2 = 0.60$ ) exists. Showing how organic matter in general is important to the speciation of Pb in soil. Negative correlations exist between the Pb extracted in steps I, II and III and content of phosphate, while a positive correlation exists with step IV, verifying that phosphates are important to the strength of the bonding of Pb in soil as shown by e.g. (Laperche *et al.*, 1996; Chen *et al.*, 1997). A positive correlation also exists between carbonate and amount extracted in step IV. This is not explicable, taking the information from the predominance diagrams in figures 2.2 and 2.3 into consideration. We suggest that it is either a coincidence that the soils with high carbonate-content are also the soils with large residual fractions, or it is a possibility that a high carbonate-content functions as a buffer protecting original and stable Pb-contaminants from disintegration as suggested by (Essington *et al.*, 2004).

## 6 Conclusions

The first factors determining the bonding of Pb in industrially contaminated soil are: contamination level, and the stability of the originally contaminating Pb-species. Soil characteristics are of secondary importance. Pb is concentrated in the small (< 0.063mm) grain-fractions of most soils. This concentration is less dominant in soils contaminated with very stable Pb-compounds. In all soils, discrete particles of concentrated Pb are found during SEM-EDX. Pb is bound strongly to the soils with > 50% extracted in step III and IV of sequential extraction for all soils but one. With few exceptions, desorption of Pb is close to 0 between pH 4 and 12.5. For the soils which show desorption in this interval less than 10% is extracted at pH 4.5-5.8. Below pH 2 desorption is observed for all soils. There is no relation between mobility as revealed through sequential extraction and through pH-dependent desorption. Exchangeable Pb exists only in severely contaminated soils, where the bonding capacity of organic matter and oxides is exceeded. The amount of Pb extracted during



the first steps of sequential extraction is mainly a function of the total amount of Pb in the soil, while the extracted amount in the residual fraction depends on the stability of the original contaminating species and the content of phosphate. A correlation between extracted amounts in steps I and II and content of feldspars is found, leading to the suggestion that Pb preferentially adsorbs to feldspars. No correlation exists between extracted amount in step III and content of organic matter, however leaving out results of two extreme soils, a fine correlation is revealed, showing how organic matter in general is important to the speciation of Pb. Phosphate negatively correlates with Pb-content in fractions I, II and III and positively with the residual fraction, verifying that precipitation of sparingly soluble phosphates increases the strength of the Pb-bonding in phosphate-rich soils. It is a possibility that a high carbonate-content functions as a buffer protecting original and stable Pb-contaminants from disintegration.

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## 5. The Effect of Soil Type on the Electrodialytic Remediation of Lead- Contaminated Soil

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### Abstract

This work investigates the influence of soil type on electrodialytic remediation (EDR) of lead (Pb). It is well-known in electrokinetic soil remediation that pH is a key factor, and carbonate influences remediation efficiency negatively. This work provides results from laboratory scale EDR experiments with ten representative industrially Pb-contaminated surface soils. The efficiency of the direct current is evaluated with respect to a fixed current passage. Results indicate that Pb-speciation is of primary importance. Specifically, organic matter and stable compounds like  $\text{PbCrO}_4$  can impede and possibly even preclude soil remediation. In soils rich in carbonate, where the acidic front is impeded, part of the Pb can be transferred from the soil to the anolyte as negatively charged complexes during the EDR process. The dominant complex is in this case likely to be  $\text{Pb}(\text{CO}_3)_2^{2-}$ . Efficient remediation is however not obtained until all carbonate has dissolved and  $\text{Pb}^{2+}$  is transported to the catholyte. Thus the presence of carbonate negatively influences the remediation-time. Pb bound to soluble organic matter is also transported towards the anolyte during EDR. The primary effect of the mainly insoluble organic matter commonly present in surface soil is however to immobilize Pb and impede remediation. Overall, the potential for EDR remediation of fine grained, inorganic soils is found to be feasible when the Pb is not associated with extremely stable compounds.

**Key words:** electrodialytic remediation, electrokinetic remediation, industrial contamination, Pb, soil, speciation.

### 1 Introduction

Pb is the most common heavy-metal found in contaminated soil and, due to its low mobility, one of the most difficult to remediate. One method that has been investigated is electrokinetic soil remediation (EKR), in which an electric DC current is applied for

mobilization of primarily charged Pb-species in the electric field. Electrodialytic soil remediation (EDR) is an EKR method in which ion-exchange

TABLE I  
Results obtained in laboratory scale EKR feasibility tests with Pb spiked and industrially contaminated kaolinite and soils.

Soil type	Source	Pb conc. [mg/kg]	Current [mA/cm <sup>2</sup> ] or voltage [V/cm]	Reagent added Anode/Cathode	Time [d]	Length [cm]	Removal [%]	Reference
Georgia kaolinite	Spiked	145	0.04 mA/cm <sup>2</sup>		54	20.3	90	(Hamed <i>et al.</i> , 1991)
Georgia kaolinite	Spiked	340-410	0.15 mA/cm <sup>2</sup>	Ca <sup>2+</sup>	4	10	19	(Coletta <i>et al.</i> , 1997)
kaolinite	Spiked	391	1.2mA/cm <sup>2</sup>	H <sub>2</sub> SO <sub>4</sub> / H <sub>2</sub> SO <sub>4</sub>	4	15	75	(Kim <i>et al.</i> , 2001)
Marine clay	Spiked	5000	0.1 mA/cm <sup>2</sup>	N/HAc	52	5	~ 75	(Rødsand <i>et al.</i> , 1995)
Silt loam	Spiked	1000	4 V/cm	NaNO <sub>3</sub> /HAc	18	7.5	65	(Reed <i>et al.</i> , 1995)
Silt loam	Spiked	1000	4 V/cm	HCl/HAc	14	7.5	75	(Reed <i>et al.</i> , 1995)
Silt loam	Spiked	1000	4 V/cm	NaNO <sub>3</sub> /EDTA	12	7.5	75	(Reed <i>et al.</i> , 1995)
Sand	Spiked	358	1.5 V/cm	NaOH/EDTA	2	20	100	(Wong <i>et al.</i> , 1997)
Sand	Spiked	948	1 V/cm	KNO <sub>3</sub> **	5	35	91	(Li <i>et al.</i> , 1997)
Fine sandy loam	Spiked	1000	8 V/cm	HCL/HAc	20	7.5	96	(Viadero <i>et al.</i> , 1998)
Silt loam	Spiked	1000	1 V/cm	Citric/HAc	20	20	53	(Yang and Lin, 1998)
Basic clay loam	Spiked	551	0.4 V/cm	HCl*	7	18	Little	(Sah and Chen, 1998)
Neutral loamy sand	Spiked	522	0.4 V/cm	HCl*	7	18	Little	(Sah and Chen, 1998)
Acidic clay	Spiked	533	0.4 V/cm	HCl*	7	18	Little	(Sah and Chen, 1998)
Marine clay	Spiked	5000	0.6mA/cm <sup>2</sup>	N/N	30	10	95	(Chung and Kang, 1999)
Marine clay	Spiked	5000	0.6mA/cm <sup>2</sup>	N/HAc	15	10	94	(Chung and Kang, 1999)
Illitic soil	Spiked	5000	0.2mA/cm <sup>2</sup>	NaOAc/HAc	98	12.5	80	(Li and Li, 2000)
Natural clay	Spiked	500	0.5mA/cm <sup>2</sup>	N/N	15	20	88	(Chung and Kamon, 2005)
Natural clay	Spiked	500	0.5mA/cm <sup>2</sup>	ultrasound	15	20	91	(Chung and Kamon, 2005)
Loose organic silt	Unknown	3939	0.1 mA/cm <sup>2</sup>	NaAc/NaAc*	29	10.2	11	(Mohamed, 1996)
Clay	Unknown	1990	0.05 mA/cm <sup>2</sup>	N/N	157	10	2	(Alshawabkeh <i>et al.</i> , 1997)
Clay	Unknown	1990	0.05 mA/cm <sup>2</sup>	HAc/HAc	157	10	6	(Alshawabkeh <i>et al.</i> , 1997)

TABLE I (continued)

Soil type	Source	Pb conc. [mg/kg]	Current [mA/cm <sup>2</sup> ] or voltage [V/cm]	Reagent added Anode/Cathode	Time [d]	Length [cm]	Removal [%]	Reference
Tailings soil	Mining	5175	1.2mA/cm <sup>2</sup>	H <sub>2</sub> SO <sub>4</sub> / H <sub>2</sub> SO <sub>4</sub>	5	15	10	(Kim and Kim, 2001)
Tailings soil	Mining	1438	1.2mA/cm <sup>2</sup>	H <sub>2</sub> SO <sub>4</sub> / H <sub>2</sub> SO <sub>4</sub>	4	15	50	(Kim <i>et al.</i> , 2001)
Illitic clay	Chlor-alkali factory	375	1.1 V/cm	NaCl/NaCl	182	27	0	(Suer <i>et al.</i> , 2003)
Clayey sand	Extraction of metals	1090	0.2mA/cm <sup>2</sup>	AN*** /CAT	76	5	79	(Ottosen <i>et al.</i> , 2005)
Loamy sand	Unknown	1060	0.8mA/cm <sup>2</sup>	AN*** + Am. Citr./CEM + Am. Citr.*	21	5	14	(Ottosen <i>et al.</i> , 2005)

\*Soil soaked in reagent prior to remediation

\*\* Reagent placed in extended chamber between soil specimen and cathode

\*\*\* AN = Anion Exchange Membrane, CAT = Cation Exchange Membrane

membranes separate the soil from electrolytes, physically inhibiting the intrusion of an alkaline front into the contaminated soil, while creating an acidic front due to water-splitting at the surface of the anion-exchange-membrane (Ottosen *et al.*, 2000).

It is well established that among common contaminating metals, Pb is the least amenable to EKR and EDR (Mohamed, 1996; Hansen *et al.*, 1997; Ottosen *et al.*, 2001). The progress of an electrokinetic remediation experiment depends on the applied current density or voltage gradient as well as the duration of the experiment. Generally it is agreed upon that higher current/voltage and increased remediation time positively influences remediation (Viadero *et al.*, 1998; Chung and Kang, 1999). Current densities between 0.04 and 1.2mA/cm<sup>2</sup> and voltage gradients between 0.4V/cm and 8V/cm are reported in literature (table I). In EKR the maximum current/voltage applicable depends on the individual soil and its conductivity. In electro-dialytic soil remediation an optimal current-density around 0.4 mA/cm<sup>2</sup> was reported in two cases (Hansen *et al.*, 1999; Ottosen *et al.*, 2000). Results (table I) show how decreased remediation success in experiments with spiked kaolinites and soils (Coletta *et al.*, 1997; Sah and Chen, 1998) can be explained by low energy-input and/or short duration. In contrast low energy-input cannot solely explain the less successful remediation results of industrially contaminated soils (table I). Indeed spiked Kaolinite was shown to be remediated faster than complex soils (Le Hecho *et al.*, 1998; Reddy *et al.*, 2003), and many works have reported that soil characters such as pH, buffer capacity and lime content are of primary importance to the progress of EKR and EDR (Lageman *et al.*, 1989; Hamed *et al.*, 1991; Yeung *et al.*, 1996; Hansen *et al.*, 1997). In retaliation (Ottosen *et al.*, 2001) saw that Pb was removed at higher pH values from highly carbonaceous soils (> 12% CaCO<sub>3</sub>) than in soils with < 3.7% CaCO<sub>3</sub>. This was thought to be due to the presence of Pb as PbCO<sub>3</sub>, which is soluble at relatively high pH, in the carbonaceous soils.

The influence of Pb speciation on remediation has not been well-established. (Kim and Kim, 2001) studied the relation between removal and fractionation as determined by sequential extraction in a tailings soil. They found that no residual Pb was removed, while most of the exchangeable Pb and part of the carbonate-bound,



oxide-bound and organic Pb was removed. It has also been demonstrated that remediation is more effective (in terms of % Pb removal) with highly contaminated soils than with soils with only slightly elevated Pb-concentrations (Jeong and Kang, 1997; Chung and Kang, 1999). This finding is probably due to the increased likelihood of finding a larger fraction of mobile charged Pb-ions in highly contaminated soils. In heavily contaminated soils, the capacity of sites for strong bonding is more likely to be exceeded and a larger fraction of the Pb may be present as water-soluble, exchangeable or carbonate-bound (Jensen *et al.*, 2006). Speciation was found to be of primary importance when part of the Pb in a soil contaminated by chlor-alkali industry was observed to be moving towards the anode (Suer *et al.*, 2003). The presence of sulfur in the soil and formation of the negative complex  $\text{Pb}(\text{SO}_4)_2^{2-}$  was used to explain this behavior, and implying a complex interaction between Pb, soil and co-contaminating compounds during remediation.

This purpose of this work is to advance our understanding of Pb-contaminated soil remediation by the process of electrodialysis, or EDR. The emphasis of this work is on elucidating the influence of soil properties and Pb-speciation on the feasibility of EDR. In a departure from the practice of spiking samples, the bench-scale EDR experiments described in this work are performed using industrially contaminated soils such that a range of soil physical and chemical properties are investigated for a variety of realistically occurring Pb species.

## 2 Materials and Methods

### 2.1 SOIL SAMPLES AND ANALYTICAL METHODS

Ten industrially polluted soils were collected in 1999 from sites around Denmark. All soils were analyzed and Pb-speciation was investigated. Probable contamination sources and Pb-speciation as revealed in (Jensen *et al.*, 2006) are given in table II. All soils were analyzed to quantify grain-size distribution; pH; carbonate-content; organic matter; cation exchange capacity (CEC); concentrations of Fe and Cl; conductivity; phosphate; mineralogy and the heavy metals: Pb, Ni, Cu, Cd, Zn, Sn, Cr. All results reported are the mean of at least three analyzed samples, with the exception of grain size distribution (single analysis), and phosphorus (duplicate analyses). *Grain-size distributions* were determined by wet-sieving approximately 100g natural wet soil with 0.002M  $\text{Na}_4\text{P}_2\text{O}_7$  through a 0.063mm sieve followed by separation by dry sieving of the larger size fractions ( $>0.063$  mm) and an X-ray based sedimentation method for the fractions less than 0.063 mm (Micrometritics SEDIGRAPH 5100). *pH* was measured by electrode MeterLab® CDM220 after shaking of 5.0g dry soil with 12.5mL 1M KCl constantly for 1 hour, followed by settling for 10min. *Carbonate content* was determined volumetrically by the Scheibler-method when reacting 3g of soil with 20mL of 10% HCl. The amount was calculated assuming that all carbonate was present as calcium-carbonate. *Organic matter* was determined by loss of ignition in a heating furnace at 550°C for 1 hour. *CEC* was determined after ion exchange of 10g dry soil with  $\text{NH}_4^+$ , followed by exchange of  $\text{NH}_4^+$  for  $\text{Na}^+$ . The ammonium concentration of the supernatant was measured by spectrophotometer via flow-injection.

TABLE II  
Contamination sources and likely Pb speciation as revealed by (Jensen *et al.*, 2006).  
Dominant species are in bold font.

Soil	Activity and probable Pb-source	Activity period	Pb-Associations
1	Ancient church with Pb-roof burned down	1627	Solder Phosphates (pyromorphite + plumbogummite) Al/Fe-minerals <b>Oxide-bound</b> <b>Organically bound</b>
2	Extraction of metals from scrap and ore. Smelter waste products deposited on site. Battery recycling.	1938-1985	Phosphates (pyromorphite) Alloys (smelter waste products) Sulfate (jarosite) <b>Oxide bound</b> <b>Organically bound</b>
3	Car painting. Use of lead based paints.	1900's	<b>Chromate</b> <b>Organically bound</b>
4	Harbor area, filled up with waste from porcelain production and a gasworks. Braking up and scrapping of locomotives.	1880-1988	Phosphates (pyromorphite + plumbogummite) Fe/Al-minerals Oxide-bound <b>Organically bound</b>
5	Former waste-dump with mixed industrial waste and household waste. Covered with sewage sludge, ash and mould.	1913-1937	Al/Fe-minerals <b>Alloy</b> Organically bound Oxide bound
6	Former waste-dump with mixed industrial waste and household waste. Covered with sewage sludge, ash and mould.	1913-1920	<b>Alloy</b> <b>Solder</b> <b>Phosphates</b> (plumbogummite) <b>Organically bound</b> <b>Oxide bound</b>
7	Gravel pit used as waste dump.	1900's	<b>Carbonates/oxides</b> (hydrocerussite, cerussite, litharge) <b>Oxide bound</b> Organically bound
8	Metal foundry	1921-1976	<b>Sulphates</b> (anglesite) <b>Solder</b> Organically bound
9	Harbor area filled up with harbor sludge and surface soil from central Copenhagen between 1780 and 1820. Site laid out as army ammunition site with chemical storage.	After 1780	<b>Metallic</b> <b>Oxide bound</b> <b>Organically bound</b>
10	Soil collected by contractor north of Copenhagen.	Unknown	Fe/Al -minerals <b>Metallic</b> <b>Alloys</b> <b>Solder</b> Chloride Organically bound

*Conductivity* was measured by electrode (MeterLab CDM210) in a solution prepared by constantly mixing of 10g soil and 25ml distilled water for 30min, followed by settling for 20min. Phosphate was measured after digestion of 0.2-0.5g sample at 550°C followed by boiling with HCl, reaction with ammonium molybdate to form yellow phosphor-molybden acid, and reduction by ascorbic acid in the presence of antimony. The strong blue color was measured by spectrophotometer (Shimadzu UV-1601). *pH-dependent desorption* of Pb from the soil was investigated by extraction of 5.00g dry, crushed soil with 25.00ml reagent at 200rpm for 7 days. The reagents were as follows: 1.0M NaOH, 0.5M NaOH, 0.1M NaOH, 0.05M NaOH, 0.01M NaOH, distilled water, 0.01M HNO<sub>3</sub>, 0.05M HNO<sub>3</sub>, 0.1M HNO<sub>3</sub>, 0.5M HNO<sub>3</sub>, 1.0M HNO<sub>3</sub>. pH was measured after 10min settling, after which the liquid was filtered through a 0.45µm filter for subsequent measurement on AAS. Non acidic samples were preserved with one part of conc. HNO<sub>3</sub> to four parts of liquid in autoclave at 200 kPa and 120°C for 30 minutes prior to AAS measurement. *Metals* were analyzed according to the Danish standard method DS259 (Dansk Standardiseringsråd, 1991), which entails a 30min acid digestion of 1g soil with 20.00mL of half concentrated HNO<sub>3</sub> in an autoclave at 200kPa and 120°C. The metal-content in solution was measured by atomic adsorption spectrophotometry (AAS, Perkin Elmer 5000 or GBC 932AA) following filtration through a 0.45µm filter. AAS analyses were for all metals validated through analysis of reference samples.

TABLE III  
Measured physical and chemical characteristics of the soils from Table II.

Soil number	1	2	3	4	5	6	7	8	9	10
<b>Parameter</b>										
<b>Clay (%) (&lt; 2 µm)</b>	5	35	8	8	6	11	20	13	14	10
<b>pH</b>	6.9	6.1	7.2	6.9	6.3	7.2	6.8	7.6	7.6	7.8
<b>CaCO<sub>3</sub> (%)</b>	3.7	0.5	3.7	6.7	0.9	4.9	1.0	9.1	7.7	9.2
<b>Organic matter (%)</b>	2.6	4.1	3.5	7.4	21.3	11.7	3.6	3.4	7.0	2.8
<b>CEC (meq/100g)</b>	6.6	15.3	3.7	6.3	26.0	10.3	5.3	4.9	8.2	4.5
<b>Fe (g/kg)</b>	5.2	18.8	9.5	24.4	37.6	30.4	21.5	12.0	13.6	13.6
<b>Conductivity (µS/cm)</b>	244	446	194	455	1820	351	281	1848	1659	637
<b>Phosphate [mg/kg]</b>	1200	745	2224	1257	2455	539	741	1036	1123	1547

## 2.2 EDR FEASIBILITY EXPERIMENTS

Electrodialysis experiments were carried out in cylindrical Plexiglas cells with three compartments (Figure 2.1). The center compartment contained the soil specimen which was 10 cm long and 8 cm in diameter. The anolyte and catholyte were separated from the soil specimen by anion- and cation-exchange membranes, respectively (Ionics, AR204SZRA and CR67 HVY HMR427, respectively). Electrolytes were circulated between electrolyte chambers and glass reservoirs by a mechanical pump (Masterflex® model 7553-76). Platinum-coated electrodes (Permacand) were used as working electrodes. The electrolytes initially consisted of 500mL 0.01 M NaNO<sub>3</sub> adjusted to pH 2 with HNO<sub>3</sub>. Prior to the beginning of each experiment, soil specimens were mixed with deionized water to a moist but unsaturated consistency.

A constant current of  $0.2\text{mA/cm}^2$  was maintained in all experiments except where noted in table IV. pH in the electrolytes, current and voltage were observed approximately once every 24 hours. Each experiment was terminated after approximately 67500coulomb/kg had passed through the soil. The quantification of charge with respect to mass and not volume of soil was necessary because the soil mass and water content varied considerably from one sample to another due to variations in soil organic matter and soil structural differences. During the electrodialysis experiments  $\text{H}^+$ , and  $\text{OH}^-$  were produced at the anode and cathode, respectively. The ion-exchange membranes hindered intrusion of these ions into the soil specimen, and pH-changes occurred in the electrolytes. An electrode (MeterLab CDM220) was used to measure pH in electrolyte compartments, which was maintained between 1 and 2 by manual addition of  $\text{HNO}_3$  and  $\text{NaOH}$ .

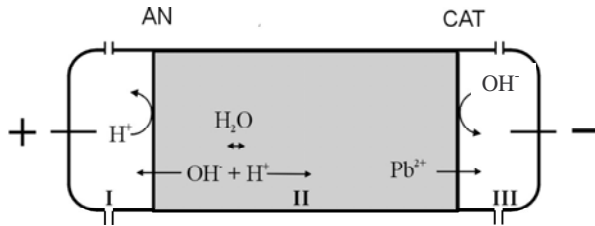


Figure 2.1: Schematic drawing of a cell used for experimental electrodialytic remediation of contaminated soil. AN = anion-exchange-membrane, CAT = cation-exchange-membrane

TABLE VI

Summary of bench-scale EDR feasibility experiments (see Tables 2 and 3 for soil origins and characteristics). The charge passage was kept constant at 67.5 C/g DW.

Exp./Soil No	Current density [mA/cm <sup>2</sup> ]	Voltage (range)***	Soil [g dry weight]	Time [days]	Initial water content [%]
1	0.2	1.8-116.8	750	59	22
2	0.2**	6.1-104.7	1131	70	27
3	0.2	2.8-44.0	764	60	20
4	0.2	3.2-29.6	700	55	24
5	0.2	4.1-33.4	508	40	49
6	0.2	4.8-137.2	566	44	30
7	0.2*	3.0-139.3	848	78	19
8	0.2	2.4-137.1	854	67	18
9	0.2*	4.3-135.8	696	86	27
10	0.2*	3.1-138.3	889	71	17

\*Due to imperfect contact between soil and membranes current decreased during a period of the remediation. This was compensated for by longer remediation, to reach the wished passage of current.

\*\*During part of the period current was increased to  $0.4\text{mA/cm}^2$

\*\*\* The high voltages were observed only during short periods, when catholytes needed pH adjustment in all experiments but 7, 9 and 10.

After each experiment, the soil specimen was divided into five sections perpendicular to the current-direction. Pb, pH and water content were measured in each slice. Membranes were cleaned overnight in 1M HNO<sub>3</sub> and electrodes were cleaned overnight in 5M HNO<sub>3</sub>. Volumes of the cleaning acids as well as the electrolytes were measured followed by analysis of the Pb-concentration by AAS.

### METAL-MOBILIZATION LENGTH

Results from electrokinetic soil remediation feasibility experiments presented in terms of the percentage of metal removed clearly dependent on experimental geometry all else being equal, shorter systems will exhibit greater removal. Coletta *et al.*, (1997) suggested evaluation of the moments of synoptic concentration distributions for comparison. We modified this approach in order to facilitate comparisons between distributions observed over various soil specimen lengths, and suggest the metal-mobilization-length ( $M_m$ ) parameter defined as:

$$M_m = \frac{M_1}{M_0} \quad (1)$$

Where  $M_1 = 1^{\text{st}}$  moment of contaminant (position of the center of mass of contaminant being mobilized) and  $M_0 = 0^{\text{th}}$  moment (total mass of contaminant in the sample). For a discretely sampled experiment,  $M_0$  and  $M_1$  can be approximated as:

$$M_0 = \frac{\sum_i c_i l_i}{c_0 L} \quad M_1 = \frac{(\sum_i c_i l_i d_i)}{\sum_i c_i l_i} - \frac{L}{2} \quad (2a, b)$$

For our experiments,  $c_0$  is the initial Pb concentration in the soil sample,  $c_i$  is the final concentration in the soil slice  $i$ ,  $L$  is the length of the soil specimen and  $l_i$  is the length of soil slice  $i$ , while  $d_i$  is the distance of slice  $i$  from the anode-end of the soil-specimen. With  $M_m$  it is possible to express the extent of contaminant transport obtained in a single number, which simplifies evaluation of experiments significantly: A positive  $M_m$  is obtained if the contaminant is transported towards the cathode; a negative  $M_m$  is obtained if the contaminant is transported towards the anode; greater  $|M_m|$ , the better remediation.

