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Effect of pulse current on energy consumption and removal of heavy metals during electrodialytic soil remediation

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Effect of pulse current on energy consumption and removal of heavy metals during electrodialytic soil remediation

PhD thesis, 2013

DTU

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Preface

This dissertation includes the results of my PhD study carried out at the research group "Environmental Electrochemistry", Department of Civil Engineering in the Technical University of Denmark (DTU) during the period from January 2010 to March 2013. This PhD study was funded by the Department of Civil Engineering, DTU. The main supervisor was Associate Professor Lisbeth M. Ottosen and co-supervisors were Associate Professor John Mortensen from Roskilde University and Professor Mette R. Geiker from Norwegian University of Science and Technology.

I wish to acknowledge all my colleagues in the "Environmental Electrochemistry Group" for a dynamic and inspiring research environment. I would like to express my special gratitude to my supervisor Lisbrth M. Ottosen for always having faith in me and my work and being a huge inspiration. Her guidance, good advices, support, encouragement and discussions regarding problems accompany me along with my PhD study. In addition, thanks for the fruitful scientific discussions and help from my co-supervisors John Mortensen and Mette R. Geiker and my colleagues Pernille E. Jensen and Gunvor M. Kirkelund.

Laboratory technicians Ebba Cederberg Schnell, Sabrina Madsen, and Malene Grønvold are greatly thanked for assistance with the experimental work and sample measurement.

During my PhD study, I spent three months at Lehigh University, Bethlehem, Pennsylvania, USA for exchange study. I felt so welcome and at home thanks to the faculty, staff and graduate students. I especially thank Professor Sibel Pamukcu for inspiration, discussion and interest in my work.

Finally, I would like to thank my wife Xiao Ying Liu for her thoughtful care and love, and friends and family for their support and cheering during my work.

Tian Ran Sun

April 2013

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Abstract

Contamination of soils and groundwater keep attracting attention of worldwide. The contaminants of concern include a wide range of toxic pollutants such as heavy metals, radionuclides, and organic compounds. The environment and humans are exposed to these pollutants through different exposure pathways to unacceptable dosages, leading to intolerable adverse effects on both public health and the environment. In the last decades, soil and water remediation have gained growing awareness, as the necessity becomes clearer for development of such techniques for elimination of the negative impact from the contamination on human health and land use.

Electrochemical remediation has been recognized as a promising group of technologies for remediation of contaminated sites, leading to several research programs worldwide for the development. Electrochemical remediation is also synonymously referred to as electrokinetics, electrokinetic remediation, electroremediation or electroreclamation. Electrochemical remediation technologies are part of a broader class of technologies known as direct current technologies. The techniques utilize the transport processes obtained by application of the electric DC field: transport of water (electroosmosis) and ions (electromigration), with electromigration being the most important transport process when treating heavy metal contaminated soils.

Electrodialytic remediation (EDR), one of the enhanced electrochemical remediation techniques, is developed at the Technical University of Denmark in the early 1990s and aims at removal of heavy metals from contaminated soils. The electrodialytic remediation method differs from the electrokinetic remediation methods in the use of ion exchange membranes for separation of the soil and the processing solutions in the electrode compartments. Therefore no current is wasted for carrying ions from one electrode compartment to the other.

The EDR technique has been tested for decontamination of a variety of different heavy metal polluted particulate materials: mine tailings, soil, different types of fly ashes, sewage sludge, freshwater sediments and harbor sediments. In previous works including both lab and pilot scale experiments, this technique has demonstrated effective removal of heavy metals from all the contaminated materials. In the PhD project, the focus turns to energy saving aspect of EDR which influencing costs and thus the applicability for remediation beyond bench and pilot scale.

The overall aim of the present PhD study is to clarify and understand the underlying mechanisms of the effect of pulse current on energy consumption and removal of heavy metals during electrodialytic soil remediation. Series of experiments with constant and pulse current in two different industrially polluted soils were conducted.

Results showed that the pulse current gave positive effect in relation to energy saving and improvement of removal of heavy metals during EDR. The positive effect was related to enhancement of the acidification process, increasing the electric conductivity in soil pore fluid, and diminishing the polarization process of membranes and soil particles. The efficacy of pulse current was found dependent on applied current density, soil buffering capacity, and applied pulse frequency. In stationary EDR, the efficacy of pulse current was more significant at higher current densities, higher buffering capacities, and lower pulse frequencies (i.e. adequate relaxation time with respect to the current "ON" time). On the contrary in suspended EDR, higher pulse frequency was preferred, and the difference was due to the different transport process of ions between stationary and suspended EDR. The major energy was consumed by the fouling of cation exchange membrane in stationary EDR, whereas major energy consumption was found in soil suspension in suspended EDR. Compared with stationary EDR (maximum 70% energy saving), less energy was saved (maximum 33%) in suspended EDR, even with higher applied current densities.