## 3 Results and Discussion

### 3.1 OVERALL MASS BALANCES AND PB REMOVAL

Results in terms of the initial Pb-concentrations, Pb mass balances, Pb removal (%) and metal-mobilization lengths for the 10 experiments are summarized in table V. The final Pb amount in each soil specimen was estimated by duplicate analyses of each of the 5 soil slices (10 samples). The experimental mass balances varied between 80% (experiment 2) and 143% (experiment 1). Pb removal varied from negligible (0.7%) for soil 3 to almost 40% for soil 7. Similarly,  $|M_m|$  varied between 0.01cm for soil 3 and 2.92cm for soil 7. The overall direction of Pb-transport was towards the cathode for soils 1-3, 6, and 7 and towards the anode (negative  $M_m$ ) for soils 4, 5 and 8-10, as quantified by the direction that the center of mass of Pb moved within the soil specimen. However, examination of the Pb removed from the soil and found on electrodes and in electrolytes suggests that this conclusion is inconsistent for experiments 1 and 6, where the major part of the removed Pb was found in the anolytes. The inconsistent transport directions suggest that various Pb-species are

transported simultaneously towards the anolyte and the catholyte during remediation. This finding suggests that the concept of  $M_m$  should be employed with care, since equal amounts of transport in each direction would result in  $M_m$  being zero, which does not properly reflect the transport. Nevertheless the magnitude and sign of  $M_m$ , together with soil characteristics and analysis of process fluids soil, provide valuable insight into the prevailing processes and Pb-speciation in EDR.

TABLE V  
Results of the bench-scale EDR feasibility experiments.

Experiment	1	2	3	4	5	6	7	8	9	10
<b>Pb start [mg/kg]*</b>	296	964	568	761	1005	914	4115	286	854	1144
<b>Mass balance [%]</b>	143	80	89	107	100	115	101	122	111	109
<b>Removal [%]</b>	5.7	19.1	0.7	1.1	1.8	2.0	39.4	4.5	0.8	7.2
<b><math>M_m</math> [cm]</b>	0.59	2.18	0.01	- 0.44	- 0.69	1.26	2.92	- 0.37	- 0.39	- 1.12
<b>Direction of transport</b>	Cat/ An	Cat	Cat	An	An	Cat/ An	Cat	An	An	An

\*Calculated as the final amount of Pb found in soil and liquids divided with initial soil mass.

### 3.2 pH

Acid front migration is quantified in terms of pH profiles for all post treatment soil specimens in figure 3.1. Differences in front migration are directly related to the soil carbonate content, which is noted in the figure 3.1 legend. Despite the presence of ion-exchange membranes, an acid front evolved from the anode-end in all cases. Because soils commonly contain particles (clay and organics) which are negatively charged and surrounded by a layer of mobile cations, they act as cation-exchangers.

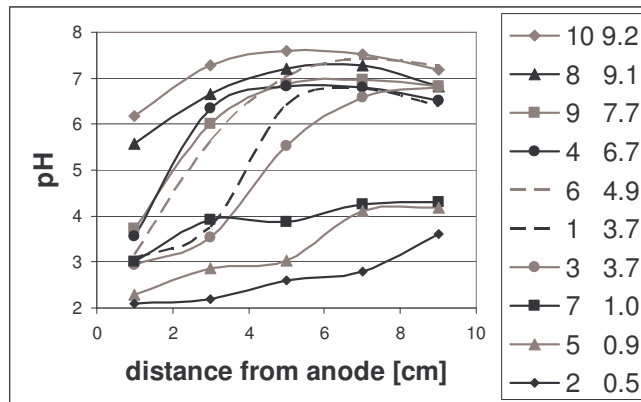


Figure 3.1: pH profiles of all soils after remediation experiments.  
 $\text{CaCO}_3$  concentration [%] is given next to the soil number.

The mobile cations are transported in the electric field (electromigration), while the soil particles are transported to a lesser extent (electrophoresis), and not at all through

the ion-exchange membranes. In order to meet the requirement of electro-neutrality equal amounts of positive and negative charges have to be transported out of the soil. The lack of transportable anions causes water-splitting at the surface of the anion-exchange membrane followed by immediate transport of the hydroxide-ions into the anolyte with acidification of the soil as a consequence. The phenomenon of water-splitting in electrodialysis and its relation to ion-concentration is well recognized in water treatment technology (Mulder, 1996). In the present systems, the extent of the acid front propagation varied from slight acidification in the first few cm (soils 10 and 8) to the full soil specimen (soils 2, 5 and 7).

### 3.3 REMEDIATION

The extent of soil acid front propagation is an important factor to consider in relation to the observed Pb profiles in the soil specimens. Figure 3.2 summarizes the Pb profiles for the soils in which Pb was transported towards the cathode. Of these, significant Pb removal occurred from soils 2 and 7, as expected based on the low pH and large fraction of fines in these soils (35 and 20% clay respectively) which demonstrates the potential of the EDR process in fine-grained soils. Pb appears to be removed at greater pH values from soil 7 than from soil 2. This observation is in accord with previous reports (Reed *et al.*, 1996; Jeong and Kang, 1997; Chung and Kang, 1999), and is a reflection of the greater contamination levels for this soil and the associated looser bonding of a large portion of the Pb. In soils 1 and 3, the pH values within the 4cm closest to the anode are as low as in soil 7. Removal of Pb from this section of soil 1 is commensurate with the low pH values. However, only very limited Pb transport has occurred in soil 3. A likely reason for this difference is that the Pb in soil 3 may be bound to organic matter and as insoluble  $\text{PbCrO}_4$  (see table II) while Pb in soil 7 is primarily bound as carbonates and oxides (table II). Soil 6 is the least acidified of the five soils, which is reflected by low removal. Although the center of mass of Pb in this soil moved towards the cathode, the major Pb removed from this soil was collected in the anolyte (table V), suggesting reverse transport of species with opposite charge.

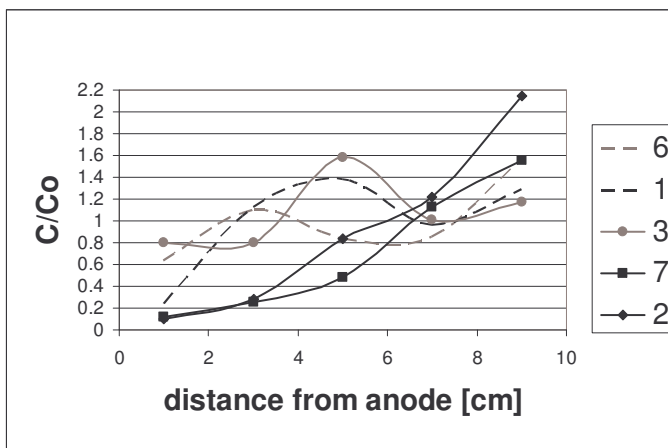


Figure 3.2: Pb profiles of five soils in which Pb transport was towards the cathode.

The profiles in Figure 3.3 summarize the cases for which Pb was primarily transported toward the anode. Relatively less transport occurred in these soils suggesting that the dominance of negatively charged Pb-complexes in general affects remediation negatively. In addition, a bimodal distribution of Pb in some of the soils (4 and 5) is pointing to different transport for different species (as for soil 6 – see figure 3). An explanation of this behavior may be found in the fact that soils 4-6 are the most organic soils of the ten. The fact that organic matter is insoluble at low pH may well explain the low removal (table V) obtained from soil 5 despite the low pH obtained. Although only part of the Pb in these soils is bound to organic matter, a process where Pb re-adsorbs to the organic phase after having been released from other fractions due to acidification could have taken place. If that is the case, the organic matter is likely to preclude remediation because the organically bound Pb will stay immobile as the acidic front proceeds, and addition of complexing or oxidizing agents would be necessary to obtain remediation.

In contrast, when looking at the removal obtained from soils 8 and 10 (table V), some apparent transport into the anolyte has taken place despite of the high carbonate content and limited acid front propagation in these soils. Furthermore no sign of opposite transport is observed, suggesting that other mechanisms govern Pb-transport in these soils. The fact that these two soils are the most carbonaceous of the ten suggests that the transport may be related to the dissolution of carbonate resulting from the acid production at the anion-exchange membrane: According to the speciation diagram for Pb shown in figure 3.4, an increased carbonate concentration in the pore-liquid of the soil, may at neutral pH results in formation of soluble and negatively charged lead-carbonate ( $\text{PbCO}_3^{2-}$ ) which would be transported towards the anode. In support of this hypothesis, the transport of Pb into the anolyte among soils 8-10 was observed to correlate with the carbonate content of the soils. No overall remediation of carbonaceous soils through this mechanism is however possible, because as the soil closest to the anode becomes acidic, Pb-carbonates, which continue to travel from the neutral sections towards the anode, precipitate or change sign of valence as they reach the acidic region and therefore remain in the soil until the full soil has become acidic and transport of  $\text{Pb}^{2+}$  into the catholyte is made possible. The combined effect of a high concentration of dissolved carbonates and an extended period of prevailing neutral conditions throughout the soil specimen are primarily responsible for the greater transport into the anolyte from carbonaceous soils like soils 8 and 10.

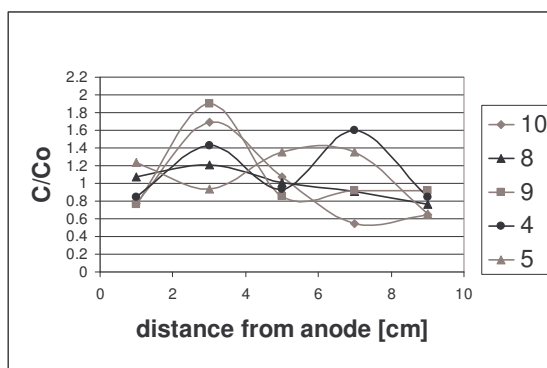


Figure 3.3: Pb profiles for soils in which Pb was transported towards the anode.



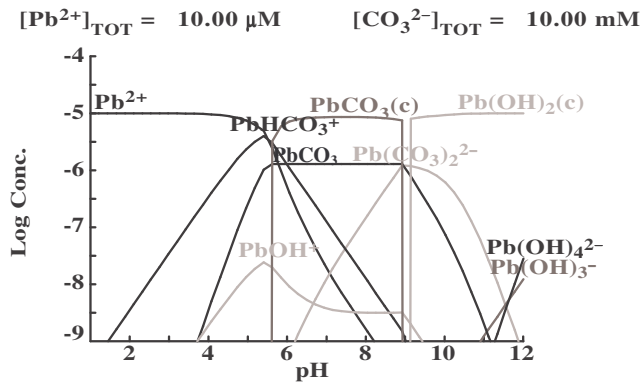


Figure 3.4: Speciation of Pb in solution with excess carbonate as a function of pH (Puigdomenech, 2002).

The fact that dissolution of carbonates results in dissolution of Pb at neutral pH is supported by the information found in figure 3.5, where removal (%) in the soil slices of all experiments is plotted (figure 3.5a) as a function of pH together with results of batch extraction of Pb with nitric acid (figure 3.5b). The effect of the current is obvious here since at pH-values between 2 and 8, Pb has been removed to a much larger extent from the soil-slices of the EDR experiments than by batch extractions. Two separate groups of points are apparent in figure 6a: Up to 90% extraction of Pb has been obtained at pH 2-4, while up to 45% extraction was obtained at pH 6-8, while removal was absent at pH 4-6. From batch extractions some extraction of Pb (up to 32%) between pH 2 and 4 occurred, but to a much lesser extent than in the soil subjected to EDR, and no extraction was observed in the higher pH interval (6-8). In the low pH-interval we attribute the difference to the current transporting the dissolved Pb out of the soil, and thereby shifting the equilibrium. In the high pH-interval we believe the difference is the effect of dissolved carbonates, resulting in increased  $\text{CO}_3^{2-}$  concentrations in the pore-liquid and dissolution of  $\text{PbCO}_3^{2-}$ .

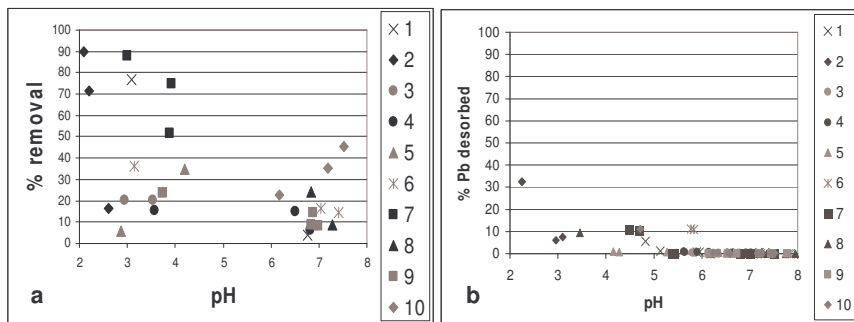


Figure 3.5: (a) % removal in the soil slices of all experiments is pictured as a function of pH. Only the slices in which Pb has been removed are pictured, while the slices where Pb has been concentrated are omitted. (b) desorption dependency of Pb from all 10 soils in the relevant pH interval.

## 4 Conclusions

The development of an acidic front in soil during electrodialytic remediation is governed by the buffer-capacity of the soil. Severely contaminated soils, where a large fraction of the Pb is bound in the mobile fractions, are remediated at higher pH than less contaminated soils where Pb is strongly bound to the soil. EDR shows a great potential in remediation of fine-grained soils, for which no other efficient treatment has yet been developed. In the case of soils, for which the original polluting Pb-species are extremely stable (e.g. where  $\text{PbCrO}_4$  dominates), remediation will proceed very slowly, and may not be feasible, as seen for soil 3, in this work. In highly organic soils remediation is hindered by the redistribution of Pb, which readsorbs to insoluble organic matter under acidic conditions. Remediation of such soils may not be possible without any preconditioning (with complexing agents/oxidizing agents) because only a minor fraction of the organic matter is soluble. In carbonate-rich soils, the first period of remediation is dominated by dissolution of carbonates. This results in an increased carbonate concentration in the pore-liquid and dissolution of  $\text{Pb}(\text{CO}_3)_2^{2-}$  which is transported into the anolyte. However, as the acidic front develops, transport towards the cathode will take over and dominate the remediation. Pb-contaminated soils low in organic matter and where Pb does not exist in extremely stable compounds can be remediated by electrodialysis. In that case the remediation-time depends on the carbonate content of the soil.

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## 6. Electrodialytic Remediation of Soil Fines (< 63 $\mu$ m) in Suspension

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### Abstract

Current treatment of the remaining soil fines from soil wash is onerous and expensive, and therefore, in this work, we investigated the feasibility of electrodialytic remediation (EDR) as an alternative treatment. The study focuses on EDR efficiency as a function of current strength, liquid-to-solid-ratio (L/S), pH and time. We found out that during the experiments, Pb was easily dissolved by the acidification resulting from water splitting at the anion-exchange membrane. When higher currents and/or higher L/S ratios were applied, it was found that water splitting occurring at the cation-exchange membrane increased the pH, and this resulted in decreased remediation efficiency. It was shown that complete remediation of the soil-fines is possible, with the majority of the Pb being transported into the catholyte and precipitated at the cathode. Based on the results it is recommended that EDR is implemented using a number of reactors in series, where the initial reactor works at the highest possible removal rate, and the final reactor works at the target Pb-concentration.

**Keywords:** Electrodialysis; Pb; soil remediation; soil washing; water splitting.

### 1 Introduction

#### 1.1 SOIL WASHING

Particle separation techniques based on size or density differences are standard operations in the supply of clean sand for concrete, road-building and in mining technology (Hinsenveld, 1991). Variations of such techniques namely soil washing have been investigated for their potential application in remediation of contaminated soil (VanBenschoten *et al.*, 1997; Mann, 1999; Kuhlman and Greenfield, 1999), and constitute one of few options in the treatment of heavy metal (HM) contaminated soil. Through soil washing, the oversize material can be cleaned simply by water-rinse. The fine and coarse sands can be treated by density/gravity separation processes, followed by an extractive soil washing where an appropriate extractant is added. The

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remaining silts and clays, which generally contain the highest concentrations of contaminants, are dewatered and treated by stabilization/solidification techniques to immobilize the contaminants (VanBenschoten *et al.*, 1997; Mann, 1999; Kuhlman and Greenfield, 1999). However, fines are dewatered with difficulty: minimum 45% water-content after thickening and pressurized belt filter press (Mann, 1999). Including a volume increase due to the stabilization/solidification-process, the final volume of contaminated material may well resemble the initial even though a considerable volume of clean materials has been obtained. The limited success of soil washing can largely be attributed to this troublesome treatability and handling of the fine fraction. Attempts have been made to use the contaminated fines for brick- and roof-tile fabrication for which clay is a natural raw material. However, legacy- and confidence matters have restrained this solution (Hinsenveld, 1991). An introduction of an efficient unit-process for decontamination of the fines is necessary to make soil washing an environmentally and economically profitable process, where contaminated soil is remediated and well-defined materials for construction-purposes are produced.

With the objective to develop a method for treatment of the remaining fines from soil washing, this work aims at investigating the feasibility of Electrodialytic remediation (EDR) of Pb-contaminated fines in suspension. Influence of L/S and current were identified as important, basic parameters, and therefore this work focuses on elucidation of remediation dependency on these.

## 1.2 EDR OF PB FROM FINE-GRAINED MATERIAL IN SUSPENSION

EDR is an electrokinetic remediation method, where ion-exchange membranes function as barriers, which physically hinder intrusion of hydrogen and hydroxide-ions from the electrode processes into the contaminated material. EDR of HM contaminated soils has up till now been tested only for stationary set-ups. However, EDR of fine materials was already tested in suspension (non-stationary set-up) for fine-grained material, such as municipal solid waste incineration (MSWI) fly ash (Pedersen, 2002; Ferreira *et al.*, 2005), wood combustion fly-ash (Pedersen, 2003), straw combustion fly-ash (Pedersen *et al.*, 2004), wastewater sludge (Jakobsen *et al.*, 2004) and contaminated harbor sediments (Nystroem *et al.*, 2005b). These materials are difficult to handle in solid form, and therefore the suspended EDR setup was introduced (Pedersen, 2003; Nystrom *et al.*, 2005). In MSWI fly ash, Pb was found to be the least mobile of the contaminating metals, and only 8% was removed after 3 weeks of remediation ( $0.796 \text{ mA/cm}^2$  and L/S-ratio 6.5) (Pedersen *et al.*, 2003). The low removal led to introduction of desorbing agents, such as sodium-citrate (12% removal after 2 weeks for the same ash and experimental conditions) (Pedersen, 2002) and ammonia/ammonium citrate (20% removal after 70 days) (Pedersen *et al.*, 2005). From a different fly ash, 30.7% Pb was removed after 12 days ( $0.8 \text{ mA/cm}^2$  and L/S 5.25) (Ferreira *et al.*, 2005). From contaminated harbor sediments, Pb was removed more efficiently: 76% Pb was removed after 21 days ( $0.6 \text{ mA/cm}^2$  and L/S 4) in distilled water (Nystrom *et al.*, 2005). Remediation was shown to depend on L/S-ratio and current-strength as well as time, and 91-96% was removed from various harbor sediments after 14 days ( $1.393 \text{ mA/cm}^2$  and L/S 8) (Nystroem *et al.*, 2005b).

## 1.3 ION-EXCHANGE MEMBRANES AND WATER SPLITTING

For all the fine-grained materials referred above, as well as in EDR of soil in stationary set-up (Hansen *et al.*, 1999; Ottosen *et al.*, 2000), water splitting was

observed at the surface of the anion-exchange membrane. The occurrence of water splitting is well known from dialysis of liquid samples (Kang *et al.*, 2004), and *accelerated water splitting* is used for electro-synthesis of acids and bases in industry. *Accelerated water splitting* is obtained through application of bipolar ion-exchange membranes at the surface of which the dissociation rate is  $10^7$ - $10^8$  times faster than in free solution (Desharnais and Lewis, 2002). The presence of soil also affects the water splitting rate positively e.g. application of iron hydroxide/oxide and silica sol at cation-exchange membranes increased the rate up to  $10^4$ - $10^5$  times (Kang *et al.*, 2004). Due to the negatively charged surface of soil-constituents such as clay and organic matter, the interface between an anion-exchange membrane and soil constituents is in effect bipolar, and very little cation-exchange capacity or clay is necessary for water splitting to occur at the bipolar interface between anion-exchange membrane and soil (Desharnais and Lewis, 2002).

Initiation of water splitting is related to the limiting current ( $i_{\text{lim}}$ ). As current is increased, the ion-concentration at the surface of the membrane approaches zero (concentration polarization), and  $i_{\text{lim}}$  is reached:

$$i_{\text{lim}} = \frac{zDFc_b}{\delta(t^m - t^{bl})} \quad (1)$$

Here  $z$  is the charge,  $F$  is Faraday's constant,  $c_b$  is the ion-concentration in the bulk solution,  $\delta$  is the boundary layer thickness.  $t^m$  and  $t^{bl}$  are the transport numbers of the counter-ions transported in the membrane and the boundary layer respectively, and  $D$  is the diffusion coefficient of the counter ions in the boundary layer (Mulder, 1996). A region exists, where voltage is increased dramatically with an increase in the current. In this region the additional energy ( $\Delta V$ ) is a result of increasing resistance associated with the concentration polarization in the boundary layer at the polarized membrane side (Mavrov *et al.*, 1993). The limiting current density increases with increasing ionic concentration ( $c_b$ ) and decreases with thickness of the boundary layer ( $\delta$ ). Consequently the limiting current increases with decreased L/S-ratio (more ions available). Furthermore  $i_{\text{lim}}$  increases in a stirred system compared to a stationary set-up because the boundary layer is decreased. In EDR of soil in stationary systems, the limiting current density for the cation-exchange membrane was in two cases found to be around  $0.4 \text{ mA/cm}^2$  (Hansen *et al.*, 1999; Ottosen *et al.*, 2000), while the limiting current for the anion-exchange membrane is close to zero. The water splitting at the anion-exchange membrane results in acidification of the soil with dissolution of HM's as a consequence. This acidification is the foundation of unenhanced EDR of HM-containing materials (Nystroem *et al.*, 2005a). Water splitting at the cation-exchange membrane is in most cases unwanted due to production of hydroxide-ions and decreased mobility of most HM's under alkaline conditions, why the ideal current density is found just below  $i_{\text{lim}}$  for the cation-exchange membrane.

## 2 Materials and Methods

### 2.1 SOIL

The experimental soil is an industrially contaminated Danish soil of unknown origin, characterized in (Jensen *et al.*, 2006) as soil 10 to be rich in carbonate and feldspar, low in organic matter and relatively rich in phosphate. SEM-EDX analysis revealed a



mixed Pb-pool, where Pb was identified in association with iron/aluminum-minerals, metallic alloys, solder, chloride and pure (possible metallic) Pb (Jensen *et al.*, 2006)F.

The soil-fines were obtained by simple wet-sieving of the original soil with distilled water through a 0.063mm sieve. A concentrated slurry of fines was obtained by centrifugation at 3000rpm for 10 min. followed by decantation of the supernatant. The soil-fines were kept in as slurry and stored at 5°C in presence of oxygen. Prior to an experiment, distilled water was added to the slurry to obtain the wished L/S-ratio.

## 2.2 CHARACTERIZATION

The original soil as well as the fines were analyzed for the following parameters: *Metals* (Fe, Pb) were measured by AAS/graphite furnace. Soil samples were digested according to the Danish standard method DS259 (Dansk Standardiseringsråd, 1991), which includes acid digestion of 1g soil with 20.00mL of half concentrated HNO<sub>3</sub> in autoclave at 200kPa and 120°C for 30 minutes and filtration through a 0.45µm filter. Liquid samples with pH > 4 were digested with one part of conc. HNO<sub>3</sub> to four parts of liquid in autoclave at 200 kPa and 120°C for 30 minutes prior to AAS measurement. *Carbonate* content was determined volumetrically by the Scheibler-method when reacting 3g of soil with 20mL of 10% HCl. The amount was calculated assuming that all carbonate is present as calcium-carbonate. *Organic matter* was determined by loss of ignition in a heating furnace at 550°C for 1 hour. CEC was decided by ion exchange of 10g dry soil with NH<sub>4</sub><sup>+</sup>, followed by exchange of NH<sub>4</sub><sup>+</sup> for Na<sup>+</sup>. The ammonium concentration of the centrifugate was measured by spectrophotometer via flow-injection. *Phosphate* was measured after digestion of 0.2-0.5g sample at 550°C followed by boiling with HCl. The sample was reacted with ammonium molybdate to form yellow phosphor-molybden acid, which was reduced by ascorbic acid in the presence of antimony. The strong blue color was measured by spectrophotometer Shimadzu UV-1601. *pH* was measured by electrode MeterLab® CDM220 after shaking of 5.0g dry soil with 12.5mL 1M KCl constantly for 1 hour, followed by settling for 10min. *Pb concentration in each grain-size fraction* was measured according to DS 259 after wet-sieving (with 0.002M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) approximately 100g naturally wet soil through a 0.063mm sieve followed by separation by dry sieving of the larger fractions (>0.063 mm). Each fraction was ground thoroughly with a mortar and pestle in order to obtain as homogeneous a distribution of Pb as possible. *Desorption dependency on pH*: 5.00g of dry, crushed soil was mixed with 25.00ml reagent at a shaking table at 200rpm for 7 days. pH was measured after 10min settling, and the liquid was filtered through a 0.45µm filter for subsequent measurement on AAS. The reagents were: 1.0M NaOH, 0.5M NaOH, 0.1M NaOH, 0.05M NaOH, 0.01M NaOH, distilled water, 0.01M HNO<sub>3</sub>, 0.05M HNO<sub>3</sub>, 0.1M HNO<sub>3</sub>, 0.5M HNO<sub>3</sub>, 1.0M HNO<sub>3</sub>. *Sequential extraction* was made according to the method from the Standards, Measurements and Testing Program of the European Union (Mester *et al.*, 1998): 0.5g of dry, crushed soil was treated in four steps as follows: I) Extraction with 20.0ml 0.11M acetic acid pH 3 for 16 hours. II) Extraction with 20.0 ml 0.1M NH<sub>2</sub>OH·HCl pH2 for 16 hours. III) Extraction with 5.0ml 8.8M H<sub>2</sub>O<sub>2</sub> for one hour and heating to 85°C for one hour with lid followed by evaporation of the liquid at phase 85°C until it had reduced to < 1ml by removal of the lid. The addition of 5.0 ml 8.8M H<sub>2</sub>O<sub>2</sub> was repeated followed by resumed heating to 85°C for one hour and removal of the lid for evaporation until almost dryness. After cooling down, 25.0 ml 1M NH<sub>4</sub>OOCCH<sub>3</sub> pH 2 was added, and extraction took place for 16 hours. IV) Finally digestion according to DS 259 was made for identification of the residual fraction. Between each step the sample was centrifuged at 3000rpm for

15min, and the supernatant was decanted and stored for AAS analysis. Before addition of the new reagent the sample was washed with 10.0ml distilled water for 15min, centrifuged at 3000rpm for 15min and the supernatant was decanted. All extractions were performed at room temperature while shaking at 100rpm unless otherwise mentioned. All analyses were made in triplicate except CEC and sequential extraction which were made in double.

## 2.3 REMEDIATION EXPERIMENTS

Electrodialysis experiments were made in cylindrical Plexiglas-cells with three compartments. Compartment II, which contained the soil-slurry was 10 cm long and 8 cm as an inner diameter. The slurry was kept in suspension by constant stirring with plastic-flaps attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). The anolyte was separated from the soil specimen by an anion-exchange membrane, and the catholyte was separated from the soil specimen by a cation-exchange membrane. Figure 2.1 shows a schematic drawing of the setup. Both membranes were obtained from Ionics® (types AR204SZRA and CR67 HVY HMR427). Electrolytes were circulated by mechanical pumps (Totton Pumps Class E BS5000 Pt 11) between electrolyte chambers and glass bottles. Platinum coated electrodes from Permascand® were used as working electrodes, and the power supply was a Hewlett Packard® E3612A. The electrolytes initially consisted of each 500mL 0.01 M  $\text{NaNO}_3$  adjusted to pH 2 with  $\text{HNO}_3$ .

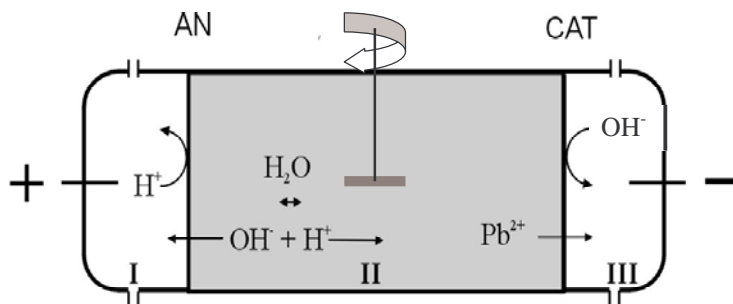


Figure 2.1: Schematic view of a cell used for experimental EDR of soil fines in suspension. AN = anion-exchange membrane, CAT = cation-exchange membrane.

Current, voltage and pH in all chambers as well as conductivity in chamber II, were measured approximately once every 24 hours. During the electrodialysis experiments current passed between the electrodes. Due to electrode processes pH-changes occurred in the electrolytes, and pH in the electrolytes was manually kept between 1 and 2 by addition of  $\text{HNO}_3$  and  $\text{NaOH}$ .

To investigate the influence of current strength and L/S, 12 experiments were made according to table I. It was earlier shown (Jensen *et al.*, 2006) that Pb in this soil and most other soils desorb at  $\text{pH} < 2$ , why all experiments were run until pH in chamber II was decreased to  $< 2$  by the water splitting process. Apart from these 12 experiments, 2 additional experiments were made (C1a and D1a). These experiments worked at L/S 3.5, while running for the same amount of time pr. g. soil as experiment C2. Constants and variables of the four compared experiments are summarized in table II.

TABLE I  
Experimental plan

L/S	3.5	7.0	10.5	14.0
Current density (J) [mA/cm <sup>2</sup> membrane area]				
0.2	A1	A2	A3	A4
0.4	B1	B2	B3	B4
0.6	C1	C2	C3	C4

TABLE II  
Constants and variables of two additional experiments and  
the experiments with which they are compared.

Experiment	C1	C1a	C2	D1a
Current density ( <i>i</i> ) [mA/cm <sup>2</sup> membrane area]	0.6	0.6	0.6	0.8
L/S	3.5	3.5	7.0	3.5
Treatment-time (hours/gram soil)	6.0	11.5	11.5	11.5

### 3 Results and Discussion

#### 3.1 SOIL CHARACTERISTICS

Characteristics of the original soil and the soil fines are listed in table III. The soil fines contain more Pb, carbonate, organic matter and iron than the original soil. Also CEC is higher, probably due to higher fraction of organic matter and clay-minerals. In contrast the phosphate-content is lower.

TABLE III  
Characteristics of the soil fines and the original soil

	Pb [mg/kg]	pH	CaCO <sub>3</sub> [%]	Organic matter [%]	CEC [meq/100g]	PO <sub>4</sub> <sup>3-</sup> [mg/kg]	Fe [g/kg]
Soil fines	1170	7.8	17.3	7.8	14.1	559	27.3
Original soil	1090	7.8	9.2	2.8	4.5	1547	13.6

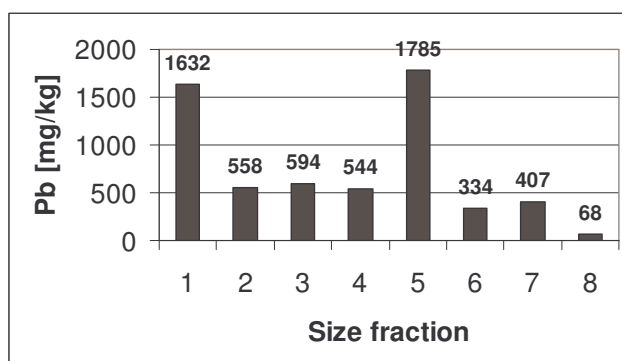


Figure 3.1: Distribution of Pb in soil fractions. 1: 0-0.063mm; 2: 0.063-0.080mm; 3: 0.080-0.125mm; 4: 0.125-0.250mm; 5: 0.250-1.000mm; 6: 1.000-2.000mm; 7: 2.000-4.000mm; 8: > 4.000mm.

Figure 3.1 reveals that Pb is concentrated in the  $< 63\mu\text{m}$  fraction as well as in the fraction between 0.25 and 1mm. In this larger fraction Pb is unevenly distributed (large standard deviation on analysis of Pb), and may well be found as discrete particles of contaminating metal, which may be separated from the soil matrix by density-separation during soil washing. It should be stressed that no attempts have been made to optimize the soil washing process, and an even more pronounced concentration in the fines could be expected if this was done.

In figure 3.2, the desorption dependency on pH from the original soil and the soil fines is illustrated. At pH below 2 most of the Pb is desorbed from both materials, and their extraction-patterns are very similar.

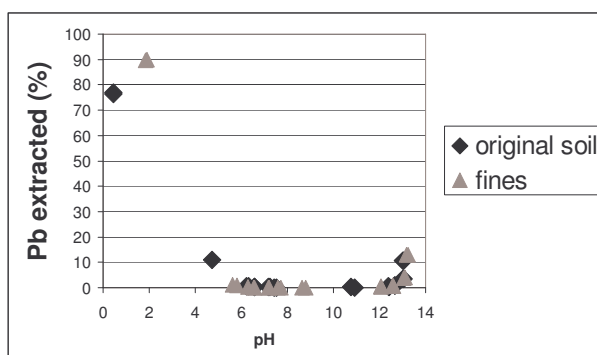


Figure 3.2: Desorption dependency of Pb in original soil and soil fines.

Sequential extractions of the soil-fines show (figure 3.3), how a large residual fraction of Pb is found in the original soil, while most of the Pb in the fines is released during oxidization. The higher mobility of Pb in the fine fraction suggests that Pb in the coarse fractions may exist in stable e.g. metallic compounds. As the stable compounds are slowly transformed under environmental conditions, the Pb may preferably bind to organic matter and clay-particles prevailing in the fine fraction.

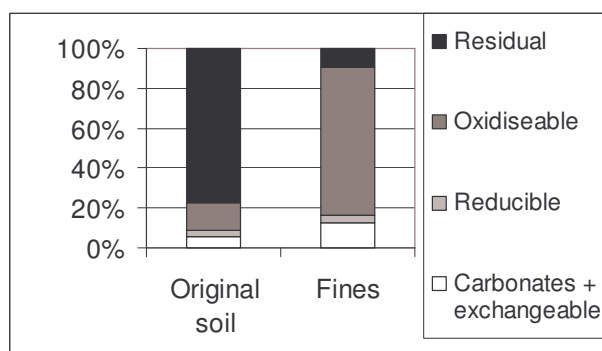


Figure 3.3: Sequential extraction of Pb from soil fines and original soil.

### 3.2 EDR EXPERIMENTS

Table IV gives results of the 12 experiments listed in table I.

TABLE IV  
Results of EDR experiments  
Best results in each series are emphasized by bolding

	Hours to reach pH < 2	Hours pr. g soil	Current efficiency [%]	Hours pr. mg Pb removed	Mass- balance [%]	Pb removed from M [%]	Pb in liquid in M [%]	Final Pb soil conc. [ppm]
<b>A1</b>	713	<b>6.9</b>	1.1	29.5	126	21	43	681
<b>A2</b>	403	7.5	1.3	22.9	130	25	35	753
<b>A3</b>	330	8.9	2.6	9.9	125	63	14	<b>407</b>
<b>A4</b>	<b>265</b>	9.5	<b>3.1</b>	8.5	134	<b>72</b>	<b>5</b>	426
<b>B1</b>	495	<b>4.8</b>	1.1	13.9	113	32	38	584
<b>B2</b>	334	6.2	1.6	8.2	133	51	21	506
<b>B3</b>	<b>240</b>	6.5	<b>2.3</b>	5.6	115	<b>86</b>	<b>0.6</b>	224
<b>B4</b>	474	17.0	1.2	10.4	161	<b>87</b>	1.6	<b>212</b>
<b>C1</b>	<b>621</b>	<b>6.0</b>	<b>1.9</b>	4.6	159	72	15	309
<b>C2</b>	<b>621</b>	11.5	0.7	12.7	87	90	0.7	119
<b>C3</b>	788	21.3	0.6	14.3	132	<b>96</b>	1.4	<b>42</b>
<b>C4*</b>	809	28.9	0.3	29.3	91	93	<b>0.0</b>	133

\*Reached maximum voltage (137.1V) after 330 hours and continued with variable current (0.3-0.5mA/cm<sup>2</sup>) until 447hours, where the current increased to 0.6mA/cm<sup>2</sup> again and remained stable. pH in this experiment did not reach 2 when the experiment was terminated.

#### 3.2.1 Mass balances

Mass-balances for Pb were obtained between 87 and 161%. Since the initial Pb-concentration was determined as a triplicate measurement in a batch of soil-slurry, containing slurry for several experiments, and the final amount was specifically calculated for the single experiment, the final concentration is regarded the most precise, and therefore used when calculating removal percentages. In each experiment a weight-loss approximately equivalent to the amount of CaCO<sub>3</sub> in the soil was observed.

#### 3.2.2 Water splitting and current efficiency

In the A-series of experiments, the time to reach pH <2 decreased with increased L/S as expected due to the presence of less soil and therefore less buffer capacity of the slurry. In the B-series and even more pronounced in the C-series however, other mechanisms influence the acidification of the slurry. In the B-series time to reach pH <2 was decreasing from experiment 1 through 3; while increasing dramatically in experiment 4. In the C-series time to reach pH <2 is increased compared to the B-series although current was increased, and within the series itself an increase was observed throughout the whole series. The effect was even more pronounced when calculated as hours to reach pH <2 pr. g of soil. The reason for this increase we believe is the exceeding of the limiting current-density for the cation-exchange membrane resulting in production of hydroxide-ions. The lack of ions becomes more

pronounced as L/S and current increases due to less soil material to supply the ions and more ions necessary for transport. With production of both hydrogen and hydroxide-ions in the cell, acidification was impeded. In addition, part of the current was transported by hydrogen and hydroxide-ions, resulting in a decreased current efficiency (% of the charge carried by  $\text{Pb}^{2+}$ ) as seen for experiments B4 and C2-C4. The described processes became more pronounced the more current was forced at the system. In general however, current efficiency was at least a size order larger than when remediating harbor sludge (Nystroem *et al.*, 2005a) probably because the soil contains less soluble salts competing for the current. Experiment C4 is an example of the utmost consequence of forcing too much current over the system: the lack of ions became pronounced, and even water splitting was unable to compensate. As a result resistance increased dramatically, and the constant current-density could not be kept.

The mechanisms are illustrated in detail in figure 3.4 showing the conductivity of the soil-slurry as a function of time; figure 3.5 illustrating the pH-development and figure 3.6 showing the voltage-development. After a “lag-period”, conductivity increased in all experiments except C4. The extent of the “lag-period” was related to the current-density and L/S relationship with a longer “lag-period” for experiments with high current density and high L/S. The conductivity of the soil-slurry in all experiments in the A-series, as well as B1-B3 and C1 started to increase after approximately 150 hours. While the conductivity increase for experiment B4, C2 and C3 appeared after almost 400, 450 and 620 hours respectively and the conductivity increase in C4 was never observed.

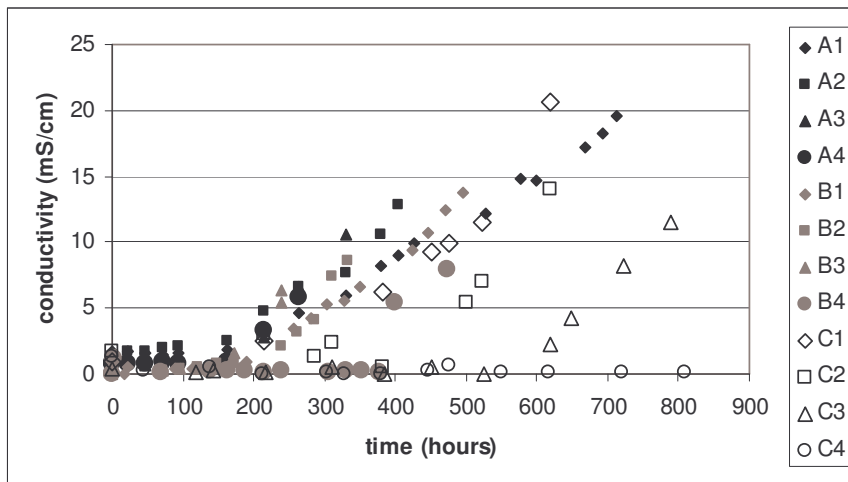


Figure 3.4: Conductivity in the soil slurry of the 12 experiments as a function of time.

In figure 3.5 the pH-development is illustrated. All experiments except C4 reached  $\text{pH} < 2$ , and were then terminated. As already discussed, the time to reach  $\text{pH} < 2$  within each series of experiments depends on the L/S-ration for experiments not affected by water splitting at the cation-exchange membrane (A1, A2, A3, A4, B1, B2, B3). During the lag-phase we believe that soluble salts including carbonates were removed from the soil. As the buffer-capacity was spent, the excess production of  $\text{H}^+$ -ions in the soil-slurry resulted in the simultaneous pH-decrease and conductivity increase.

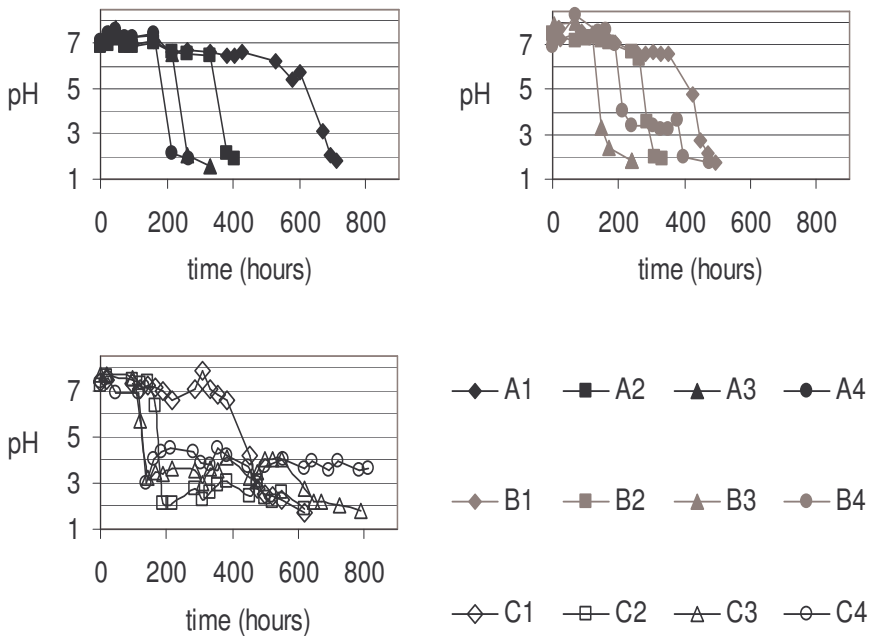


Figure 3.5: pH-development in the 12 experiments as a function of time.

In figure 3.6 it is illustrated how the voltage in all experiments in the A-series was low ( $<10V$ ) throughout the experimental time. Experiment B2, B3, C1 and C2 showed a few incidents of high voltage caused by precipitation of hydroxides in the cation-exchange membrane in connection with high pH in the catholyte. In these cases voltage decreased immediately after pH-adjustment. In comparison the voltage-increases in experiments B4, C3 and C4 were more constant and not related to pH-increases in the catholyte. These voltage increases we believe appear due to extensive concentration polarization and water-splitting at the anion-exchange membrane, and the observations suggest that under continuous pH-control, voltage can be used as a control-parameter for avoidance of water splitting at the cation-exchange membrane. In this experimental setup water splitting could be avoided by keeping a voltage-drop between the working electrodes below approximately 20. It should however be stressed that the major voltage-drop in that case is found over the membranes and that reactor up-scaling therefore cannot be made with a simple linear voltage-increase.

### 3.2.3 Pb-removal

In the 12 experiments, between 21% and 96% of the Pb was removed from chamber II into electrolytes or precipitated in membranes and at electrodes. Pb remaining in the liquid in chamber II constituted up to 43% of the total Pb after the end of the experiments. Final soil Pb-concentrations, ranging between 42 and 753 mg/kg, were obtained, showing how remediation of soil-fines was possible with the suspended EDR-setup.

An expected effect of acidification was that current-efficiency decreased with time due to production of  $H^+$ -ions competing with  $Pb^{2+}$  for transport. Therefore longer

acidification-times per gram of soil were expected to result in an increased current-efficiency for Pb-removal. Indeed this was seen in the experiments not affected by water splitting at the cation-exchange membrane (A1 through B3 and C1). In addition, when looking at the remediation rate (hours pr. mg Pb removed), the experiments with the longer acidification-time (A4 and B3) showed better remediation results than those with very fast acidification. Therefore, in the search of the most efficient remediation, it is not necessarily the fastest acidification which is preferential. Considering the total Pb removal, experiments affected by water splitting at the cation-exchange membrane (B4 and C2-C4) showed superior due to the longer remediation times. In addition the low concentration of ions in the liquid phase of chamber II of these experiments resulted in immediate removal of any ions released and higher removal of Pb from the soil solution.

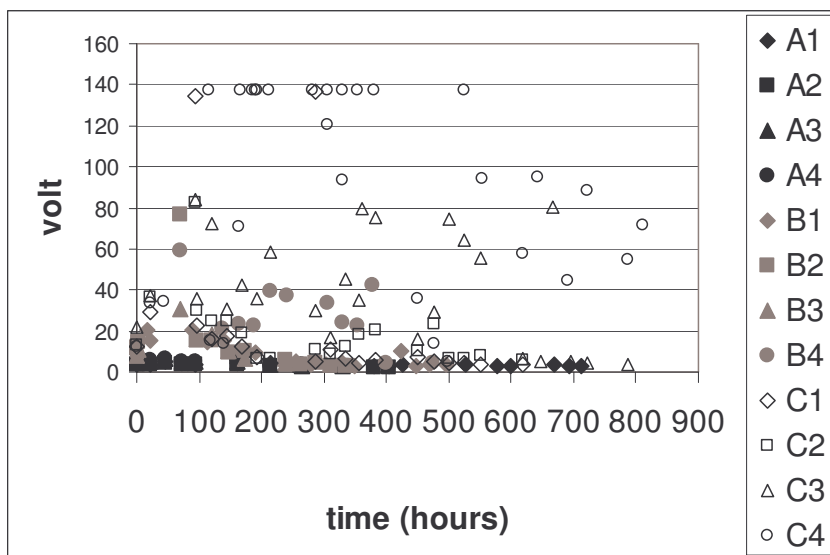


Figure 3.6: Voltage as a function of time in the 12 experiments

### 3.2.4 Final distribution of Pb

Figure 3.7 shows the final distribution of Pb in the experimental cells. The majority of the Pb was transported towards the cathode as  $\text{Pb}^{2+}$ . Only in experiments where a large fraction of the Pb remained in solution in chamber II, Pb was found in small amounts in the anolyte, and Pb appears to have been transferred into the anolyte as co-ions. Both at the anode- and the cathode-sides a negligible fraction of the Pb was found in the membranes. At the anode-side all Pb was found dissolved in the anolyte, while at the cathode-side the major Pb-pool was found in the catholyte in experiments A1, A2 and precipitated at the cathode as a porous substance in the remainder experiments.



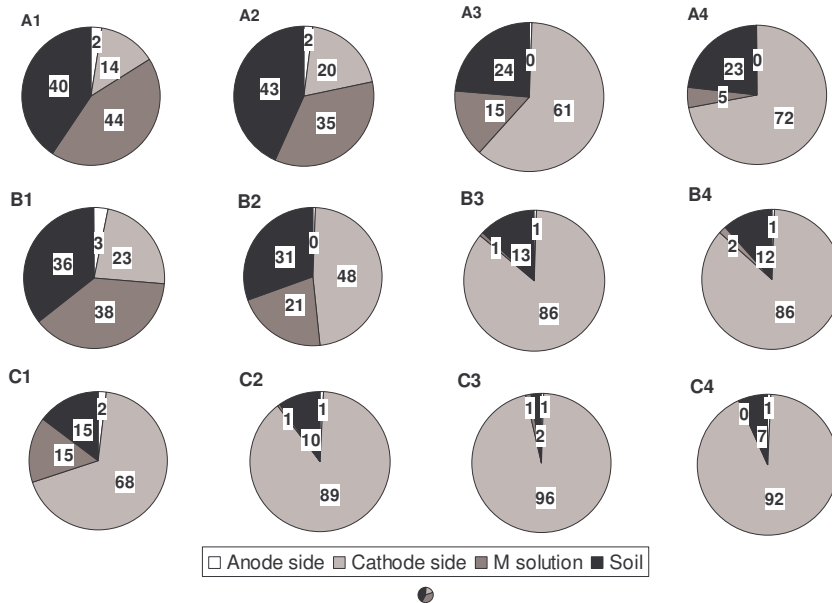


Figure 3.7: Final distribution of Pb in the 12 experiments (%).

### 3.2.5 Influence of time

At figure 3.8 the relation between final Pb concentration and remediation-time is visualized. Time pr. g. soil is thought to be a crucial parameter in the case of up-scaling and commercial benefit, because it relates directly to residence-time and thereby size of equipment. It is evident that a relation exists; however, some experiments show higher removal-rates than others. The experiments with the lowest removal-rates (points above the line in figure 3.8) are A1, A2 and C4. A1 and A2 due to the low current and C4 due to ion-deficiency caused by the combination of high L/S and high current. The experiments that show faster remediation than average (points below the line in figure 3.8) are B3, C1 and C2.

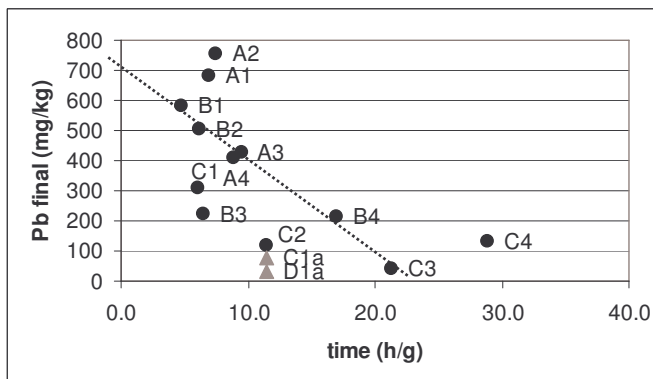


Figure 3.8: Relation between remediation-time (hours/g soil) and final Pb concentration (mg/kg). Initial Pb- concentration  $\approx 1170$  mg/kg.