Although it was demonstrated that the pulse current is a possible way to decrease the energy consumption and increase the removal efficiency of heavy metals during EDR, long-term tests are still needed in future research to evaluate the possible decay of the enhancing effect induced by pulse current as a function of remediation time. Although the influences of applied current density and soil buffering capacity on pulse current were investigated, the test range of current density and buffering capacity was relatively narrow; therefore more experiments are needed to make the conclusions more general. Moreover, clarification on the redistribution of ionic species in the soil pore fluid and interaction between ions and soil particles at the relaxation period are also needed for fundamental understanding the mechanisms related to pulse current.

Sammendrag

Forurening af jord og grundvand tiltrækker til stadighed opmærksomhed verden over. De forskellige typer af forurening, som giver bekymring, inkluderer en lang række toksiske forbindelser så som tungmetaller, radioaktive stoffer og organiske forbindelser. Miljøet og mennesker eksponeres for disse forureninger gennem forskellige eksponeringsveje og i uacceptabelt høje doser, hvilket leder til uacceptable, uønskede bivirkninger på både folkesundhed og miljøet. I de seneste årtier har jord og grundvandsrensning fået stigende opmærksomhed i takt med at det tydeliggøres, at der er behov for disse teknikker for at eliminere den negative effekt fra forureninger.

Elektrokemisk rensning er generelt anerkendt som en lovende gruppe af teknikker til rensning af forurenede arealer, hvilket har ledt til flere forskningsarbejder verden over til udvikling af disse teknikker. Elektrokemisk jordrensning har flere navne, som anvendes synonymt; elektrokinetisk jordrensning, electro-remediering eller electroreclamation. De elektrokemiske rensningsteknologier er en del af en større gruppe af teknologier kendt som jævnstrømsteknologier. Elektrokemisk jordrensning bygger på de transportprocesser, som opnås når jorden påtrykkes et elektrisk jævnstrømsfelt: transport af vand (elektroosmose) og ioner (elektromigration), og af disse er elektromigration den væsentligste transportproces i forbindelse med tungmetalforurenet jord.

Elektrodialytisk jordrensning (EDR) er en af de udbyggede elektrokemiske jordrensningsmetoder. Den er udviklet på Danmarks Tekniske Universitet i starten af 1990erne med det formål at fjerne tungmetaller fra forurenet jord. Den elektrodialytiske jordrensningsmetode adskiller sig fra de øvrige ved at ionbyttermembraner adskiller jord og procesvæsker i elektrodekamrene, hvilket betyder, at der ikke spildes strøm på at bære harmøse ioner fra det ene elektrodekammer til det andet.

EDR er blevet testet til tungmetalfjernelse fra en lang række forskellige partikulære materialer: jord, mineaffald, forskellige typer af flyveasker, spildevandsslam, ferskvandssedimenter og

havnesedimenter. I alle tilfælde har teknikken vist sig effektiv til tungmetalfjernelsen, og det gælder både de forsøg, som er udført i laboratorieskala og pilotskala. Dette PhD projekt fokuserer på energibesparende aspekter i relation til EDR, idet disse er væsentlige for den overordnede behandlingspris, når metoden anvendes i fuldskala.

Det overordnede formål med PhD projektet var at klarlægge effekten af pulserende strøm på energiforbrug og tungmetalfjernelse, og samtidig forstå baggrunden for herfor. Arbejdet er eksperimentelt baseret og bygger på serier af eksperimenter med pulserende og konstant strøm med to forskellige industrielt forurenede jorde.

Det eksperimentelle arbejde viste, at den pulserende strøm havde en positiv effekt i relation til både mindre energiforbrug og forbedret fjernelse af tungmetaller under EDR. De positive effekter var relateret til forbedring af forsuringen af jorden under processen, øget elektrisk ledningsevne i jordvæsken og reduktion af polarisationsprocesser ved membraner og jordpartikler.

Virkningen af pulserende strøm blev fundet afhængig af den påtrykte strømtæthed, jordens bufferkapacitet og den anvendte puls. I stationær EDR var effekten af den pulserende strøm større ved høj strømtæthed, høj bufferkapacitet og lav puls frekvens (dvs. tilstrækkelig tid uden strøm i forhold til tid med strøm). Modsat blev det fundet for EDR på suspenderet jord, at høj puls frekvens gav det bedste resultat. Forskellen var pga. de forskellige transportprocesser i de to opstillinger. Den største elektriske modstand lå over kationbyttermembranen i stationær EDR (pga. udfældninger), medens det var suspensionen af jord, som gav den højeste modstand i suspenderet EDR. I sammenligning med stationær EDR, hvor energiforbruget blev reduceret med op til 70%, var energibesparelsen mindre for suspenderet EDR, hvor der blev sparet op til 33% ved den højeste påtrykte strømtæthed.