Based on these findings, it was decided to repeat experiments C1 (experiment C1a) however, now running for 11.5 hours/gram soil for direct comparison with experiment C2. An additional experiment with further increased current density and high L/S (D1a) was also run for 11.5 hours/gram soil (see table II for details). Results of these two experiments are included in figure 3.8. The result of experiment D1a showed that remediation is possible to levels below the governmental limit set by the Danish EPA for sensitive land use (40 mg/kg). Results of experiments C1 and C1a show how the removal rate decreases as the removal proceeds, because increasing amounts of  $H^+$ -ions compete for the transport. In consistence with this, current efficiency also decreases. In order to remediate efficiently it could therefore be beneficial to apply a number of reactors in series, where the initial reactor works at the highest possible removal rate, and the final reactor works at the target Pb-concentration. As conductivity increases with time the removal rate could be increased in secondary reactors by increasing current. In table VI the optimal experiments at each L/S-ration are highlighted. It appears that the optimal current density increases linearly with decreased L/S in this region with the relation:

$$J_{\text{opt}} = 0.057(L/S) + 1 \quad (2)$$

TABLE V  
Results of experiments C1a and D1a

Exp. No.	Mass-balance [%]	Current efficiency [%]	Pb removed from II [%]	Pb in liquid in II [%]	Hours pr. mg Pb removed	Final Pb soil conc. [mg/kg]
<b>C1a</b>	111	0.8	95	1.5	10.7	78
<b>D1a</b>	104	0.6	100	0	11.0	34

TABLE VI  
Dependency of optimal current density (bolded) on L/S.

L/S J [mA/cm <sup>2</sup> ]	3.5	7.0	10.5	14.0
0.2	A1	A2	A3	<b>A4</b>
0.4	B1	B2	<b>B3</b>	B4
0.6	C1	<b>C2</b>	C3	C4
0.8	<b>D1</b>	-	-	-

## 4 Conclusions and Future Recommendations

With EDR in suspension, it is possible to remediate soil-fines completely, even from a soil with a high carbonate-content. During EDR of soil-fines in suspension, the lack of free anions results in water splitting at the anion-exchange membrane, resulting in acidification of the soil-slurry and mobilization of Pb. At high current densities and/or L/S, the lack of free cations results in water splitting at the cation-exchange membrane, resulting in production of hydroxide-ions and impeding the acidification of the soil. Water-splitting and remediation are highly dependent on L/S and current density. The optimal current density decreases linearly with increased L/S in the investigated region. The most efficient remediation is obtained when applying a

current just below the limiting current for the cation-exchange membrane. Best results considering remediation rate were obtained at L/S 3.5 and current density of 0.8 mA/cm<sup>2</sup>. Voltage can be used as a control-parameter for application of the ideal current. In this experimental setup water splitting can be avoided by keeping a voltage-drop between the working electrodes below 20. The removal rate decreases as the removal proceeds. In order to remediate efficiently it could therefore be beneficial to apply a number of reactors in series, where the initial reactor works at the highest possible removal rate, and the final reactor works at the target Pb-concentration at an increased current density.

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## 7. Organic Acid Enhanced Electrodialytic Extraction of Pb from Contaminated Soil Fines in Suspension

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### Abstract

In the search of an efficient, low-cost remediation method for soil fines, which constitute a major process residue after soil wash, the feasibility of heterotrophic leaching combined with electrodialytic remediation was investigated. The ability of 11 organic acids to extract Pb from the fine fraction of a Danish industrially polluted soil was investigated at pH-values between 2 and 7, where acid-producing fungi grow. The choice of acids was based upon the ability of harmless fungi to produce them. Five of the acids (citric acid, DL-malic acid, gluconic acid, tartaric acid and fumaric acid) showed ability to extract Pb from the soil fines at neutral and slightly acidic pH in excess of the effect caused by pure pH-changes. No extraction of Pb was observed with six of the acids (oxalic acid, pyruvic acid, lactic acid, formic acid, acetic acid and L-glutamic acid). Extraction of Pb, Fe, Al and Mn with citric acid and DL-malic acid was further investigated, and the best extraction was obtained with 0.4 and 0.6M citrate and 1.0M malate at near neutral pH, which in all cases gave 35% extraction of Pb. Application of DL-malic acid, citric acid, potassium-citrate and nitric acid as enhancing reagents during electrodialytic remediation (EDR) of Pb-contaminated soil fines in suspension was tested in 10 experiments. Addition of organic acids severely impeded EDR, and promotion of EDR by combination with heterotrophic leaching was rejected. In contrast enhancement of EDR with nitric acid showed promising results at current densities increased beyond what is ideal with addition of only distilled water. Consequently addition of nitric acid is recommended in cases where the removal rate is considered important, while suspension in pure water is to be recommended cases where energy expenditure and chemical consumption are limiting factors.

**Keywords:** Contamination, Electrodialytic remediation, Heterotrophic leaching, Organic acid, Pb, Remediation, Soil wash.

## 1 Introduction

Electrodialytic soil remediation (EDR) is an electrokinetic remediation (EKR) method, where ion-exchange membranes are applied as barriers between soil and electrolytes. In order to solve an essential waste-problem of the remaining sludge after soil-wash, EDR of soil fines in suspension was suggested as a potential treatment method (Jensen *et al.*, 2006a). EDR of Pb-contaminated soil was however shown to be a slow process (Jensen *et al.*, 2006b), and the aim of this work is therefore to investigate enhancement of the process by addition of a suitable reagent.

### 1.1 ENHANCING REAGENTS

The suitability of various reagents for extraction of Pb and other heavy metals from soil during soil wash has been extensively investigated. The strong chelating agent ethylenediaminetetraacetic acid (EDTA) was repeatedly and successfully tested by e.g. (Barona and Romero, 1996; Kim and Ong, 1996; VanBenschoten *et al.*, 1997), although its suitability was questioned because of its low biodegradability and potential hazard to the environment (Hinck *et al.*, 1997; Henneken *et al.*, 1998). Similarly, enhancement of EKR with EDTA is well documented (Reed *et al.*, 1995; Yeung *et al.*, 1996; Wong *et al.*, 1997), with the important note that although extraction of Pb from soil with EDTA was shown to be pH-independent (Wasay *et al.*, 1998), enhancement of EKR was obtained only at pH-values above 5 (Yeung *et al.*, 1996). Chelating agents more susceptible to biodegradation like [s,s]-ethylenediaminedisuccinic acid (EDDS) and nitrilotriacetic acid (NTA) were shown to be as efficient as EDTA for extraction of Cu and Zn (Tandy *et al.*, 2004). Similar success was however not obtained for Pb due to a much stronger complexation of Pb by EDTA, which was superior for extraction of Pb (Tandy *et al.*, 2004).

Besides chelating agents, organic acids possess heavy-metal extraction potential due to their complexing behavior. In contrast to EDTA, extraction of Pb from soil by a number of organic acids and their ammonium-salts (citric, oxalic, tartaric, acetic, itaconic, fumaric and pyruvic acids) was shown to be highly pH-dependent (Wasay *et al.*, 1998), but at pH's 2-7 citrate (0.2M) and tartrate (0.5M) extracted Pb as effectively as EDTA. In addition, the organic acids were shown to act more gentle towards the soil by removing 80% less macronutrients (Ca, Mg, Fe) compared to EDTA (Wasay *et al.*, 1998). In accordance, substantial improvement of EKR of Pb from a spiked silt loam with citric acid was demonstrated at pH's between 3.3 and 5.4 (Yang and Lin, 1998), while EDR of Pb from MSWI fly ash was enhanced by sodium-citrate (Pedersen, 2002) and ammonium citrate (Pedersen *et al.*, 2005) at alkaline pH's. Although acetate was shown to be a moderate extractant of Pb from soil (Wasay *et al.*, 1998), several works reported on successful enhancement of EKR with acetic acid at low pH (Reed *et al.*, 1995; Mohamed, 1996; Viadero *et al.*, 1998; Yang and Lin, 1998); however not as efficient as with citric acid (Yang and Lin, 1998).

Altogether current knowledge supports the feasibility of enhancing EDR of soil by addition of either chelating agents or organic acids. The fact that organic acids were shown to extract Pb as efficiently as the superior, but environmentally hazardous chelating agent EDTA, encourages the use of organic acids, among which citric acid and tartaric acid seems promising, although more knowledge is needed to make a reasoned selection of an appropriate acid.

## 1.2 HETEROTROPHIC LEACHING

In order to render soil remediation economically realistic, an important consideration is the cost of any applied chemicals. Several authors suggested leaching by heterotrophic bacteria or fungi as an economical alternative for extraction of valuable metals from non-sulfide, low-grade ore (Groudev, 1987; Burgstaller and Schinner, 1993; Sayer *et al.*, 1995). This technique is based upon the ability of selected microorganisms to produce organic acids during growth, and their potential growth on cheap organic waste-products. Heterotrophic leaching was later suggested for treatment of industrial wastes, sewage sludge and heavy metal contaminated soil (Bosecker, 1997; Krebs *et al.*, 1997; White *et al.*, 1997). Most research within heterotrophic leaching of contaminated material was conducted with fly ash. It was shown that *A. niger* grew and produced gluconate in the presence of 10% (w/v) fly ash, while citrate was produced in its absence. Chemical leaching with commercial citric acid was only slightly higher than microbiological leaching (Bosshard *et al.*, 1996). In another study *P. simplicissimum* was shown to produce citric acid in the presence of Zn-contaminated filter dust while no acid production was seen in its absence (Franz *et al.*, 1991). Finally it was shown how extraction of Pb from filter dust by yeasts isolated from seeping water, waste compost, and sewage was possible (Wenzl *et al.*, 1990). This documented microbial growth and organic acid production in the presence of heavy-metal contaminated fine-grained materials, suggests that growth and acid production would also be possible in the presence of heavy-metal contaminated soil fines. The fact that microbial extraction of even very stable Pb-compounds is possible was supported by a work in which it was discovered how *A. niger* grew with pyromorphite as sole phosphate source (Sayer *et al.*, 1999). In addition it was shown that application of direct current increased metabolism of bacteria in soil slurries (Jackman *et al.*, 1999), which supports the feasibility of heterotrophic leaching in combination with EDR/EKR.

In this work the feasibility of combining heterotrophic leaching and EDR of Pb contaminated soil fines in suspension is subjected to preliminary investigation. The potential of the technology depends on the ability of organic acids to extract Pb from soil under acidic conditions, as well as on demonstrated promotion of EDR of Pb from soil fines under influence of the organic acids. Our research comprises experimental extraction of Pb from contaminated soil fines with 11 organic acids at neutral to slightly acidic pH. The acids were chosen upon to the ability of heterotrophic microorganisms to produce them (Krebs *et al.*, 1997). Based on the results of these extractions, and included in this work, the effect of addition of selected organic acids on EDR of Pb-contaminated soil fines is studied in 10 EDR experiments.

## 2 Materials and Methods

**Soil:** An industrially contaminated Danish soil of unknown origin, obtained from a pile after excavation, was used as experimental soil. The soil fines were obtained by simple wet-sieving of the original soil with distilled water through a 0.063mm sieve. Concentrated slurry of fines was obtained by centrifugation at 3000rpm for 10 min. and decantation of the supernatant. The soil fines were kept in slurry and stored at 5°C in access of oxygen. The *content of metals* (Fe, Mn, Al, Pb) was determined by AAS. Prior to analysis of soil samples, 1.00g soil fines were digested in autoclave with 20.00mL 1:1 HNO<sub>3</sub> for 30min at 120°C and 200kPa according to the Danish standard method DS259 (Dansk Standardiseringsråd, 1991), and filtered through a 0.45µm filter by vacuum. Liquid samples with pH > 4 were identically digested with



concentrated  $\text{HNO}_3$  (1:4). Validation of AAS results was for all metals obtained by measurement of liquid reference samples. The *carbonate content* was determined volumetrically by the Scheibler-method when reacting 3g of soil with 20mL of 10% HCl. In calculations it was assumed that all carbonate is present as calcium-carbonate. *Organic matter* was determined by loss of ignition at 550°C for one hour. *CEC* was measured after ion exchange of 10g dry soil with  $\text{NH}_4^+$ , followed by exchange of  $\text{NH}_4^+$  for  $\text{Na}^+$ . The ammonium concentration of the centrifugate was measured on spectrophotometer via flow-injection. For *pH*-measurements 5.0g dry soil was shaken with 12.5mL 1M KCl for one hour followed by settling for 10min and measurement by a Radiometer Analytical electrode. *Sequential extraction* was performed according to the method from the Standards, Measurements and Testing Program of the European Union (Mester *et al.*, 1998): 0.5g of dry, crushed soil was treated in four steps as follows: I) Extraction with 20.0ml 0.11M acetic acid pH 3 for 16 hours. II) Extraction with 20.0 ml 0.1M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  pH2 for 16 hours. III) Extraction with 5.0ml 8.8M  $\text{H}_2\text{O}_2$  for one hour and heating to 85°C for one hour with lid followed by evaporation of the liquid phase at 85°C until it had reduced to < 1ml by removal of the lid. The addition of 5.0 ml 8.8M  $\text{H}_2\text{O}_2$  was repeated followed by resumed heating to 85°C for one hour and removal of the lid for evaporation until almost dryness. After cooling down, 25.0 ml 1M  $\text{NH}_4\text{OOCCH}_3$  pH 2 was added, and extraction took place for 16 hours. IV) Finally digestion according to DS 259 was made for identification of the residual fraction. Between each step the sample was centrifuged at 3000rpm for 15min, and the supernatant was decanted and stored for AAS. Before addition of the new reagent, the sample was washed with 10.0ml distilled water for 15min, centrifuged at 3000rpm for 15min and the supernatant was decanted. All extractions were performed at room temperature while shaking at 100rpm unless otherwise mentioned. All analyses were made in triplicate except CEC and sequential extraction which were made in double. *Extraction experiments:* Soil fines (5.00g) were allowed to equilibrate with 25ml reagent at room temperature for 7 days while shaken at 180rpm. pH and metal content was measured in the liquid phase.  $\text{HNO}_3$  extractions were made at concentrations between 0.01 and 2M. Organic acids (acetic acid, citric acid, DL-malic acid, formic acid, fumaric acid, gluconic acid, lactic acid, L-glutamic acid, oxalic acid, pyruvic acid, tartaric acid) were all 0.2M and adjusted to pH values of 2, 3, 4 and 5 with  $\text{HNO}_3/\text{NaOH}$ . Citric acid and DL-malic acid were chosen for further study, and prepared in concentrations between 0.2M and 1M at pH's 5 and 6 prior to extraction in accordance with the describe procedure. All extractions were made in double.

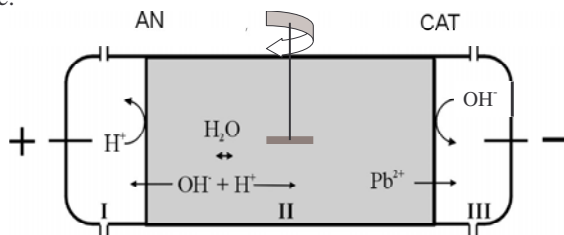


Figure 2.1: Schematic view of a cell used for experimental EDR of soil fines in suspension.

*Remediation experiments:* Electrodialysis experiments were made in cylindrical Plexiglas-cells with three compartments. Compartment II, which contained the soil-slurry was 10 cm long and 8 cm in inner diameter. The slurry was kept in suspension

by constant stirring with plastic-flaps attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). The anolyte was separated from the soil specimen by an anion-exchange membrane, and the catholyte was separated from the soil specimen by a cation-exchange membrane. Both membranes were obtained from Ionics® (types AR204SZRA and CR67 HVY HMR427). Figure 2.1 shows a schematic drawing of the setup. Electrolytes were circulated by mechanical pumps (Totton Pumps Class E BS5000 Pt 11) between electrolyte chambers and glass bottles. Platinum coated electrodes from Permascand® were used as working electrodes and the power supply was a Hewlett Packard® E3612A. The electrolytes initially consisted of each 500mL 0.01 M NaNO<sub>3</sub> adjusted to pH 2 with HNO<sub>3</sub>. Conductivity in chamber II, pH in all chambers, and voltage between the working electrodes were observed approximately once every 24 hours. pH in the electrolytes was accordingly kept between 1 and 2 by manual addition of HNO<sub>3</sub>/NaOH. Experiments were made according to the experimental plan in table I. All experiments lasted 240 hours and were designed with a liquid-to-solid-ratio (L/S) of 10.5 (37g soil, 390 ml liquid). pH of malic and citric acid solutions was adjusted with NaOH. In the last three experiments (MA40N, CA40N and KC40) the reagent was allowed to react with the soil fines for 24 hours prior to application of the current.

TABLE I  
Experimental plan

Exp. Name	Reagent (pH of reagent)	J** [mA]	Adjustment of pH in II with NaOH
DW20	Distilled Water (pH 6.5)	20	-
MA20	1 M Malic acid (pH 5)	20	-
CA20	0.5M Citric acid (pH 5)	20	-
MA20N*	1 M Malic acid (pH 7)	20	Kept at 6-7
CA20N*	0.5M Citric acid (pH 7)	20	Kept at 6-7
NA20	HNO <sub>3</sub> (pH 1.4)	20	-
NA40	0.5 M HNO <sub>3</sub> (pH 0.0)	40	-
MA40N*	1 M Malic acid (pH 5)	40	Kept at 5-6
CA40N*	0.5M Citric acid (pH 5)	40	Kept at 5-6
KC40	0.5M Potassium-citrate (pH 8.5)	40	-

\*N = neutral conditions

\*\*20mA is equivalent to 0.4mA/cm<sup>2</sup>, 40mA is equivalent to 0.8mA/cm<sup>2</sup>

### 3 Results

#### 3.1 SOIL CHARACTERISTICS

Characteristics of the soil fines are listed in table II. Pb was analyzed in triple in each batch of soil-fines produced. Three different batches were used in this work containing between 670 and 1170mg/kg Pb. Sequential extraction (figure 3.1) shows how Fe and Al are more strongly bound in the soil than Pb and Mn. It is a soil with a high carbonate content and a significant content of organic matter. Both carbonate and organic matter concentrations are increased in the soil fines compared to the original soil (Jensen *et al.*, 2006a). The speciation of Pb in the original soil was investigated in (Jensen *et al.*, 2006b) as soil 10, while unenhanced EDR in a traditional stationary setup was investigated for the original soil (soil 10) in (Jensen *et al.*, 2006b).

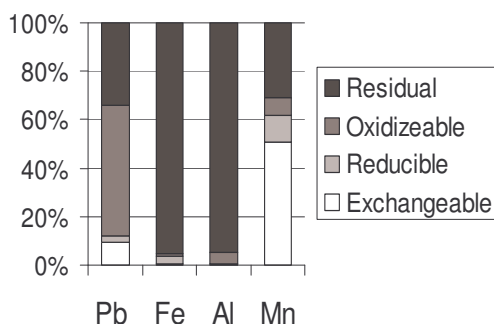


Figure 3.1: Sequential extraction of Pb, Fe, Al and Mn from the soil fines

TABLE II  
Characteristics of the soil fines

Pb [mg/kg]	670-1170
pH	7.8 +/-0.2
CaCO <sub>3</sub> [%]	17.3 +/-0.1
OM [%]	7.8 +/-0.1
CEC [meq/100g]	14.1 +/-0.3
Fe [g/kg]	27.3 +/-0.3
Mn [mg/kg]	587 +/-26
Al [g/kg]	9.9 +/-0.2

### 3.2 EXTRACTION EXPERIMENTS

The ability of the 11 organic acids to extract Pb is illustrated in figure 3.2. Six of the acids showed similar or worse extraction results than HNO<sub>3</sub> in this slightly acidic to neutral pH (pH3-7), while five of the acids (citric acid, DL-malic acid, gluconic acid, tartaric acid and fumaric acid) showed pronounced improvement at near neutral pH due to complexation between Pb and the organic ligands of the acids. In consistence with the results of (Wasay *et al.*, 1998), citrate and tartarate showed particularly promising, however extraction with malate, which was not included in the previous investigation, showed slightly better results than tartarate. The promising Pb-extracting properties of malic acid are in consistence with the findings of (Qin *et al.*, 2004). Citric acid extracted 22% Pb at pH 7.2 (initial pH of extractant was 5.0) while DL-malic extracted 11% of the Pb at pH 6.8-7.1 (initial pH of extractant was 5.0). The results were not as promising as those obtained by (Wasay *et al.*, 1998) when extracting Pb from a loam and a sandy clay loam with citrate and tartarate. This discrepancy may be caused by the 5 times lower L/S and the more fine grained material used in the present study; but could also be due to the high carbonate content or presence of less soluble Pb-compounds. Extraction results with oxalic acid are not visible from figure 3.2 because the final pH's of the slurry was above 7. The fact that pH of the soil increased after addition of oxalic acid at pH's 2-5 (well below the initial soil pH) indicates a complex interaction between soil constituents and oxalate, which may include dissolution of iron-oxides and -hydroxides resulting in the observed pH-increase. The maximum extraction of Pb with oxalic acid was 1% obtained at pH 9-10.

Based on the results shown in figure 3.2, further investigation of the ability of citric and DL-malic acid to extract Pb from soil fines was initiated. Results of increased extractant concentration are shown in figure 3.3, where also extraction of Fe, Mn and Al is shown. Increased extraction of Pb could be obtained by increasing the concentration of both citric acid and DL-malic acid, however at the highest concentration of citrate (1M), a significantly declined extraction was observed. This coincided with a decreased extraction of Mn, Fe and Al, and could be due to precipitation of the formed complexes.

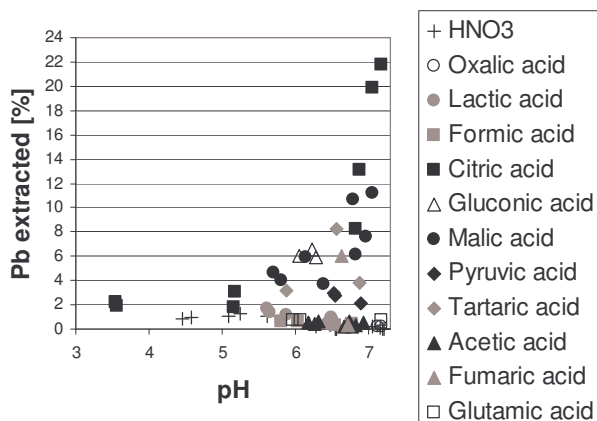


Figure 3.2: Extraction of Pb from soil fines with  $\text{HNO}_3$  and organic acids (0.2M).

With both acids significantly higher extraction of Mn than of Pb occurred. Concerning the mineral dissolution taking place during Pb-extraction, it was obvious that no Pb-extraction with these acids could be obtained without complete extraction of Mn. Fe, and in particular Al, were dissolved to a smaller extent than Pb. Mn, Fe and Al were all extracted beyond the extraction obtained during steps I-III of sequential extraction, while Pb was less affected by the organic acids than by the first three steps of sequential extraction. The best organic acid extraction of Pb was obtained with 0.4 and 0.6M citrate and 1.0M malate which extracted equivalent amounts of all metals including 35% of the Pb.

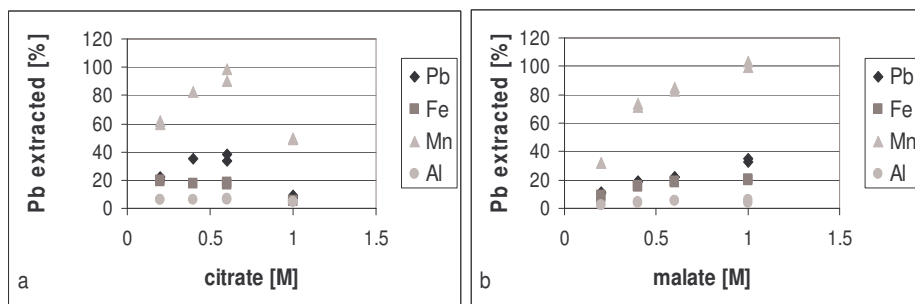


Figure 3.3: Extraction of Pb, Fe, Mn and Al from soil fines with a) citric acid (final pH between 7.1 and 7.7) and b) DL-malic acid (final pH between 6.8 and 7.2). Results of both double decisions are plotted.

### 3.3 REMEDIATION EXPERIMENTS

Main results of the 10 EDR experiments are summarized in table III. Soil fines from three different batches with Pb-concentrations of 670, 1040 and 1170 mg/kg respectively were used. Mass balances for Pb between 61 and 115% were obtained. Although the low mass balances in some of the experiments mean that interpretation of the data should be made with caution, the results of the experiments are significant enough to draw final conclusions. The final Pb-concentrations in the soil-fines obtained were between 40 and 980 mg/kg however in some of the experiments a

considerable amount of the released Pb remained in the solution in chamber II (up to 55%), while in other experiments all the released Pb was transported into the electrolytes. Between 0.05 and 2.31‰ of the current was transferred by Pb-ions (calculated as the ‰ of the total transferred charges carried by  $\text{Pb}^{2+}$  into the electrolytes).

TABLE III  
Experimental results

Exp. Name	Pb Mass balance [%]	Start Pb [mg/kg]	Final Pb [mg/kg]	% Removed From soil*	% Pb in Solution in chamber II*	Current efficiency [%]
DW20	115	1170	220	87	1	2.31
MA20	86	1040	400	63	53	0.20
CA20	84	1040	980	6	1	0.11
MA20N	94	1040	540	54	48	0.11
CA20N	61	1040	560	26	15	0.16
NA20	84	670	48	93	55	0.34
NA40	96	670	40	90	9	0.93
MA40N	89	670	355	51	41	0.09
CA40N	69	670	315	43	21	0.17
KC40	70	670	519	8	3	0.05

N = neutral conditions in chamber II

\*Calculated as fraction of the total final amount of Pb

### 3.3.1 Effect of acid addition

The effect of addition of malic acid (MA20), citric acid (CA20) and nitric acid (NA20) on remediation is compared to the reference experiment with distilled water (DW20) in figure 3.4. Of these, the lowest final Pb-concentration in the soil-fines was 48 mg Pb/kg obtained with nitric acid. The final Pb-concentration in the soil fines was considerably higher in both of the experiments with organic acid compared to the experiments with distilled water and nitric acid. In addition, the transport of Pb from the middle-chamber (II) into the electrolyte-chambers was impeded in the experiments with malic acid and nitric acid compared to the experiment with distilled water. The reduced Pb-transport in the experiments with acid addition is confirmed by the low current efficiency obtained in NA20, MA20 and CA20 compared to DW20. The overall result is that distilled water is superior for EDR of Pb-contaminated soil-fines in suspension. In DW20, 86% of the Pb was transported towards the cathode end, where 79% was precipitated at the cathode itself. Less than 1% was found in the anolyte and in solution in chamber II respectively. In MA20 and NA20 7% of the Pb was transported into the anolyte, while more than 50% was found in solution in the middle-chamber. In MA20 the remainder was still bound to the soil while in NA20 32% was transported into the catholyte. Pb released from the soil in CA20 was transported towards the anode. In this experiment however, 94% of the Pb was still bound to the soil-fines after 240 hours in contrast to what was expected from the extraction results.

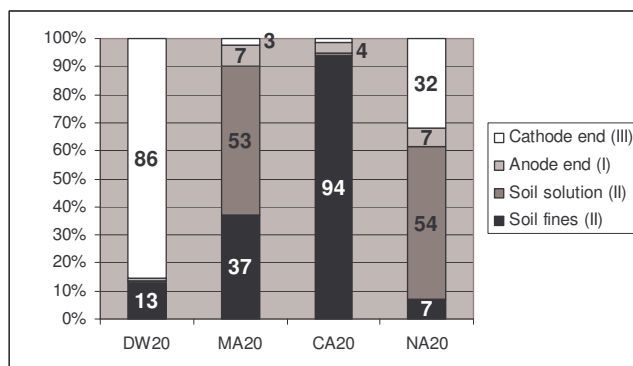


Figure 3.4: Final distribution of Pb in the chambers of the electrodiolytic cell after experimental remediation for 240 hours at 20 mA at L/S 10.5. Enhancing reagents were distilled water (DW), 1M malic acid (MA), 0.5M citric acid (CA) and nitric acid pH 1.4 (NA).

### 3.3.2 pH

The pH-development in the middle chamber (II) during the four electrodiolytic remediation experiments is illustrated in figure 3.5. The figure shows how pH was decreasing in the experiment with distilled water due to water-splitting at the anion-exchange membrane as discussed in (Jensen *et al.*, 2006a). pH in the experiment with nitric acid was initially slightly lower than in the experiment with distilled water; however pH was increasing during the first 80 hours to reach values similar to the distilled-water experiment. pH in the organic acid experiments was decreasing slowly through out the experimental period to reach a final pH of approximately 4.5. This development is a consequence of addition of a high enough concentration of mobile anions to result in a significant decrease of the water-splitting at the anion exchange membrane. The slightly slower pH-decrease in NA20 compared to DW20 could likewise be a result of the added  $\text{NO}_3^-$ .

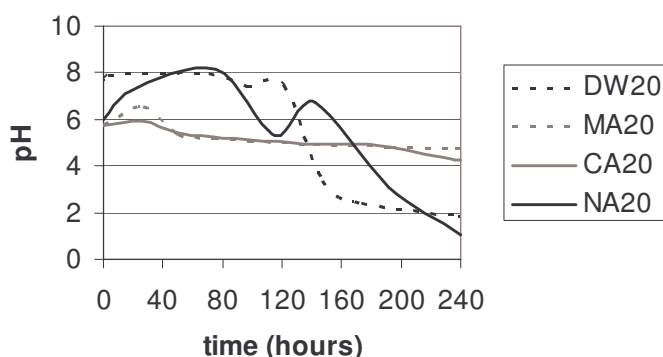


Figure 3.5: pH in the soil solution during experimental remediation with distilled water (DW), malic acid (MA), citric acid (CA) and nitric acid (NA) as reagents at 20mA ( $0.4\text{mA}/\text{cm}^2$ ).

### 3.3.3 Conductivity

The conductivity of the soil solution was directly related to the concentration of added acid. The highest conductivity was seen in MA20 where 1M malic acid was added. Compared to this, the conductivity was about halved in CA20, where 0.5M citric acid was added, and in NA20 with nitric acid (pH 1.4); the initial conductivity was only slightly elevated compared to DW20, and by the end of the experiments conductivity had increased in DW20 beyond that of NA20 due to more water-splitting taking place in DW20.

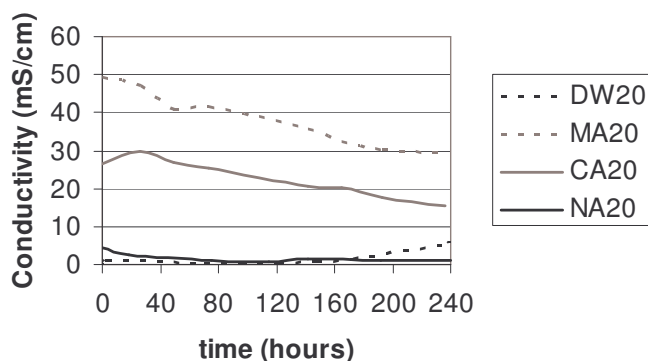


Figure 3.6: Conductivity in the soil solution during experimental remediation with distilled water (DW), malic acid (MA), citric acid (CA) and nitric acid (NA) as reagents at 20mA ( $0.4\text{mA/cm}^2$ ).

The conductivity of the organic acid experiments was decreasing constantly during the experimental period, suggesting transport of organic ligands out of the soil solution. This transport was confirmed by visible inspection of CA20 where the anolyte turned yellow after only 24 hours with a clear invigoration of the color during the experimental time. This information may keep the explanation of the low extraction of Pb obtained in CA20: transport of citrate into the anolyte may be hindering complexation with Pb. Figure 3.7 illustrates the speciation of citrate as a function of pH and confirms the dominance of negatively charged citrate-species at pH 4-6 which are available for transfer into the anolyte.

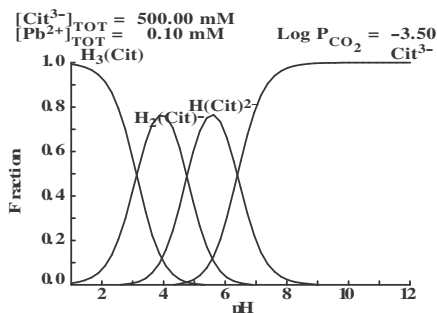


Figure 3.7: Speciation of citrate in solution in the presence of Pb and carbonate in equilibrium with the atmosphere as a function of pH (Puigdomenech, 2002).

### 3.3.4 Voltage

The high conductivities in the experiments with organic acid result in correspondingly low voltages (figure 3.8). During most of the experimental period DW20 showed the highest voltage in consistence with the low ion-concentration and conductivity in this experiment. By the end of the NA20-experiment one incident of very high voltage was however observed. This incident was connected to high pH (12.2) in the catholyte, and voltage decreased immediately after adjustment of pH in the catholyte. This voltage-increase is likely to have occurred as a response to impeded transport across the cation-exchange membrane due to precipitation of hydroxides within the membrane. Also in the DW20, MA20 and CA20 incidents of high pH in the catholyte were observed, however no voltage increase was registered. In DW20 the concentration of ions available for precipitation was probably too low (as suggested by the low Pb-concentration in the solution) to provoke substantial precipitation, while in the two organic acid experiments complexation by the organic ligands may have prevented precipitation.

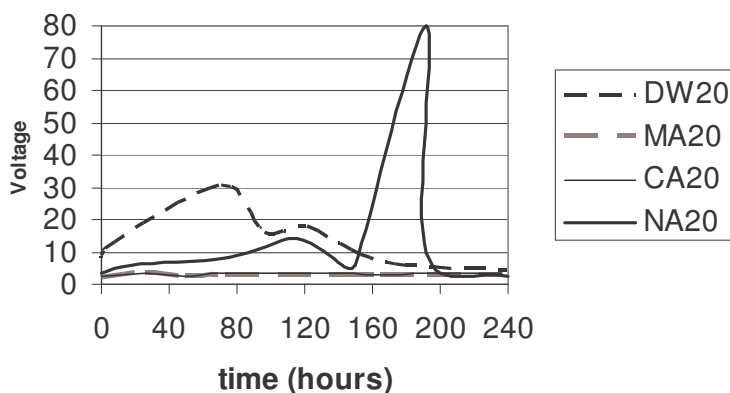


Figure 3.8: Voltage over electrodialytic cell during experimental remediation with distilled water (DW), malic acid (MA), citric acid (CA) and nitric acid (NA) as reagents at 20mA ( $0.4\text{mA}/\text{cm}^2$ ).

### 3.3.5 pH-dependency of remediation with organic acids

Speciation of Pb in the presence of citrate and malate is illustrated in figure 3.9. Impeded transport of Pb into electrolytes after addition of the organic acids could well be explained by the prevalence of neutral complexes at pH-values below 5. In particular between malate and Pb, neutral complexes dominate, explaining the observed extraction without subsequent transfer of Pb in MA20. A possible means of improvement could therefore be to adjust pH during remediation to remain at values, where charged complexes prevail. Consequently experiments were made in which pH of the soil-slurry was adjusted manually with NaOH in order to maintain pH-values between 6 and 7 during the whole experiment (experiments MA20N and CA20N). The results of these experiments are shown in figure 3.10. Increased dissolution and transfer of Pb in CA20N compared to CA20 was indeed observed, but 75% Pb was still bound to the soil fines after termination of the experiment, and in contrast to our



expectations, the remediation in MA20N was impaired slightly compared to MA20. This unexpected result may appear, because the Pb-malate system is incompletely described and further complexes may exist and dominate.

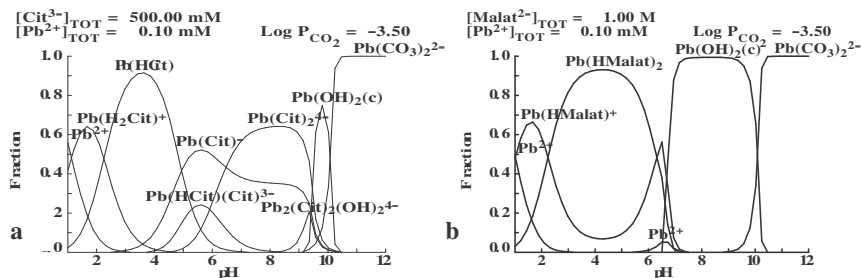


Figure 3.9a: Speciation of Pb in solution in the presence of excess citrate and b: malate and carbonate in equilibrium with the atmosphere as a function of pH (Puigdomenech, 2002). Equilibrium constants for malate from (Smith and Martell, 1977) with the reservation that the Pb-malate system may not be fully described.

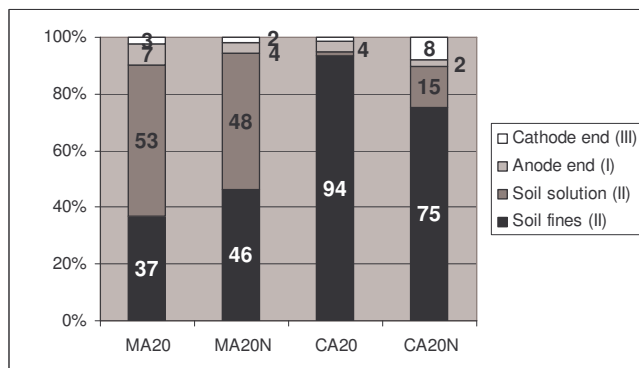


Figure 3.10: Final distribution of Pb in the chambers of the electrodialytic cell after experimental remediation for 240 hours with malic acid (MA), malic acid at neutral pH (MA20N), citric acid (CA) and citric acid at neutral pH (CA20N) as reagents at 20mA ( $0.4 \text{ mA/cm}^2$ ).

### 3.3.6 Influence of current density

It was previously shown that 20mA is the optimal current density for EDR of soil fines in suspension at L/S 10.5 with distilled water as reagent (Jensen *et al.*, 2006a), however the fact that the conductivity was increased substantially MA20 and CA20 compared to DW20 suggested that current density in these experiments could be increased beyond what is ideal for remediation with distilled water. This hypothesis was tested by increasing current to 40mA in experiments with malic acid and citric acid (MA40N and CA40N) in experiments where pH of the soil slurry was adjusted to 5-6 by addition of NaOH during the experiments. Additional experiments with nitric acid (NA40), and potassium-citrate (KC40) at increased current densities were made. Potassium citrate was chosen because it required quite a large amount of NaOH to adjust the organic acids to near neutral values, and addition of the salts of the acids

seemed more practical. In NA40 the concentration of nitric acid was increased compared to the concentration in NA20 in order to exceed the buffer-capacity of the soil and increase the conductivity enough to be able to apply the higher current without inducing water splitting at the cation-exchange membrane. In addition the reagents were allowed to react with the soil fines for 24 hours prior to application of the current in MA40N, CA40N and KC40. The results are visualized in figure 3.11: Increasing current with malic acid seemed to have no or even adverse effects on the remediation. Adverse effects could be caused by faster removal of the malate from the soil solution and therefore decreased extraction of Pb. In the experiment with citric acid CA40N increased current density seemed to have a positive influence on extraction and transport of Pb into the anolyte, however by no means reaching the efficiency of DW20. Addition of potassium citrate strongly impeded remediation compared to all experiments even the ones with citric acid.

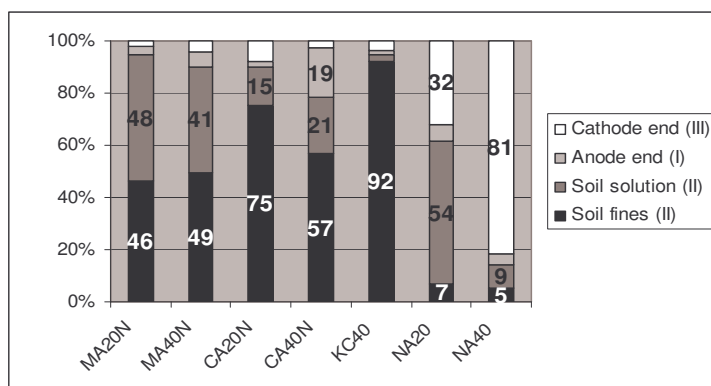


Figure 3.11: Final distribution in the chambers of the electrodiolytic cell after experimental remediation for 240 hours at 20mA with malic acid (MA20), citric acid (CA20) and nitric acid (NA20) and at 40mA with malic acid (MA40), citric acid (CA40), sodium-citrate (KC40) and nitric acid (NA40) as reagents.

Figure 3.12 illustrates how the buffer capacity in NA40 was successfully overcome by addition of 0.5M  $\text{HNO}_3$ . The combined effect of decreased pH and increased current density gave significantly improved remediation compared to NA20. The final Pb concentration in the soil fines after NA40 was 40 mg/kg which is below the concentration obtained in DW20 (220 mg/kg) and corresponds to the governmental limit set by the Danish EPA for sensitive land use. Addition of nitric acid in combination with an increased current density is therefore well suggested for promotion of EDR of Pb contaminated soil fines in cases where removal-rate is considered to be more important than energy-expenditure and acid consumption.

The remaining high conductivity (figure 3.13) in the experiments with acid at increased current densities suggests that current density may be increased further in favor of remediation with nitric acid as a reagent. An important consideration prior to addition of nitric acid is however the condition of the soil fines and any potential application of those succeeding remediation. If relevant the implication of acid addition on nutrients and minerals should be investigated.

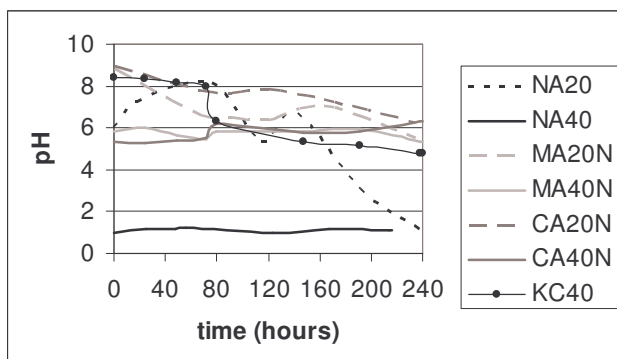


Figure 3.12: Implication on pH of elevated current density.

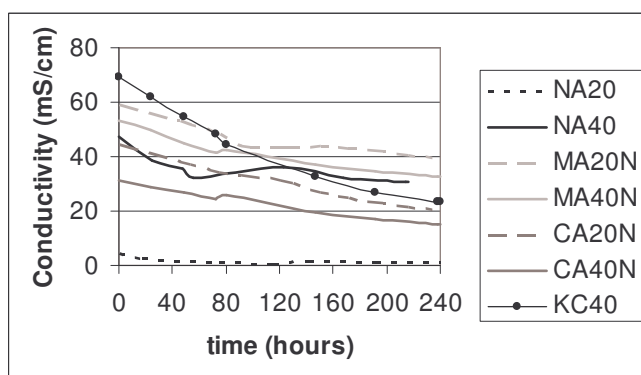


Figure 3.13: Implication on conductivity of elevated current density.

## 4 Conclusions

Citric acid, DL-malic acid, gluconic acid, tartaric acid and fumaric acid (0.2M) are able to extract Pb from contaminated soil fines in excess of the extraction obtained due to pure pH-changes at neutral to slightly acidic conditions. The most efficient extraction is obtained with citric and malic acids, with which extraction results are improved when increasing concentrations to 0.5 and 1.0M respectively. Maximum 35% Pb was extracted from the present soil. Mn is completely extracted by the organic acids while Fe and Al are extracted to a smaller extent than Pb. Electrodialytic remediation of soil-fines in suspension is impeded strongly by addition of citric acid and malic acid (0.5M and 1.0M) independently on pH-control of the suspension to intervals where the Pb-complexes with those acids ought to be charged and allowance for time to react prior to application of current. Increased current densities did also not improve results with organic acid as reagent, and the idea of combining EDR and heterotrophic leaching of soil fines in suspension is rejected. In contrast enhancement of EDR with nitric acid show promising results at current densities increased beyond what is feasible with addition of only distilled water. Nitric acid addition is therefore preferable in situations where removal rate is considered more important than energy expenditure and chemical consumption. Increased changes in soil characteristics by addition of nitric acid could however be expected, and should be investigated when relevant for the succeeding application of the remediated soil fines.

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## 8. Kinetics of Electrodialytic Extraction of Pb and Soil Cations from Contaminated Soil Fines in Suspension

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### Abstract

The objective of this work was to investigate the removal rates of Pb and common soil cations from soil-fines during electrodialytic remediation in suspension. This was done in six identical experiments of various duration, followed by analysis of Pb, Al, Ca, Fe, Mg, Mn, Na and K in the remediated soil. The Pb-remediation process could be divided into four phases 1) a “lag-phase”, where removal was substantially absent, 2) a period with a high removal rate involving dissolution of Pb in the soil-solution, 3) a period with a low removal-rate, where the dissolved Pb was removed from solution, and 4) a period where no further Pb-removal was obtained as the treatment proceeded. The maximum removal rate for Pb obtained during phase 2) was 4(mg/kg)/hour. During phase 3) the high conductivity and low voltage suggested that removal may be accelerate by increasing current density. During the first phase dissolution of carbonates was the prevailing process. This dissolution resulted in a corresponding loss of soil-mass. During this phase, the investigated ions accounted for the major current transfer, while, as remediation proceeded, hydrogen-ions increasingly dominated the transfer. The overall order of removal-rates was: Ca > Pb > Mn > Mg > K > (Al and Fe). Na was found to enter the soil from the electrolytes why a careful choice of electrolytes in order to meet any requirements by subsequent applications of the soil-fines is recommended. It is also recommended to limit the dissolution of Fe and Al-minerals by terminating remediation as soon as Pb-extraction ceases in order not to waste energy and to avoid the toxic effects of aluminum in solution.

**Keywords:** Contamination, Electrodialytic remediation, Macronutrients, Pb, Remediation, Soil wash.

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## 1 Introduction

Sludge of heavy metal contaminated soil fines is the main process residue limiting the success of the soil washing process as a remediation solution for contaminated soil. Electrodialytic soil remediation (EDR) is an electrokinetic remediation (EKR) method, where ion-exchange membranes are applied as barriers between soil and electrolytes. It was recently shown that during EDR of soil fines in suspension, Pb is easily dissolved by the acidification resulting from water splitting and transferred to the catholyte (Jensen *et al.*, 2006b). Potential applications of the remediated soil fines include: ceramics (bricks and tiles), lightweight-expanded aggregates, cement, concrete, soil amendment, and landfill liners. Besides the content and leachability of heavy metals, the applicability of soil-fines depends on their final characteristics including content of salts, nutrients and minerals. Examples of limitations are: production of bricks and roof tiles, where iron-oxides are unwanted (Ferreira *et al.*, 2003); lightweight-expanded aggregates, where the expanding qualities depend on the grain size and the composition of the clay-minerals; cement production in which chloride is problematic (Ferreira *et al.*, 2003); production of concrete, where water soluble species in general are unwanted (Ferreira *et al.*, 2003); and application in landfill liners and as soil amendment, which is limited by the acidity of the soil fines.

During the EDR process, the character of the soil fines is subject to alterations, and attention needs to be paid towards the quality of the treated product prior to application. Dissolution of natural soil constituents during EDR/EKR was demonstrated in several studies (Hansen *et al.*, 1997; West *et al.*, 1999; Suer *et al.*, 2003). Ca dissolution was observed to precede contaminant removal and coincided with the pH-shift in the soil (Hansen *et al.*, 1997; Suer *et al.*, 2003). Also Fe, Mg and Mn were removed from soil as a response to EKR (Suer *et al.*, 2003). Here removal of Mg and Mn was directly related to the pH decrease, while no relation between pH and Fe-removal was observed. Mineral dissolution was further demonstrated by (West *et al.*, 1999), who observed transfer of Na, Mg, Ca, K, Al, Fe, and Si ions from kaolinite into the electrolytes during EKR of spiked kaolinite.

Studies on the influence of direct current on clay minerals were made in the mid 1900's. It was shown that extensive hydration of common minerals (olivine, augite, hornblende, pargasite, biotite, chlorite, muscovite and feldspar) took place as a response to direct current (Hla, 1945). The hydration was accompanied by dissolution and transport of K, Na, Ca, Fe, Mg, Al and Si. The authors held that the drastic changes imply a partial or complete destruction of the geometry of the original minerals. Evidence of mineralogical changes in a thin surface-film covering the original mineral was given, however the XRD-technique was not sophisticated enough to make ultimate conclusions. A great variance in stability among minerals towards electrodialysis was demonstrated in a study, where extensive dissolution of saponite clay and removal of Si was demonstrated, while only little Si was removed from nontronite clay (Caldwell and Marshall, 1942). Similarly biotite and jeffersite were almost completely decomposed while muscovite and phlogopite only gave off small quantities of cations (Roy, 1949). Interestingly the XRD-patterns of the biotite and jeffersite did not change during treatment. A recent study showed how montmorillonite exhibited color-changes (grey to green), shrinkage cracks, water loss and an increased Fe(II)-content upon the influence of the current and the acidic front. These reactions concurrently pointed towards reduction of octahedral Fe(III) to Fe(II) within the lattice of the clay mineral (Grundl and Reese, 1997).

In order to perform a preliminary investigation of the condition of soil-fines remediated by EDR in suspension, we present a study of the electrodialytically

induced dissolution and removal of major soil cations (Fe, Al, Mg, Na, Mn, Ca, K). The option of adjusting the alteration of soil-characteristics to suit specific application purposes through process control is elucidated by studying the removal of soil cations as a function of time, and in relation to the Pb-removal. Thereby this study also illuminates the kinetics of the Pb-removal itself.

## 2 Materials and Methods

### 2.1 ANALYTICAL

Pb, Fe, Al, Mg, Na, Mn, Ca, and K were analyzed by flame AAS. Samples with Pb concentrations below the detection limit (1mg/L) were measured by graphite furnace AAS. Prior to analysis of soil samples, 1.00g soil fines were digested in autoclave with 20.00mL 1:1 HNO<sub>3</sub> for 30min at 120°C and 200kPa according to the Danish standard method DS259 (Dansk Standardiseringsråd, 1991), and filtered through a 0.45µm filter by vacuum. Validation of AAS results was obtained by measurement of liquid reference samples. Carbonate was measured volumetrically by the Scheibler-method when reacting 3g of soil with 20mL of 10% HCl. In calculations it was assumed that all carbonate is present as calcium-carbonate. Organic matter was determined by loss of ignition at 550°C for one hour. CEC was measured after ion exchange of 10g dry soil with NH<sub>4</sub><sup>+</sup>, followed by exchange of NH<sub>4</sub><sup>+</sup> for Na<sup>+</sup>. The ammonium concentration of the centrifugate was measured on spectrophotometer via flow-injection. pH and Conductivity were measured by a Radiometer Analytical electrode.

### 2.2 SOIL

An industrially contaminated Danish soil of unknown origin was used as experimental soil. The soil fines were obtained by simple wet-sieving of the original soil with distilled water through a 0.063mm sieve. Concentrated slurry of fines was obtained by centrifugation at 3000rpm for 10 min. and decantation of the supernatant. The soil fines were kept in slurry and stored at 5°C in access of oxygen.

TABLE I  
Characteristics of the soil fines

<b>Pb [mg/kg]</b>	<b>673 ±101</b>
<b>Mn [mg/kg]</b>	<b>542 ±49</b>
<b>Ca [g/kg]</b>	<b>64.7 ± 4.7</b>
<b>Mg [g/kg]</b>	<b>4.3 ±0.7</b>
<b>Fe [g/kg]</b>	<b>23.2 ±4.6</b>
<b>Al [g/kg]</b>	<b>12.5 ±3.1</b>
<b>K [g/kg]</b>	<b>4.0 ±0.9</b>
<b>Na [mg/kg]</b>	<b>410 ±50</b>
<b>CaCO<sub>3</sub> [%]</b>	<b>17.3 ±0.1</b>
<b>Organic matter [%]</b>	<b>7.8 ±0.1</b>
<b>CEC [meq/100g]</b>	<b>14.1 ±0.3</b>

### 2.3 REMEDIATION EXPERIMENTS

Electrodialysis experiments were made in cylindrical Plexiglas-cells with three compartments. Compartment II, which contained the soil-slurry was 10 cm long and 8 cm in inner diameter. The slurry was kept in suspension by constant stirring with plastic-flaps attached to a glass-stick and connected to an overhead stirrer (RW11



basic from IKA). The anolyte was separated from the soil specimen by an anion-exchange membrane, and the catholyte was separated from the soil specimen by a cation-exchange membrane. Both membranes were obtained from Ionics® (types AR204SZRA and CR67 HVY HMR427). Figure 2.1 shows a schematic drawing of the setup. Electrolytes were circulated by mechanical pumps (Totton Pumps Class E BS5000 Pt 11) between electrolyte chambers and glass bottles. Platinum coated electrodes from Permascand® were used as working electrodes and the power supply was a Hewlett Packard® E3612A. The catholyte and anolyte initially consisted of 0.01M  $\text{NaNO}_3$  adjusted to pH 2 (500 and 300mL respectively) with  $\text{HNO}_3$ . In previous experiments the build-up of an osmotic pressure difference between the two compartments was observed to result in extensive water transfer from chamber I to II. This water transfer was avoided by decreasing the amount of liquid to be circulated in the anolyte from 500mL, used in previous works (Jensen *et al.*, 2006a; Jensen *et al.*, 2006b) to 300mL, whereby the hydraulic pressure was decreased and overflow avoided.

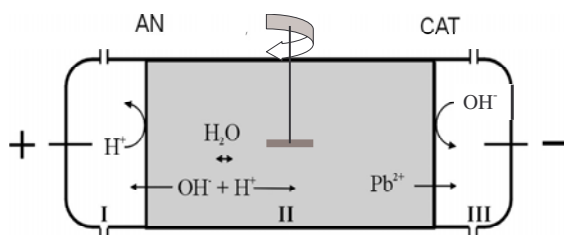


Figure 2.1: Schematic view of a cell used for experimental EDR remediation of soil-fines in suspension.

Current, voltage and pH in all chambers as well as conductivity in chamber II were measured approximately once every 24 hours. pH in the electrolytes was kept between 1 and 2 by manual addition of  $\text{HNO}_3/\text{NaOH}$ . Experiments were made according to the experimental plan in table II. In all experiments the liquid to solid ratio (L/S) was 4.3 (87g soil and 375ml distilled water), and the current density was  $0.8\text{mA}/\text{cm}^2$  (40mA).

TABLE II  
Experimental plan

Exp.	Experimental time (hours)
K1	188
K2	330
K3	503
K4	671
K5	838
K6	930

After each experiment, membranes were cleaned overnight in 1M  $\text{HNO}_3$  and electrodes were cleaned overnight in 5M  $\text{HNO}_3$ . Volumes of the cleaning acids, the electrolytes, and the solution in the middle chamber were measured followed by analysis of the cation-concentrations by AAS, the remaining soil mass was decided and the cation concentrations in the soil were measured by AAS after digestion

according to DS259 as described above. The mass balances for Pb and soil cations were calculated as the mass of the ions found in the whole system after remediation (in soil, soil solution, electrolytes and at membranes and electrodes) in percent of the amount found in the soil prior to remediation (concentration times initial amount of soil).

### 3 Results

#### 3.1 PB REMOVAL

Main results of the experiments are summarized in table III. Pb mass balances between 73 and 108% were obtained. The final amount of soil was reduced with 13-26% compared to the initial amount. This general reduction is likely to reflect a partial dissolution of soil constituents. The final Pb-concentration in the soil-fines was between 798 and 23mg/kg with a clear reduction as remediation time increased, and with 97% removal in the two experiments of longest duration (calculated at the fraction of the Pb in the whole system after remediation, which was found elsewhere than the soil). In one experiment (K2) 33% of the Pb appeared in the soil-solution in chamber II, while in all other experiments the amount of Pb in dissolution in II was minor. The final pH of the soil solution was between 1 and 2 for all experiments except the one with the shortest duration, where pH had only decreased slightly from the initial value (7.5) to 6.9.

Pb removal as a function of time is illustrated in figure 3.1 (one point for each experiment). Also illustrated is the concentration build-up in the cathode section (catholyte, cathode and cation-exchange membrane), the anode section (anolyte, anode and anion-exchange membrane), as well as the Pb dissolved in the solution in the middle chamber (II). In all experiments >90% of the Pb in the cathode section was precipitated at the cathode itself.

TABLE III  
Experimental results

Exp. Name	Pb Mass balance [%]	Soil mass balance [%]	Final Pb [mg/kg]	% Pb Removed From soil	% Pb in Liquid II	Final pH
<b>K1</b>	108	87	798	5	0	6.9
<b>K2</b>	102	84	224	73	33	1.5
<b>K3</b>	103	82	110	87	1	1.5
<b>K4</b>	86	81	44	94	2	1.1
<b>K5</b>	73	74	23	97	6	1.0
<b>K6</b>	93	78	27	97	1	1.4

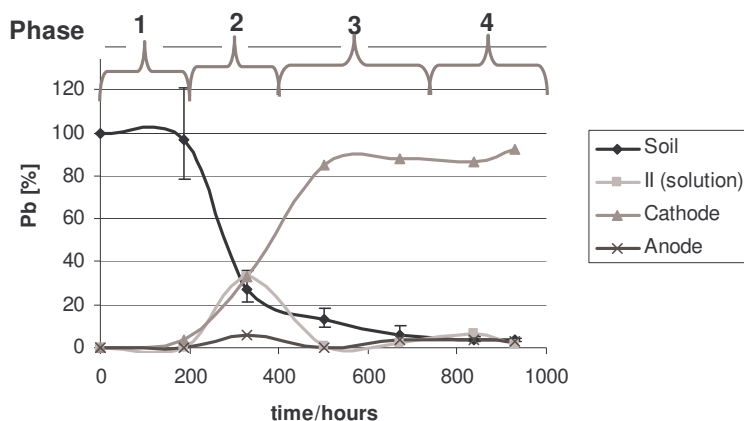


Figure 3.1: Removal of Pb from soil, dissolution in solution in soil-solution (II) and concentration in anode and cathode sections. Removal proceeds in four phases: (1) Lag-phase (2) High removal rate (3) Low removal rate (4) Removal stopped.

The highest removal rate was obtained between 188h and 330h. Here the average rate was 4.0 (mg/kg)/hour. In order to determine the maximum obtainable rate, more experiments in this interval would be necessary, and further optimization options should be investigated. This work however clearly illustrates how the removal undergoes four phases (1) a “lag-phase”, where removal is substantially absent, (2) a period with a high removal rate involving dissolution of Pb in the soil-solution, (3) a period with a low removal-rate, where the dissolved Pb is removed from solution, and (4) a period where no further Pb-removal is obtained as the treatment proceeds.

### 3.2 PH, CONDUCTIVITY AND VOLTAGE

The pH-development in the soil solution during remediation is illustrated in figure 3.2. pH was more or less constant during the first 200-240 hours, followed by a sharp decline to 1-2, where pH stabilized after 360-400 hours. This pH-decline is in consistence with previous observations (Jensen *et al.*, 2006b), and is believed to occur due to water splitting at the surface of the anion-exchange membrane induced by insufficient amounts of anions in the solution available for current transfer (Jensen *et al.*, 2006b). The sharp pH-decrease coincided with the maximum rate of Pb-removal, and confirms that acidification is the foundation of unenhanced EDR of HM-containing materials (Nystroem *et al.*, 2005). In addition, the attainment of the low pH plateau coincided with the change from high to low removal rate suggesting that the removal rate decreases due to an overflow of the suspension with  $H^+$ -ions, which compete successfully for the current transfer. The last phase (4), where no removal took place was not related to any pH-changes, but rather occurred because most of the anthropogenic Pb at that point had been removed.

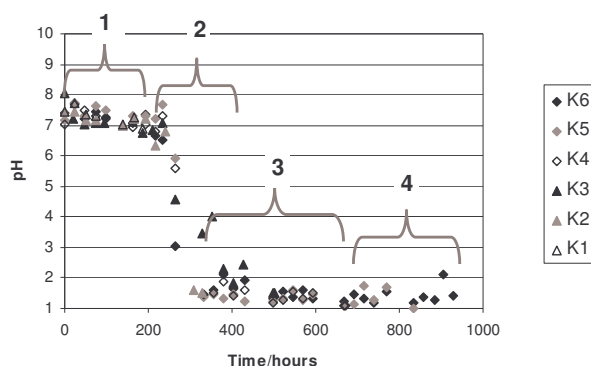


Figure 3.2: pH development in the soil-slurry during remediation

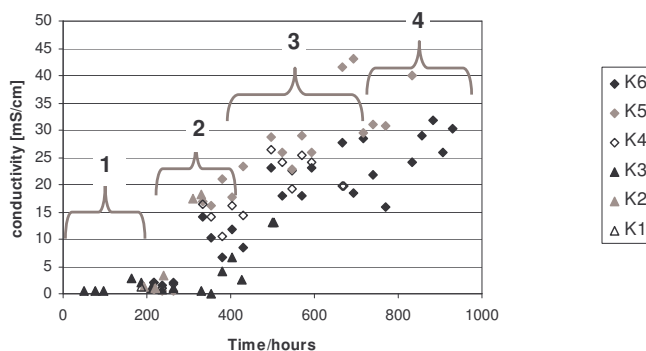


Figure 3.3: Conductivity of soil-slurry during remediation

Developments in the conductivity of the soil-slurry are illustrated in figure 3.3. During remediation, the conductivity increased as a prompt response to the pH-decrease (phase 2), confirming how the Pb-removal declined due to preferential transfer of hydrogen-ions in the acid environment. Although pH stabilized in phase (3), conductivity seemed to continue to increase. This could be due to dissolution of soil-constituents. The voltage between the working electrodes decreased (figure 3.4) as a response to the acidification and the resulting increased conductivity. In the period prior to acidification several incidents of high voltage occurred. These incidents coincided with observations of high pH in the catholyte caused by  $\text{OH}^-$  production by the electrode-process. As soon as pH in the catholyte was regulated down by addition of nitric acid, voltage decreased again.

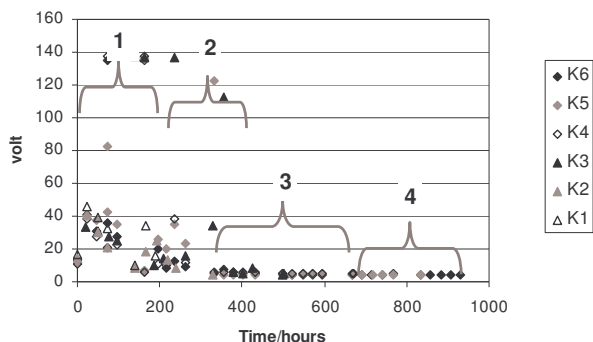


Figure 3.4: Voltage between working electrodes during remediation

These incidents of high voltage are likely to have occurred due to precipitation of hydroxides within the cation-exchange-membrane, and suggest that faster removal and/or lower energy consumption could have been obtained through pH-static control of the catholyte. By the end of the acidification, the simultaneous conductivity increase and voltage-decrease suggest that a higher current might have been forced on the system during phase (3) in order to obtain a higher removal rate. During phase (1) however, voltage in general was between 20 and 40 which is above the previously (Jensen *et al.*, 2006b) recommended value (max. 20), suggesting that some water splitting at the cation-exchange membrane may have taken place and prolonged this phase unnecessarily. A lower current density might have accelerated the process during this phase.

### 3.3 EXTRACTION OF SOIL CATIONS

Figures 3.5-3.7 illustrates the influence of the electrodialytic treatment on soil content of common soil cations. In general it should be noted that, due to the extraction procedure, only the fraction of the elements which is not bound within the silica matrix is included in the discussion, as we also expect that only this fraction is affected by the electrodialytic treatment. In figure 3.5 the extraction of the cations most affected by the electrodialytic treatment (Mn, Ca and Mg) are illustrated in relation to the extraction of Pb.

Ca was completely extracted during phase (1), and prior to Pb. The early extraction of Ca is in accordance with results of (Hansen *et al.*, 1997; Suer *et al.*, 2003), and shows that a prevailing process during phase (1) is elimination of the soils buffer-capacity. The dissolution of primarily calcium carbonates followed by removal of Ca explains the observed soil-mass reduction (table III) well: a) the reduction in soil-mass in the experiment with the shortest duration and with incomplete Ca-removal was 13%, which is below the content of calcium carbonate (17.3%); b) the average reduction in the remainder experiments was 20.2% which is just above the amount of calcium carbonate in the soil, confirming that calcium carbonate is the primary soil-constituent undergoing dissolution; c) the total amount of extracted Ca is equivalent to a calcium carbonate content of 15.7%, suggesting that other minor carbonates are dissolved as well. Of those, the most common is dolomite  $\text{CaMg}(\text{CO}_3)_2$ , dissolution of which was confirmed by a slight decrease in Mg-content was observed during phase (1), where in contrast the content of Pb and Mn increased.

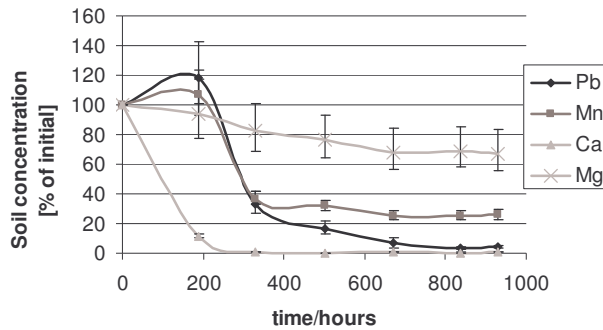


Figure 3.5: Kinetics of dissolution of Pb, Mn, Ca and Mg from the soil.

During the following phases (2 and 3) slow dissolution of Mg continued while it ceased completely in phase (4) after the Mg concentration had been reduced with 25% (50% Mg-extraction). The fact that Mg-dissolution was not related to the pH-shift is in contrast to the findings of (Suer *et al.*, 2003). This suggests that a main fraction of the Mg was bound in soil-minerals, which were less affected by the EDR process.

The increased concentrations of Pb and Mn observed after 188 hours of EDR appeared due to the described preferential extraction of carbonates and the resulting reduced soil-volume, which caused unaffected elements to concentrate in the soil-phase. Mn-extraction further resembled Pb-extraction in that it occurred at a high rate during phase (2), at a low rate during phase (3) and ceased in phase (4). The relation between the pH-shift and Mn-release is in consistence with the results of (Suer *et al.*, 2003). The Mn-concentration was however only reduced with 75% (80% Mn-extraction) before extraction ceased, suggesting that for as for Mg, a fraction was bound in stable soil-minerals, which were less affected by the EDR process.

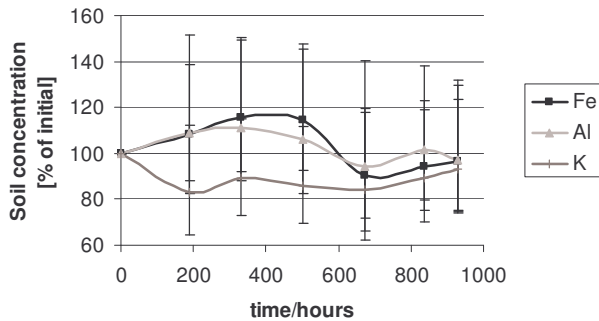


Figure 3.6: Kinetics of dissolution of Al, Fe and K.

Extraction of Fe, Al and K is illustrated in figure 3.6 (note the different y-scale). The large variation on analytical results primarily reflects a large variation on the analysis of initial content. Cautious interpretations may however still be made. It seems that the concentration of Fe and Al increased throughout phases (1), (2) and part of phase (3). This shows how Fe- and Al-minerals were relatively unaffected by the EDR process during those phases. At the low pH-level prevailing in phases (3) and (4), they

however began to dissolve, and probably acted as buffers at this low pH-level. Dissolution of particularly Al is undesirable during EDR due to its toxicity. Therefore, according to these results, it is recommended to terminate remediation as soon as the Pb-extraction ceases. K was dissolved during phase (1) to a larger extent than Fe and Al, but dissolution ceased after phase (2). Because of the reduced soil mass, the concentration of all three elements had only decreased slightly compared to the initial concentration by the end of the experimental remediation. This however does not mean that the mineral composition is unaffected, and the final amount of extracted Fe, Al and K constituted 25-30%.

Finally in figure 3.7 the behavior of Na during EDR is illustrated. This graph shows how the content of Na increased continuously during phases (2), (3) and (4). Sodium nitrate (0.01M) constituted the initial electrolyte solutions, and clear evidence of intrusion of Na into the soil solution is given here. This intrusion appeared despite the separation of anolyte and suspension by an anion-exchange membrane and could be due to transfer of Na as co-ions over this membrane and/or diffusion against the current-direction due to the concentration-difference over the cation-exchange membrane, which separated the slurry from the catholyte. The final amount of Na adsorbed to the soil exceeds the initial amount of Na in electrolytes, proving that transfer of Na from the anolyte, which was adjusted to 1-2 regularly by addition NaOH takes place. In addition the soil may have been enriched in  $\text{NO}_3^-$  due to regulation of pH in the catholyte with  $\text{HNO}_3$ . This observation illustrates how the ion-exchange membranes are not to be conceived as perfect barriers, and demonstrates how the electrolytes should be carefully chosen in order to fulfill any requirements of the soil-fine condition prior to subsequent application.

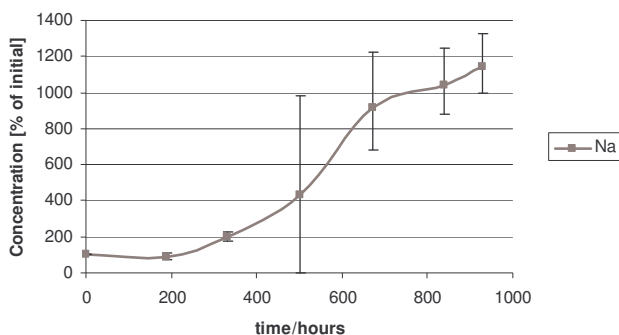


Figure 3.7: Intrusion of Na into soil.

The overall order of removal-rate found was:  $\text{Ca} > \text{Pb} > \text{Mn} > \text{Mg} > \text{K} > (\text{Al and Fe})$ . This is in consistence with the order of extraction observed for the clays saponite and nontronite (both smectites), while for attapulgite (palygorskite, not a smectite), Mg was extracted at a higher rate than Ca (Caldwell and Marshall, 1942).

### 3.4 CURRENT EFFICIENCY

The current efficiency understood as the fraction of the current transferred by a specific element is given in table IV for all investigated elements. The calculation was based on the assumption that the individual elements were transferred with the following valences:  $\text{Pb}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ . In experiment K1

almost all the current was accounted for by calcium transport, which again shows how dissolution of carbonates and removal of Ca was the prevailing process during the first stage of EDR. As the remediation proceeded, less and less current was transferred by the investigated soil cations due to the preferential transfer of the produced hydrogen ions. Although concentrations of Ca, Pb, and Mn were reduced significantly, only Ca-transfer constituted a significant fraction of the current transfer due to the relatively small initial concentrations of Pb and Mn. Conversely, Fe and Al ions, which were not particularly reduced in concentration, constitute a substantial fraction of the current transfer due to their initially high concentrations.

Table IV  
Current efficiency (%)

Element Time	Pb	Al	Ca	Fe	K	Mg	Mn	Na	Total
188	0.10	25	900	23	9	20	1	1	980
330	0.59	17	567	7	5	19	5	-2	618
503	0.67	22	373	9	4	15	4	-5	422
671	0.45	29	279	30	3	14	3	-10	348
838	0.30	24	224	27	2	12	2	-8	283
930	0.36	22	202	19	2	11	2	-9	248

#### 4 Conclusions

Several potential applications of soil-fines after electrodialytic remediation in suspension exist depending on the characteristics of the remediated product. The process of electrodialytic remediation of Pb-contaminated soil fines can be divided into four phases: In phase 1) the soil buffer capacity is being eliminated by the production of hydrogen-ions at the surface of the anion-exchange membrane where water-splitting takes place. During this phase soil-carbonates are extracted, resulting in complete extraction of Ca and partial extraction of Mg and K. The carbonate extraction results in a corresponding loss of soil mass, and imply a concentration of elements unaffected by EDR during this phase, including Pb. In this phase the major current transfer can be accounted for by Ca. During phase 2) a sharp pH-decrease of the soil-slurry takes place along with increased conductivity. During this phase Pb-removal occurs at a high rate and a significant fraction of the Pb is dissolved in the soil-solution. Along with Pb, also Mn is extracted. Mg is continuously being extracted during this phase, however at a much lower rate than that of Pb and Mn. In phase 3) pH stabilizes at 1-2, while the conductivity continues to increase and the voltage between working electrodes decreases. During this phase Pb is extracted at a lower rate simultaneous with low-rate extraction of Mn and Mg. Furthermore Fe and Al-oxides start to act as buffers, resulting in some extraction of these elements as well. In phase 4) extraction of Pb and most soil-cations has ceased, and the primary transport is that of hydrogen-ions complemented by a continuing slow dissolution of Fe and Al-oxides. It is recommended to terminate remediation as soon as Pb-extraction ceases to limit the dissolution of Fe and Al-minerals. Due to intrusion from the electrolytes, the soil content of Na is continuously increasing during remediation, and a careful choice of electrolytes in order to meet requirements by the succeeding application of soil-fines is necessary. From this soil 97% of the Pb could be extracted, reducing the final Pb-concentration to 25mg/kg. The overall order of removal-rate found was: Ca > Pb > Mn > Mg > K > (Al and Fe). In order to establish a complete evaluation of any



potential applications of the soil-fines after remediation, this investigation should be complemented by investigations of the fate of phosphate, nitrate, chloride and organic matter as well as the mineralogical condition of the fines after remediation.

### Acknowledgements

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## 9. Suspended Electrodialytic Remediation of Soil Fines Contaminated with As, Cd, Cr, Cu, Hg, Ni, Pb and Zn

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### Abstract

This work investigated the feasibility of treating residual sludge after soil-wash by electrodialytic remediation (EDR) in suspension. Ten experiments with five industrially heavy metal contaminated soils (As: 3030-9260 mg/kg, Cd: 4-43 mg/kg, Cr: 196-2310 mg/kg, Cu: 163-6820 mg/kg, Ni: 55-75 mg/kg, Pb 281-418 mg/kg, Hg: 173 mg/kg, and Zn: 496-7210 mg/kg) demonstrated the repeatability of the method. It was shown that the method is feasible for removal of As, Cd, Cu, Ni, Pb and Zn. Among these, the last five elements were transported to the catholyte, where Cu and Pb precipitated at the cathode, while Cd, Ni and Zn remained in solution. Arsenic was transferred almost exclusively to the anolyte, where it remained in solution. Our results demonstrated that As(III) is oxidized to As(V) during remediation, and that the prevalence of charged As(V)-species facilitates a successful mobilization and removal of arsenic under the influence of direct current. Chromium was amenable to remediation, although removal from most of the soils was slow compared to the other elements. Chromium was primarily transferred to the catholyte, where it remained in solution, leading to the conclusion that Cr(III) was the dominating species in all investigated soils, and that no oxidation to Cr(VI) took place during remediation. In general preconditioning of Cr-contaminated soil by addition of an oxidizing or a complexing agent is recommended. Mercury was unsusceptible to EDR in suspension with 100% remaining in the soil after termination of the experiments. Some changes in the Hg-speciation towards mobilization were, however, established. As for Cr-contaminated soil preconditioning of Hg-contaminated soil with oxidizing or complexing agents is recommended. The maximum removals obtained after 10 days of treatment were: 79% As, 92% Cd, 55% Cr, 96% Cu, 0% Hg, 52% Ni, 53% Pb and 88% Zn.

**Keywords:** Electrodialysis; heavy metals; soil remediation; soil washing.

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## 1 Introduction

The residual sludge remaining after soil wash of heavy metal contaminated soils is often contaminated with heavy metals at higher levels than the original soil. An efficient, practical and environmentally responsible treatment method for the sludge is a main issue in full scale application of soil washing. It was recently shown that electrodynamic remediation (EDR) of soil fines in suspension easily dissolved and removed Pb from industrially contaminated soil fines in the acid environment produced by the process (Jensen *et al.*, 2006a). Several works on electrokinetic remediation (EKR) and EDR of heavy metal contaminated soil showed that among toxic elements, Pb is one of the most recalcitrant towards remediation (Mohamed, 1996; Hansen *et al.*, 1997; Ottosen *et al.*, 2001). This gives reason to believe that EDR of soil fines in suspension may succeed for other contaminating and toxic elements like As, Cd, Cu, Cr, Hg, Ni and Zn as well. Among those, the behavior of Cd, Cu, Ni and Zn is expected to resemble that of Pb during remediation, because free, hydrated cations dominate their aqueous chemistry at the low pH values prevailing during remediation. For As, Cr and Hg, however, the redox-chemistry may complicate the remediation process.

This study investigates the feasibility of suspended EDR of soil fines contaminated by As, Cd, Cu, Cr, Hg, Ni and Zn. The validity of the hypothesis stating that elements are removed in an order corresponding to their hydrolysis constants during EKR (Suer *et al.*, 2003) is tested for EDR in suspension. Finally an insight into the influence of soil-type and contamination-origin on remediation feasibility is given by comparison of removals of As, Cd, Cu, Cr, Ni, Pb, and Zn from several different soils.

## 2 Materials and Methods

### 2.1 SOILS

Five soils, all industrially contaminated by several heavy metals, were chosen for the investigation. Soils 1-4 were collected in Denmark and soil 5 in Sweden. Previous EDR results and speciation characteristics concerning Pb for soil 2 are found in (Jensen *et al.*, 2006c; Jensen *et al.*, 2006d) (referred to as soil 8). Previous EDR results concerning removal of Cu, Cr and As from soil 4 are found in (Hansen *et al.*, 1997; Ottosen *et al.*, 2000). Previous EKR results concerning removal of Hg, Pb, Cu and Zn from soil 5 are found in (Suer and Allard, 2003; Suer *et al.*, 2003). The soil fines were obtained by wet sieving (soils 3 and 4) or dry sieving (soils 1, 2 and 5) through a 0.063mm sieve. The *Carbonate content* was determined volumetrically by the Scheibler-method when reacting 3g of soil with 20mL of 10% HCl. The carbonate was calculated assuming that all carbonate is calcium-carbonate. *Organic matter* was determined by loss of ignition in a heating furnace at 550°C for 1 hour.

### 2.2 ELEMENT ANALYSIS

Digestion of the soil-fines and analysis of the selected elements was made prior to and after experimental remediation. After remediation all process liquids were similarly analyzed for the relevant elements. The digestion procedure and the analysis equipment varied according to the specific elements: For analysis of *Cd*, *Cr*, *Cu*, *Ni*, *Pb* and *Zn* samples were digested according to the Danish standard method DS259 (Dansk Standardiseringsråd, 1991), which includes acid digestion of 1g soil with 20.00mL of 7M HNO<sub>3</sub> in autoclave at 200kPa and 120°C for 30 min. followed by filtration through a 0.45µm filter. The element-concentrations in the liquid phase were

analyzed by flame-AAS. Samples with Pb and Cd concentrations below the detection limit of the flame-AAS for those elements were measured by GF-AAS. *Arsenic* was measured by ICP-MS after treatment of samples according to DS259 as above. For *Mercury* analysis 0.2g soil-sample (air-dried at room temperature) was digested with 10mL conc.  $\text{HNO}_3$  in microwave oven (160psi for 5min, 180psi for 5 min, 190psi 20min). The digested samples were conserved by addition of 10mL 5%<sub>w/v</sub>  $\text{KMnO}_4$  and 1mL conc.  $\text{H}_2\text{SO}_4$ . 1mL conc.  $\text{HCl}$  was added prior to dissolution to 100mL. Aqueous samples were conserved by addition of 2mL 5%<sub>w/v</sub>  $\text{KMnO}_4$  + 0.2mL conc.  $\text{H}_2\text{SO}_4$  to 17.8mL sample. Excess  $\text{KMnO}_4$  was reduced by addition of hydroxylammoniumchloride immediately prior to analysis by CV-AAS.

TABLE I  
Experimental soils, and metal concentrations measured prior to remediation.

Soil	Contamination origin	$\text{CaCO}_3$ [%]	Org. Mat. [%]	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
				[mg/kg]							
1	Unknown	13.5	7.3	178	43	80	504	-*	55	383	7210
2	Metal Foundry	14.4	7.9	24	6	97	1520	-*	75	418	1270
3	Wood preservation	0.0	2.9	9260	0.5	2310	6820	-*	<20	5	241
4	Wood preservation	0.0	5.0	3030	0.5	1680	2780	-*	<20	5	288
5	Chlor-alkali processing	0.5	4.8	<0.1	3.7	196	163	43	57	281	496
Limiting value in Sweden****				15	0.4	120**	100	1	35	80	350
Limiting value in Denmark****				20	0.5	500***	500	1	30	40	500

-\*Not analyzed, \*\*Valid for Cr(III), Cr(VI) maximum 5mg/kg, \*\*\*Valid for Cr(III), Cr(VI) maximum 20mg/kg, \*\*\*\* for soils to be applied for sensitive land use.

## 2.3 REMEDIATION EXPERIMENTS

Electrodialysis experiments were made in cylindrical Plexiglas®-cells with three compartments. Compartment II, which contained the soil-slurry was 10 cm long and 8 cm in inner diameter. The slurry was kept in suspension by constant stirring with plastic-flaps attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). The anolyte was separated from the soil slurry by an anion-exchange membrane, and the catholyte was separated from the soil slurry by a cation-exchange membrane. Figure 2.1 shows a schematic drawing of the setup. Both membranes were obtained from Ionics (types AR204SZRA and CR67 HVY HMR427). Electrolytes were circulated by mechanical pumps (Totton Pumps Class E BS5000 Pt 11) between electrolyte compartments and glass reservoirs. Platinum-coated electrodes from Permascand were used as working electrodes, and the power supply was a Hewlett Packard E3612A. The anolyte and catholyte initially consisted of 300 and 500mL of 0.01 M  $\text{NaNO}_3$  adjusted to pH 2 with  $\text{HNO}_3$  respectively. The conductivity in compartment II, pH in all compartments, and voltage between working electrodes were monitored approximately once every 24 hours. pH in the electrolytes was kept between 1 and 2 by manual addition of  $\text{HNO}_3/\text{NaOH}$ . After termination of the experiments, the soil solution was separated from the soil fines by dripping off through filter paper overnight. Volumes of electrolytes were recorded and samples stored, electrodes and membranes were rinsed overnight in 5M and 1M

HNO<sub>3</sub> respectively, tubes and pumps were rinsed by pumping through 1M HNO<sub>3</sub> overnight. All liquid volumes were recorded and samples stored for subsequent element analysis according to the procedures described in section 2.2. All experiments ran for 240 hours with a current density of 20mA (0.4mA/cm<sup>2</sup>). The liquid to solid ratio (L/S) was 10 (40g soil and 400mL distilled water). Two identical experiments were made with each soil to document repeatability.

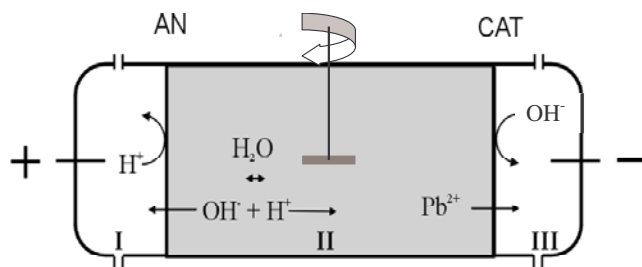


Figure 2.1: Schematic view of a cell used for experimental EDR remediation of soil-fines in suspension. AN = anion-exchange membrane, CAT = cation-exchange membrane.

### 3 Results and Discussion

#### 3.1 MASS BALANCES

Mass balances, understood as the post-treatment mass of contaminant and soil encountered in the whole system (compartment I, II, III, electrodes and membranes) in figure 2.1) in percent of the initial mass of contaminant or soil, are given for each investigated element and soil in table II.

TABLE II  
Mass balances for each element and experiment (%).

Soil	Exp.	Soil	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1	A	76		115	129	103		92	105	117
	B	74		112	118	96		92	104	106
2	A	78		72	114	101		98	100	106
	B	77		71	110	101		93	100	107
3	A	90	94		93	97				
	B	86	98		84	102				
4	A	89	101		82	102				
	B	88	94		83	95				
5	A	83		129	101	111	372	127	107	123
	B	83		136	100	94	300	111	103	120

The soil mass balances varied between the soils, while the two identical experiments (A and B) showed quite similar soil mass balances. The average amount of soil lost during remediation was 25% for soil 1, 22% for soil 2, 17% for soil 5, 12% for soil 3 and 11% for soil 4. The loss of soil mass during EDR in suspension was earlier suggested to occur primarily due to dissolution of carbonates (Jensen *et al.*, 2006b). The present work supports this hypothesis by showing a larger mass reduction

for soils with higher carbonate contents; but the mass reduction observed for the carbonate deficient soils (3 and 4) illustrates how other soil components in addition are dissolving during remediation.

Apart from the mass balances for mercury in soil 5, the mass balances for the contaminants varied between 71% and 136% with an average of 105%. Because identical experiments (A and B) in most cases showed similar mass balances for the same elements, it is likely that deviations from the ideal 100% is primarily due to inexact measurement of the initial contaminant concentrations in the soil fines. In the following sections, results are therefore given with respect to the final amount of contaminant encountered. For mercury in soil 5, the mass balances were as high as 372 and 300% (experiments A and B respectively). Because the Hg-concentration measured in the soil-fines after remediation was in better agreement with the concentrations measured in the same soil in earlier works ( $\approx 100\text{mg/kg}$ ) (Suer and Allard, 2003; Suer and Lifvergren, 2003) than the initial concentration measured in this work, the final concentrations are in this work regarded to be representative, while the much too low initial concentration is rejected. Interpretations are accordingly made with respect to the final concentration, although with care due to the unsatisfactory mass balances.

## 3.2 REMOVAL

After experimental remediation and analysis of samples, the distribution of the elements in the electrodialytic cell (figure 2.1) was calculated. The amount of the individual elements remaining in the soil (compartment II), dissolved in the suspension solution (compartment II), and transported to the cathode end (compartment III) and the anode end (compartment I) was calculated. The amount transported to the cathode end was calculated as the sum of the element mass found in the cation-exchange membrane, in the catholyte and precipitated at the cathode. Correspondingly, the amount transported to the anode end was calculated as the sum of the element mass found in the anion-exchange membrane, in the anolyte and precipitated at the anode. The results are given in table III, where standard deviations between the identical experiments (A and B) with each soil are also given. The low standard deviations (0.0-5.4%) demonstrated that the EDR-experiments were repeatable.

### 3.2.1 Removal Order

The removal-rates of various toxic metals by EKR/EDR has been observed decrease according to the following orders:  $\text{Ni} > \text{Cd} > \text{Cr} > \text{Zn} > \text{Cu} > \text{Pb}$  (Mohamed, 1996),  $\text{Zn} > \text{Cu} \approx \text{Pb}$  and  $\text{Cu} > \text{Cr}$  (Hansen *et al.*, 1997),  $\text{Cd} \approx \text{Zn} > \text{Cu} \approx \text{Pb}$  (Hansen *et al.*, 2000),  $\text{Zn} > \text{Cu} > \text{Pb}$  (Ottosen *et al.*, 2001),  $\text{Zn} > \text{Cu} > \text{Pb} > \text{Cr}$  (Alshawabkeh *et al.*, 1997) and  $\text{Ni} \approx \text{Zn} > \text{Cu} > \text{Cr}$  (Suer *et al.*, 2003). Most of these observations supported the hypothesis that removal in general follows the order of the first hydrolysis constants for the elements (Suer *et al.*, 2003), and is consistent with the observation that the selectivity of mineral soils for adsorption of heavy metals correspond to the order of increasing  $\text{pK}'\text{s}$  of the first hydrolysis product of the various metals (Elliott *et al.*, 1986).

If this hypothesis was valid for EDR in suspension as well, the removal order among the studied elements would be expected to be  $\text{Cd} > \text{Ni} > \text{Zn} > \text{Cu} > \text{Pb} > \text{Cr(III)} > \text{Hg(II)}$ . Arsenic, which is a metalloid, does not behave as a cationic metal regarding its chemistry in soil; neither does  $\text{Cr(VI)}$  or  $\text{Hg}^\circ$ , why they do not appear in the removal order. The observed removal order, however, was  $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb} >$

Ni >> Cr for soil 1. For soil 2, the order observed was: Cd > Zn > Cu > Ni  $\approx$  Pb >> Cr. In soils 3 and 4 the removal order was: Cu > As > Cr. Finally in soil 5 the removal order was: Zn > Cd > Cu > Ni > Pb > Cr > Hg. For most soils coherence with the expected removal order exists apart from Ni, which consistently seemed to be less mobile than suggested by comparison of the first hydrolysis constants of the elements. This is in contrast to results of stationary EKR of soil (Mohamed, 1996; Suer *et al.*, 2003), of which the latter work found Ni to be more amenable to remediation than Zn and Cu from the same soil referred to as soil 5 in this work. The inconsistency suggests that either the remediation processes in the stationary and suspended setup are non-identical, or the processes change as the remediation proceeds (remediation has proceeded substantially further in this work than in the previous work). Furthermore the removal order in soil 5 deviates in that Zn was more amenable to remediation than Cd. This is likely to be due to the specific heavy metal speciation prevailing in soil 5 as discussed below.

TABLE III

Distribution of contaminating elements in the electrodialytic cell after 10 days of experimental remediation (%  $\pm$  std. dev.). AN(I) includes metal at the anode, in the anion-exchange membrane and in the anolyte. CAT(III) includes metal at the cathode, in the cation-exchange membrane and in the catholyte.

Soil	Compartment	As	Cd	Cu	Cr	Hg	Ni	Pb	Zn
1	AN (I)		0 $\pm$ 0.0	0 $\pm$ 0.1	0 $\pm$ 0.2		0 $\pm$ 0.0	0 $\pm$ 0.0	1 $\pm$ 0.9
	CAT (III)		92 $\pm$ 2.1	66 $\pm$ 5.3	10 $\pm$ 0.0		38 $\pm$ 0.9	53 $\pm$ 1.4	88 $\pm$ 1.6
	Solution(II)		3 $\pm$ 1.5	9 $\pm$ 4.0	1 $\pm$ 0.2		4 $\pm$ 0.8	7 $\pm$ 1.2	6 $\pm$ 2.5
	Soil (II)		5 $\pm$ 0.6	24 $\pm$ 1.2	89 $\pm$ 0.4		58 $\pm$ 0.0	40 $\pm$ 0.2	5 $\pm$ 0.0
2	AN (I)		0 $\pm$ 0.0	1 $\pm$ 0.1	0 $\pm$ 0.0		0 $\pm$ 0.0	0 $\pm$ 0.1	2 $\pm$ 0.5
	CAT (III)		89 $\pm$ 0.7	73 $\pm$ 1.7	7 $\pm$ 0.6		52 $\pm$ 1.5	49 $\pm$ 1.4	82 $\pm$ 1.1
	Solution (II)		0 $\pm$ 0.0	11 $\pm$ 1.5	2 $\pm$ 0.1		6 $\pm$ 0.9	8 $\pm$ 1.1	8 $\pm$ 1.6
	Soil (II)		11 $\pm$ 0.7	16 $\pm$ 0.1	91 $\pm$ 0.5		42 $\pm$ 0.6	43 $\pm$ 0.2	9 $\pm$ 0.0
3	AN (I)	75 $\pm$ 0.7		0 $\pm$ 0.2	2 $\pm$ 0.5				
	CAT (III)	4 $\pm$ 0.2		95 $\pm$ 0.4	53 $\pm$ 4.9				
	Solution (II)	0 $\pm$ 0.0		0 $\pm$ 0.0	0 $\pm$ 0.0				
	Soil (II)	21 $\pm$ 0.5		5 $\pm$ 0.1	45 $\pm$ 5.4				
4	AN (I)	36 $\pm$ 4.0		0 $\pm$ 0.1	0 $\pm$ 0.0				
	CAT (III)	3 $\pm$ 0.9		96 $\pm$ 0.2	18 $\pm$ 1.5				
	Solution (II)	4 $\pm$ 3.7		0 $\pm$ 0.1	1 $\pm$ 0.3				
	Soil (II)	57 $\pm$ 1.2		4 $\pm$ 0.1	81 $\pm$ 1.3				
5	AN (I)		18 $\pm$ 0.5	3 $\pm$ 0.1	2 $\pm$ 0.4	0 $\pm$ 0.0	6 $\pm$ 2.0	4 $\pm$ 0.3	6 $\pm$ 4.0
	CAT (III)		55 $\pm$ 3.9	58 $\pm$ 3.7	15 $\pm$ 0.6	0 $\pm$ 0.0	36 $\pm$ 2.1	28 $\pm$ 3.1	65 $\pm$ 4.8
	Solution (II)		14 $\pm$ 0.4	8 $\pm$ 0.5	6 $\pm$ 0.1	0 $\pm$ 0.0	8 $\pm$ 0.5	4 $\pm$ 0.4	8 $\pm$ 0.2
	Soil (II)		13 $\pm$ 3.9	30 $\pm$ 3.1	77 $\pm$ 0.4	100 $\pm$ 0.0	50 $\pm$ 0.4	64 $\pm$ 2.4	20 $\pm$ 1.0

### 3.2.2 Speciation

Most elements were transferred primarily to the cathode end, where Cu and Pb precipitated at the cathode, while Cd, Cr, Ni and Zn were primarily or solely (for Ni) dissolved in the catholyte, showing how cationic species dominated the chemistry of these elements during remediation. For Cd, Cu, Ni, Pb and Zn this is in accordance with the expectation, because free, hydrated cations dominate the chemistry of those elements under the acidic conditions prevailing during remediation.

The only element, which was transported primarily towards the anode, was arsenic, suggesting that anionic arsenic-species dominated under the prevailing acidic conditions during remediation. In general arsenic may be present as As(III) or As(V) in soil as well as in solution. The speciation of arsenic as a function of  $p\epsilon$  and pH is illustrated in figure 3.1. It appears from the figure that anionic species of As(V) prevail over a much wider range of pH and  $p\epsilon$  conditions as compared to As(III), which is anionic only under alkaline conditions. Thus our results indicate that As(V) was the dominating specie in both investigated soils. In contrast, earlier results with stationary EKR/EDR of arsenic contaminated soils, showed that arsenic was immobile under acidic and neutral conditions (Ottosen *et al.*, 2000; Maini *et al.*, 2000), while good removal was obtained by addition of either ammonia (Ottosen *et al.*, 2000) or hydroxide (Maini *et al.*, 2000) to maintain alkaline conditions ( $pH > 9$ ), suggesting that As(III) was the dominating species in those soils. One of the soils used in this study (soil 4), however, was identical to the one used by Ottosen *et al.* (2000), thus the transfer of arsenic to the anolyte in the present study indicates that oxidation of As(III) to As(V) took place during electrochemical treatment in suspension, while it did not during traditional EKR/EDR in stationary setup.

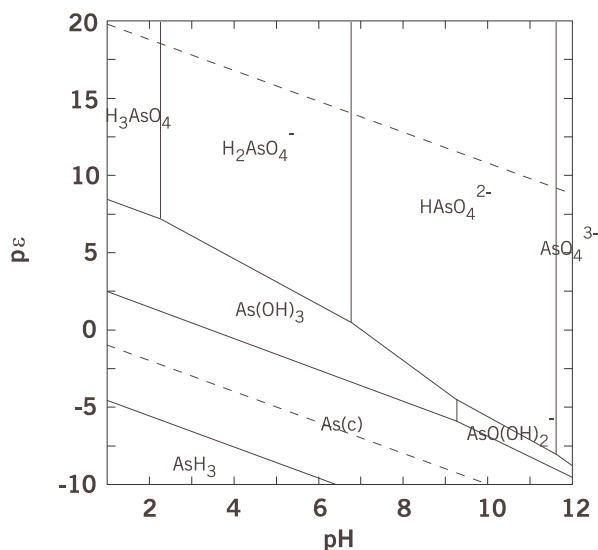


Figure 3.1:  $p\epsilon$ -pH stability diagram for arsenic ( $[As]_{tot} = 10 \text{ mM}$ ),  $T = 25^\circ\text{C}$ . The dotted lines indicate the stability field of water i.e., where  $P_{O_2}$  (upper line)  $P_{H_2}$  (lower line) reaches 1 bar (Puigdomenech, 2002).

In contrast to stationary EKR/EDR, oxygen and carbon dioxide concentrations in suspended EDR can, indeed, be assumed to be in equilibrium with the atmosphere, which should allow for oxidation of As(III) to As(V) during remediation. One important consideration, however, was the kinetics of the oxidation, since the rates of change do not always appear to be very rapid, why the proportion of various arsenic species present may not always correspond to the expected distribution (O'Neill, 1995). The results of this study demonstrated that the kinetics is fast enough to allow for oxidation of As(III) to As(V) under the acidic and oxidizing conditions prevailing



during suspended EDR. Another consideration was the lower mobility of As(V) compared to As(III): In a previous investigation EKR of As(III)-contaminated soil was enhanced by addition of an oxidizing agent (NaClO) (Maini *et al.*, 2000). This enhancement was assumed to be a result of the arsenic-release induced by oxidation of soil components and/or ion-exchange between anionic arsenic species and  $\text{ClO}^-$  (Maini *et al.*, 2000). Oxidation of As(III) to As(V) was excluded as explanation due to the lower mobility of As(V). The lower mobility was, however, observed under natural conditions (O'Neill, 1995), and may not apply to EDR/EKR, where prevalence of charged species is of crucial importance to the remediation result. Indeed, mobilization and removal of As(V) from CCA-impregnated waste wood by EDR was demonstrated in several studies (Ribeiro *et al.*, 2000; Velizarova *et al.*, 2002; Pedersen *et al.*, 2005). The observed transfer of arsenic to the anolyte in the present study proves that although As(III) is considered more mobile than As(V) under natural conditions, oxidation to As(V) facilitates a successful mobilization and removal of As(V) under the influence of direct current.

In contrast to the encouraging removal of arsenic, mobilization of chromium was low in most soils, and transport occurred almost exclusively to the catholyte, which according to the stability diagram (figure 3.2) reveal that Cr(III) was the dominating species. Removal of Cr(III) as a free, hydrated cation was expected to be more recalcitrant and require lower pH than removal of Pb. In comparison the mobility of Cr(VI) is considerably higher, and anionic species of Cr(VI), prevail in the full pH interval (fig. 3.2).

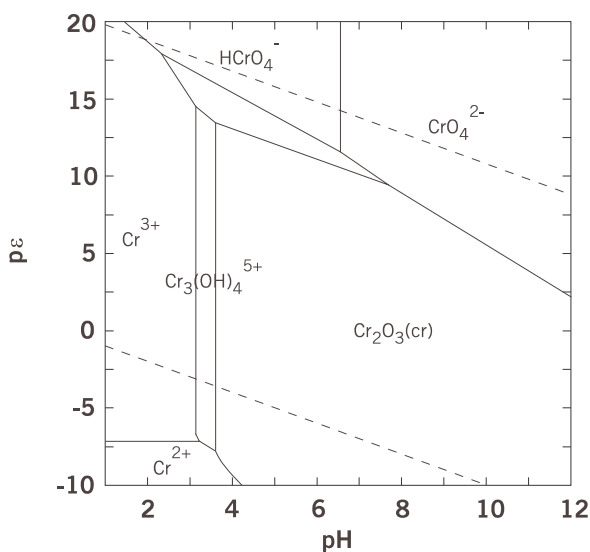


Figure 3.2: *pc*-pH stability diagram for chromium ( $[\text{Cr}]_{\text{tot}} = 10 \text{ mM}$ ),  $T = 25^\circ$  (Puigdomenech, 2002).

Previous investigations of the influence of Cr-speciation on stationary EKR showed that removal of Cr(III) occurred only under highly acidic conditions, while removal of Cr(VI) was observed to increase at neutral/alkaline conditions, although Cr(VI) was observed to be faster remediated than both Cd and Ni even under acidic conditions (Reddy and Chinthamreddy, 2003). Oxidation of Cr(III) to Cr(VI)

corresponding to the oxidation of As(III) to As(V) during remediation therefore could have been expected to improve remediation accordingly. As seen by the figures (3.1 and 3.2) oxidation of Cr(III), however, require a considerably higher  $p_e$  than oxidation of As(III), thus equilibrium with the atmosphere may not have been sufficient for oxidation to occur. Reduction of Cr(VI) to Cr(III) during stationary EKR was documented (Reddy and Chinthamreddy, 2003). In general, however, Cr was recovered in the anolyte when soils were spiked with Cr(VI) (Reddy *et al.*, 1997; Reddy and Chinthamreddy, 2003; Sawada *et al.*, 2003; Sanjay *et al.*, 2003), and in the catholyte when soils were spiked with Cr(III) (Li *et al.*, 1997a; Li *et al.*, 1997b; Weng and Yuan, 2001), suggesting that kinetics is another limiting factor. After stationary EKR of a contaminated soil from a military site, Cr was recovered from both electrolytes (Gent *et al.*, 2004), while chromium was almost exclusively recovered in the catholyte after stationary EDR of soil 4 used in this work (Hansen *et al.*, 1997), supporting the dominance of Cr(III) in this soil. Amendment with citric acid increased removal from the military site (Gent *et al.*, 2004), while ammonium-citrate improved remediation of the wood impregnation soil (Ottosen and Villumsen, 2001).

Although removal of chromium from most of the present soils was low, the possibility of mobilizing and removing Cr(III) by EDR in suspension was established after removal of 53% of the chromium from the severely contaminated soil 3. The high removal from this particular soil may be due to specific soil-characteristics and chrome speciation. It was shown previously that remediation of Pb-contaminated soil is more efficient from severely contaminated soils, while impeded by carbonate and organic matter (Jensen *et al.*, 2006c). The fact that this soil is carbonate deficient and low in organic matter suggests that removal of Cr(III) behaves similarly. In order to obtain a more efficient remediation of chromium-contaminated soils in general, the present results lead us to suggest that the effect of soil-conditioning with oxidizing/complexing agents should be tested.

As illustrated in figure 3.3, charged mercury species prevail only at very low pH and rather high  $p_e$ , complicating remediation of Hg-contaminated soil. Nevertheless, electrochemical oxidation of elemental mercury during stationary EDR of a sand containing 84% elemental Hg was documented in a previous investigation in favor of the process (Thoming *et al.*, 2000). In the present work neither oxidation nor removal of Hg was observed. In retaliation it was observed that digestion of mercury from the untreated soil failed, while mercury was successfully released from the post-treatment soil during digestion. This suggests that some changes in the speciation of Hg towards mobilization occurred during treatment. The fact that all elements seemed less mobile in the only mercury contaminated soil (soil 5) than in the remainder soils further suggests that this soil may be less amenable to remediation in general, and that final conclusions on the treatability of mercury-contaminated soils by EDR in suspension should be made only after investigation of additional mercury-contaminated soils. As for chromium, conditioning with oxidizing/complexing agents for improvement of mercury-remediation should in addition be investigated. Several previous studies of stationary EDR/EKR of mercury-contaminated soil suggest that such treatment could promote remediation considerably: In one study remediation of mercury-contaminated sand by stationary EDR showed migration towards the anode even at neutral pH (Hansen *et al.*, 1997), which, in view of the equilibrium-speciation (fig. 3.3), was surprising. The finding was explained by prevalence of the negatively charged chloride complex ( $\text{HgCl}_4^{2-}$ ) in the specific soil, which was contaminated by chlor-alkali processing (Hansen *et al.*, 1997). Another work documented a more efficient complexation of mercury by iodide than chloride (Reddy *et al.*, 2003b), which when

applied to EKR of mercury-spiked clay and soil, resulted formation of  $\text{HgI}_4^{2-}$  ions and good recovery of Hg in the anolyte (Suer and Allard, 2003; Reddy *et al.*, 2003a).

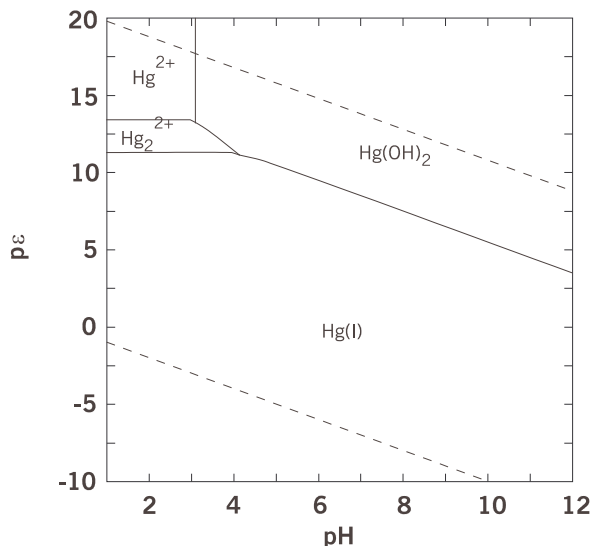


Figure 3.3: *pe-pH stability diagram mercury* ( $[\text{Hg}]_{\text{tot}} = 0.08 \text{ mM}$ ),  $T = 25^\circ\text{C}$  (Puigdomenech, 2002).

### 3.2.3 Influence of soil characteristics

The maximum removals obtained were 79% As (soil 3), 92% Cd (soil 1), 55% Cr (soil 3), 96% Cu (soil 4), 0% Hg (soil 5), 52% Ni (soil 2), 53% Pb (soil 1) and 88% Zn (soil 1). Among the soils removal from soils 1 and 2 was similar as expected based on the similar soil characteristics. Slightly better results were obtained for Pb, Cd, Cr and Zn from soil 1, and for Cu and Ni for soil 2. The removal order among the elements was identical for the two soils. In comparison removal of As and Cr from soil 3 was substantially higher than from soil 4 although these soils also resembled each other concerning the quantified soil characteristics (carbonate content and organic matter) as well as the origin of the contamination (CCA-impregnation of wood). One reason could be the higher contamination-level in soil 3, which may cause a higher fraction of the contaminants to be mobile, however more complicated speciation-issues could also be responsible as well. Cr and Cu were present as contaminants in all of the four soils, which allow for comparison of removal between the two dissimilar soil types: the organic and carbonaceous soils 1 and 2 and the less organic and non-carbonaceous soils 3 and 4. The conclusion is that removal is significantly more efficient from the latter group of soils,

The influence of specific contaminant speciation was however demonstrated by the low removal of all elements except Cr from soil 5 compared to the remainder soils. The lower removal was obtained even though this soil contained less carbonate and organic matter than soils 1 and 2. Apart from binding the contaminants stronger than the remainder soils, soil 5 was also unique in that a fraction of all contaminants (except Hg) was recovered in the anolyte. This is in consistence with the results obtained for Pb-removal from this soil by stationary EKR (Suer *et al.*, 2003), in which

the observed transfer to the anolyte was suggested to be a result of an extraordinary high sulfate content in the soil (up to 4%), which result in transfer of negatively charged lead sulfate  $\text{Pb}(\text{SO}_4)_2^{2-}$  towards the anode. In the previous work, transport towards the anode was not observed for the remainder of the studied elements: Ni, Zn and Cu (Suer *et al.*, 2003) as it was in this study. Presence of these elements in the anolyte is compromising the hypothesis of sulphates as complexing agents, because although transfer of Cd and Zn to the anode as  $\text{Cd}(\text{SO}_4)_2^{2-}$  and  $\text{Zn}(\text{SO}_4)_2^{2-}$  is a possibility, no negative complexes between sulfate and Cu and Ni are likely.

## 4 Conclusions and Future Recommendations

Experimental results of lab scale EDR of soil-fines in suspension are in general repeatable. The hypothesis that the removal order among elements is identical to the order of their first hydrolysis constants is verified for EDR in suspension with the exception of Ni, for which removal was lower than predicted. All elements except Hg were amenable to remediation with maximum removals obtained as follows: 79% for As, 92% for Cd, 55% for Cr, 96% for Cu, 52% for Ni, 53% for Pb and 88% for Zn. Oxidation of As (III) to As(V) was demonstrated with establishment of the feasibility of removing anionic As(V) species from the soil under the influence of direct current. Although Cr was removed efficiently from one soil, Cr removal from most soils was low. No oxidation of Cr(III) occurred during the remediation, and the effect of soil-conditioning with oxidizing/complexing agents should be tested. Mercury was the least amenable of the investigated elements to EDR in suspension, with no removal observed although some mobilization was documented. As for Cr, the effect of soil-conditioning with oxidizing/complexing agents should be tested, while general conclusions on the treatability of Hg-contaminated soils by EDR in suspension are recommended to be made only after investigation of additional Hg-contaminated soils. Among soil-types, contaminant removal was significantly more efficient from soils low in organic matter and carbonate, with the note that specific contaminant speciation such as prevalence of uncharged or insoluble compounds or complexing agents in a soil influences the remediation results.

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## 10. Conclusions and Recommendations

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The speciation of Pb in industrially contaminated soils was found to be determined primarily by (1) the contamination level, and (2) the stability of the originally contaminating Pb-species, while soil characteristics are of secondary importance. Pb is bound strongly to soils in general, and exchangeable Pb exists only in severely contaminated soils, where the bonding capacity of organic matter and oxides is exceeded.

When relating the electrodynamic treatability to soil characteristics and Pb-speciation, it was revealed that Pb-contaminated soils low in organic matter, where Pb does not exist in extremely kaolinite compounds, can be remediated by electrodynamic dialysis. In that case the remediation-time depends on the carbonate content of the specific soil. In the case of soils, where the original polluting Pb-species are extremely kaolinite, remediation proceeds slowly, and may not be feasible. In highly organic soils remediation is hindered by readsorption of Pb to insoluble organic matter, and remediation of such soils may not be possible without any preconditioning. Addition of microbial products such as bacterial extracellular polymers to mobilize Pb in soil during EDR showed adverse effects possibly due to the same effect as described for soil-organic matter.

In most soils Pb is concentrated in the small ( $< 0.063\text{mm}$ ) grain-fractions, and as EDR showed a great potential in remediation of fine-grained soils, the possibility of treating the residual fine soil-fraction after soil-wash by EDR in suspension was investigated. By this method it was shown to be possible to remediate Pb-contaminated soil-fines completely, even from a soil with a high carbonate-content. The performance is highly dependent on the liquid to solid ratio (L/S) and the current density. The most efficient remediation is obtained when applying a current just below the limiting current for the cation-exchange membrane, which decreases linearly with increased L/S in the investigated region.

Commercially available siderophores are able to extract a significant fraction of the Pb from contaminated soil-fines. The necessary siderophore concentration is, however, more than 1000 times higher than that commonly obtained by bacterial growth in iron-deficient substrates, and during EDR in suspension no siderophore production could be detected by an otherwise siderophore producing strain.

Citric acid, DL-malic acid, gluconic acid, tartaric acid and fumaric acid (0.2M) are, likewise, able to extract Pb from contaminated soil fines at neutral to slightly acidic conditions in excess of the extraction obtained due to pure pH-changes. The most efficient extraction is obtained with citric and malic acids, but EDR of soil-fines in suspension is impeded strongly by addition of those acids, and the idea of



combining EDR and heterotrophic leaching of soil fines in suspension is rejected. In contrast enhancement of EDR with nitric acid shows promising results at current densities increased beyond what is feasible by addition of only distilled water.

Batch extraction of Pb from contaminated soil-fines by sulfuric acid is negligible even at very low pH, probably due to the low solubility of lead-sulphate. In accordance with this, EDR of soil-fines in suspension is impeded by preceding sulfur amendment to induce autotrophic leaching as well as by suspension in sulfuric acid. In contrast, Zn-removal is enhanced by both treatments.

The process of EDR of Pb-contaminated soil fines can be divided into four phases: In phase (1) the soil buffer capacity is eliminated by the production of hydrogen-ions at the surface of the anion-exchange membrane where water-splitting takes place. The dissolution of soil-carbonates results in complete extraction of Ca, partial extraction of Mg and K, and a corresponding loss of soil mass. During phase (2) a sharp pH-decrease takes place along with increased conductivity. During this phase Pb is removed at a high rate, and a significant fraction of the Pb is dissolved in the soil-solution. In phase 3) pH stabilizes at 1-2, while the conductivity continues to increase and the voltage between working electrodes decreases. During this phase Pb is extracted at a lower rate. In phase 4) extraction of Pb and most soil-cations ceases, and the primary transport is that of hydrogen-ions. The overall order of removal-rate among soil-cations found is:  $\text{Ca} > \text{Mn} > \text{Mg} > \text{K} > (\text{Al and Fe})$ .

Among toxic, contaminating elements the overall order of removal rate from various soils is:  $\text{Cd} > \text{Zn} > \text{Cu} > \text{As} > \text{Pb} \approx \text{Ni} > \text{Cr(III)} > \text{Hg}$ . All elements except Hg are amenable to remediation with maximum removals obtained as follows: 79% for As, 92% for Cd, 55% for Cr, 96% for Cu, 52% for Ni, 53% for Pb and 88% for Zn. During remediation As (III) is oxidized to As(V), succeeded by removal of anionic As(V). In contrast, no oxidation of Cr(III) takes place during the remediation, and Cr removal is in general low. Among soil-types, EDR in suspension is more efficient from soil-fines low in organic matter and carbonate in accordance with the observations made with traditional, stationary EDR.

Among the studied options, application of microbial products to promote EDR of Pb-contaminated soil-fines does not seem feasible, while the combination of EDR and heterotrophic leaching showed potential for other toxic metals. EDR of the residual sludge after soil-wash seems to be a more promising technology for treatment of soil contaminated by Pb. In addition the method is suitable for removal of most other toxic elements enabling a simple treatment of soils affected by several contaminants. The value of the method relies upon the general validity of some observations made in this work, which should therefore be verified: (1) Pb is generally concentrated in the fine fraction of contaminated soils; (2) Pb bound in the coarser fractions is less mobile than Pb in the fine fraction; (3) the immobile Pb in the coarser fractions is concentrated in single grains, which may be separated from the soil by a density separation process during soil washing; (4) a higher current density may be applied in the suspended setup compared to the stationary method (probably due to the limited concentration polarization). The technology provides a solution for one of the most challenging obstacle to implementation of commercial soil-wash technology. The results of the present work suggest that it could be beneficiary to apply the treatment as a number of reactors in series, where the initial reactor works at the highest possible removal rate, and the final reactor works at the target heavy metal-concentration at an increased current density. Nitric acid addition is recommended in situations where the removal rate is of higher importance than energy expenditure and chemical consumptions. Increased changes in soil characteristics by addition of nitric

acid could however be expected, and should be investigated when relevant for any succeeding application of the remediated soil fines. In addition, it is recommended to terminate remediation as soon as the extraction of the relevant contaminating elements ceases in order to limit the dissolution of Fe and Al-minerals. For Cr and in particular Hg, the effect of soil-conditioning with oxidizing/complexing agents should be tested, although general conclusions on the treatability of Hg-contaminated soil-fines are recommended to be made only after investigation of additional Hg-contaminated soils. Several potential applications of soil-fines after remediation exist depending on their characteristics, which could be controlled by appropriate process management. In order to establish a complete evaluation of any potential applications of the soil-fines after remediation, this investigation should be complemented by investigations of the fate of phosphate, nitrate, chloride and organic matter as well as of the mineralogical condition of the fines after remediation. In order to be able to handle mixed contaminations, the fate of common organic contaminants, like PAH's, during EDR in suspension should also be established. A second main obstacle for implementation of commercial soil-washing is the laborious dewatering of the sludge. As changes in the sedimentation-velocity of the soil-fines during EDR was observed during the present work, it is further recommended to investigate the dewater-ability of the soil-fines before and after treatment to establish an understanding of the most optimal treatment sequence. Based on the practical experience obtained while working with the method, a few additional issues are recommended be considered prior to upscaling of the technology to bench/pilot scale. Firstly, the effect of the ion-exchange membranes needs to be elucidated, as these are expensive, and should only be employed for treatment of a low-value product such as soil if strictly necessary. Secondly it is suggested to investigate the feasibility of various optimization-options: (1) employment of pH-static control of the catholyte, (2) run the process with constant voltage in stead of constant current, (3) employ pulsed electric fields, and (4) use tap-water as electrolytes.



## Appendix I

### Abbreviations and Symbols

AAS	Flame Atomic Absorption Spectrometry	$d_i$	distance of soil slice $i$ from the anode-end
Ac	Acetate	DFO-M	desferrioxamine-M
$a_j$	hydrated ionic radius of specie $j$ [m]	DFOMTA	N-(2,3-dihydroxy-4-(methylamido)benzoyl)-desferrioxamine-B
Am. Citr.	Ammonium Citrate	DW	Distilled Water
AN	ANion-exchange membrane	$e$	charge of an electron $1.602 \times 10^{-19} \text{C}$
atm	atmosphere	EDDS[s,s]	ethylenediamine-disuccinic acid
BCR	Bureau Communautaire de Reference	EDR	ElectroDialytic Remediation
$c/c_0$	normalized concentration	EDTA	Ethylenediamine-tetraacetic Acid
$c_0$	initial concentration	EC	Electrical Conductivity
$c_b$	ion-concentration in bulk solution	EKR	ElectroKinetic Remediation
CA	Citric Acid	EPA	Environment Protection Agency
CAS	Chrome Azurol S	EU	Expandable Undefined
CAT	CATion-exchange membrane	Exp	Experiment
CCA	Chromated Copper Arsenate	F	Faraday constant $96,485 \text{ C/mol}$
CEC	Cation Exchange Capacity	GF-AAS	Graphite Furnace Atomic Absorption Spectrometry
CFU	Colony Forming Unit	G.L.	Governmental assigned Limits
$c_i$	final concentration in soil slice $i$	ha.	hektar (100m x 100m)
$c_j$	concentration of specie $j$	HM	Heavy Metal
CV-AAS	Cold Vapor Atomic Absorption Spectrometry	ICP-MS	Inductively Coupled Plasma Mass-spectrometry
$^{\circ}\text{C}$	degrees Celsius	$i_{\text{lim}}$	limiting current
(c)	Crystalline	IQ	Intelligence Quotient
D	Diffusion coefficient [ $\text{m}^2/\text{s}$ ]	J	current density [ $\text{mA}/\text{cm}^2$ ]
$D_j$	Diffusion coefficient of specie $j$ [ $\text{m}^2/\text{s}$ ]	$J_j^e$	Electroosmotic flux of specie $j$ [ $\text{mg}/(\text{m}^2 \cdot \text{s})$ ]
DC	Direct Current		
DFO-B	desferrioxamine-B		

$J_j^m$	Electromigrative flux of specie j [ $\text{mg}/(\text{m}^2\cdot\text{s})$ ]	$r^2$	correlation coefficient
$J_{\text{opt}}$	optimal current density [ $\text{mA}/\text{cm}^2$ ]	rpm	rounds pr. minute
k	Boltzmann constant $1.381 \times 10^{-23} \text{ J/K}$	SEM-EDX	Scanning Electron Microscope-Energy Dispersive X-ray
KC	Potassium Citrate	Si	Silicium
$K_d$	Equilibrium adsorption coefficient [ $\text{L}/\text{kg}$ ]	sp	specie
$k_e$	electroosmotic permeability [ $\text{mg}/(\text{m}\cdot\text{s}\cdot\text{V})$ ]	spike	contaminate artificially
$K_{\text{sp}}$	solubility constant	Std. dev.	Standard deviation
L	Length	T	temperature
$l_i$	length of soil slice i	$t^{\text{bl}}$	transport number of counter-ions in boundary layer
L/S	Liquid to Solid ration	$t^m$	transport number of counter-ions in membrane
M	Molar	$\text{Po}_2$	Partial pressure of $\text{O}_2$
$M_1$	1 <sup>st</sup> moment of contaminant	SCC	Soil Cut-of Criteria
$M_0$	0 <sup>th</sup> moment of contaminant	Sn	Tin
MA	Malic Acid	SQC	Soil Quality Criteria
Me	Metal	$u_j$	ionic mobility of specie j in free solution [ $\text{m}^2/(\text{s}\cdot\text{V})$ ]
meq	milli-equivalents	$u_j^*$	ionic mobility of specie j in soil pores [ $\text{m}^2/(\text{s}\cdot\text{V})$ ]
Mm	metal-mobilization-length	WHO	World Health Organization
MSW	Municipal Solid Waste	$x_e$	tortuosity
MSWI	Municipal Solid Waste Incineration	XRD	X-Ray Diffraction
N	Neutral conditions	z	valence
NA	Nitric Acid	$z_j$	valence of ion j
OECD	Organisation for Economic Co-operation and Development	$\eta$	viscosity [ $\text{kg}/(\text{m}\cdot\text{s})$ ]
OM	Organic Matter	$\delta$	boundary layer thickness
PbB	blood-Pb-level		
pe	$-\log[e^-]$		
pH	$-\log[\text{H}^+]$		
pK	$-\log K$ , K = equilibrium constant		
PAH	Polycyclic Aromatic Hydrocarbons		
PEM	Poul E Meier		
PNEC	Predicted No-Effect Concentration		
PTWI	Provisional Tolerable Weekly Intake		
PVC	Polyvinyl Chloride		
R	gas constant $8.31451 \text{ J}/(\text{K}\cdot\text{mol})$		

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Soil name thesis	Soil identity file	Characteristics found in chapter
<b>1</b>	P3	4
<b>2</b>	P4	4
<b>3</b>	P7 = K7013	4
<b>4</b>	P10	4
<b>5</b>	P11	4
<b>6</b>	P12	4
<b>7</b>	P15	4
<b>8/2</b>	K7036	4/9
<b>9</b>	K7048-1	4
<b>10</b>	K1487	4
<b>1</b>	K3705	9
<b>3</b>	Dansk A-træ	9
<b>4</b>	Collstrup	9
<b>5</b>	Bohus EKA	9

#### Experiments: Stationary setup

Exp. name chapter	Exp. name file	Soil J (mA/cm <sup>2</sup> )		Time (h)	Charge passage (coulomb/g)	Reagent*	Chapter
NN	Bio 10	8	0.2	1344	56	DW	3
NN	Bio 12	8	0.2	1344	56	S. cerevisiae	3
NN	Bio 9	9	0.2	1344	72	DW	3
NN	Bio 11	9	0.2	1344	72	S. cerevisiae	3
<b>1</b>	Bio 18	1	0.2	1416	68	DW	5
<b>2</b>	P4A	2	0.2	1680	68	DW	5
<b>3</b>	Bio 17	3	0.2	1440	68	DW	5
<b>4</b>	Bio 15	4	0.2	1320	68	DW	5
<b>5</b>	P11C	5	0.2	960	68	DW	5
<b>6</b>	Bio 16	6	0.2	1056	68	DW	5
<b>7</b>	Bio 19	7	0.2	1872	68	DW	5
<b>8</b>	Bio 20	8	0.2	1608	68	DW	5
<b>9</b>	Bio 22	9	0.2	2064	68	DW	5
<b>10</b>	Bio 21	10	0.2	1704	68	DW	5

\* DW = Distilled Water

## Experiments: Suspended setup:

Exp. name chapter	Exp. name file	Soil*	L/S	J (mA/cm <sup>2</sup> )	Time (h)	Charge passage (coulomb/g)	Reagent*	Chapter
NN	Bio 33	10	3.5	0.2	480	173	Siderophores	3
A1	Bio 43	10	3.5	0.2	713	249	DW	6
A2	Bio 44	10	7.0	0.2	403	269	DW	6
A3	Bio 45	10	10.5	0.2	330	321	DW	6
A4	Bio 46	10	14.0	0.2	265	341	DW	6
B1	Bio 33b	10	3.5	0.4	495	346	DW	6
B2	Bio 34	10	7.0	0.4	334	445	DW	6
B3	Bio 35	10	10.5	0.4	240	467	DW	6
B4	Bio 36	10	14.0	0.4	474	1219	DW	6
C1	Bio 39	10	3.5	0.6	621	651	DW	6
C2	Bio 40b	10	7.0	0.6	621	1242	DW	6
C3	Bio 41	10	10.5	0.6	778	2271	DW	6
C4	Bio 42	10	14.0	0.6	809	3120	DW	6
C1a	Bio 48	10	3.5	0.6	1183	1240	DW	6
D1a	Bio 49	10	3.5	0.8	1179	1648	DW	6
DW20	Bio 35	10	10.5	0.4	240	467	DW	7
MA20	Bio 51	10	10.5	0.4	240	467	Malic acid	7
CA20	Bio 52	10	10.5	0.4	240	467	Citric acid	7
MA20N	Bio 53	10	10.5	0.4	240	467	Malic acid	7
CA20N	Bio 54	10	10.5	0.4	240	467	Citric acid	7
NA20	Bio 55	10	10.5	0.4	240	467	Nitric acid	7
NA40	Bio 57	10	10.5	0.8	240	934	Nitric acid	7
MA40N	Bio 58	10	10.5	0.8	240	934	Malic acid	7
CA40N	Bio 59	10	10.5	0.8	240	934	Citric acid	7
KC40	Bio 60	10	10.5	0.8	240	934	Potassium-citrate	7
K1	Bio 66	10	4.3	0.8	188	311	DW	8
K2	Bio 67	10	4.3	0.8	330	546	DW	8
K3	Bio 68	10	4.3	0.8	503	833	DW	8
K4	Bio 63	10	4.3	0.8	671	1111	DW	8
K5	Bio 64	10	4.3	0.8	838	1387	DW	8
K6	Bio 65	10	4.3	0.8	930	1539	DW	8
1A	Bio 69	11	10	0.4	240	462	DW	9
1B	Bio 73							
2A	Bio 70	8	10	0.4	240	432	DW	9
2B	Bio 74							
3A	Bio 71	12	10	0.4	240	432	DW	9
3B	Bio 75							
4A	Bio 72	13	10	0.4	240	432	DW	9
4B	Bio 76							
5A	Bio 77	14	10	0.4	240	432	DW	9
5B	Bio 78							

\* DW = Distilled Water      •Only the fine fraction (< 63µm) is used.



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