De opnåede resultater blev fundet gennem relativt korte forsøg, og videre forskning må klarlægge effekten af den pulserende strøm over hele rensningsperioden. Forsøgsfeltet, i forhold til

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strømtæthed og jordens bufferkapacitet, var relativt smalt, og flere eksperimenter er nødvendige for at kunne generalisere konklusionerne. Yderligere skal fremtidig forskning klarlægge omfordelingen af ionforbindelser i porevæsken og interaktionen mellem ioner og jordpartikler i perioder uden strøm, for at opnå en fundamental forståelse for effekterne af den pulserende strøm på partikelniveau.

Content

1. Introduction

1.1 Electrokinetic and electrodialytic soil remediation

Many toxic chemicals like heavy metals and persistent organic pollutants have been released to the environment by industrial activities, due to accidental spills or improper management. It resulted in many contaminated sites all over the world. Soil, sediment, and groundwater contamination has been a major problem at these polluted sites, which need urgent remediation to protect public health and the environment. The absence of a specific technology solution has increased the interest in finding new and innovative techniques for the efficient removal of contaminants from soils to solve groundwater, as well as soil pollution (Shackelford and Jefferis, 2000).

Several different technologies have been developed to remediate soils, sediments, and groundwater based on physicochemical, thermal, and biological principles (Sharma and Reddy, 2004). However, they are often found to be costly, energy intensive, ineffective, and could themselves create other adverse environmental impacts when dealing with difficult subsurface and contaminant conditions. For instance, inadequate remediation has been demonstrated at numerous polluted sites (Reddy and Cameselle, 2009) due to the presence of low permeability and heterogeneities and/or contaminant mixtures (multiple contaminants or combinations of different contaminant types such as coexisting heavy metals and organic pollutants). Electrochemical remediation has been recognized as a promising technology for effective and efficient pollution remediation, both on their own and in concert with other remediation techniques, leading to several research programs worldwide for the development of this technology.

Electrochemical remediation is also referred to as electrokinetics, electrokinetic remediation, electroremediation, electroreclamation, and other such terms in published literature (Reddy and Cameselle, 2009). Electrochemical remediation technologies are part of a broader class of technologies known as direct or alternate current technologies. Electrokinetics includes transport of water (electroosmosis) and ions (electromigration) as a result of an applied electric field with electromigration the more common application for treating metal-contaminated soils (Athmer and Ho, 2009). The first field-scale application of electrokinetics for soil remediation was carried out by Geokinetics in 1987 (Lageman, 1993). Similar techniques were previously reported as used in the former Soviet Union since the early 1970's to concentrate metals and explore for minerals in deep soils (USEPA, 1997). Electrokinetic techniques have an extended history in development for treatment of clay soils since their introduction as a construction technique in 1939 (Glendinning et al., 2007). For these applications, electrokinetics is defined as the application or induction of an electrical potential difference across a soil mass containing fluid or a high fluid content slurry/suspension, causing or caused by the motion of electricity, charged soil and/or fluid particles. A typical field electrochemical remediation system is shown in Figure 1.
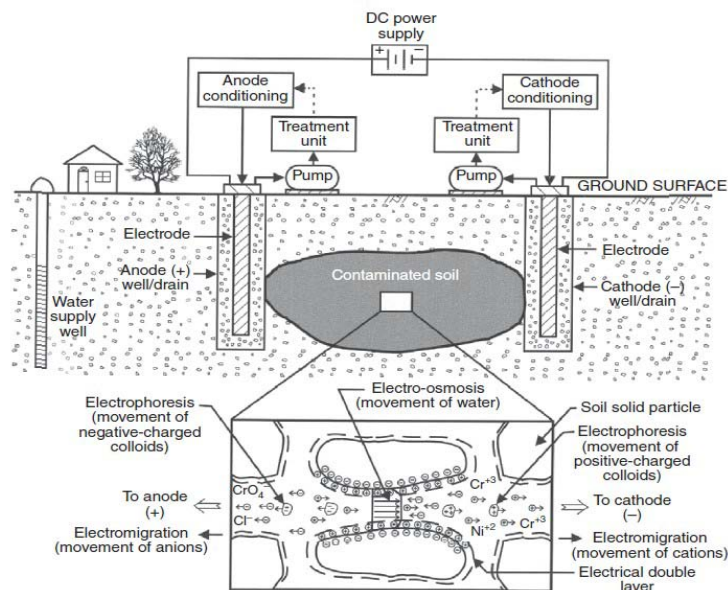

Figure 1: Schematic of implementation of in situ electrochemical remediation systems (Reddy and Cameselle, 2009).

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Wells/drains are configured and drilled to surround a contaminated region. Electrodes are then inserted into each well/drain and a low direct current (DC) or a low potential gradient to electrodes is applied. As a result of the applied electric field several transport, transfer, and transformation processes are induced which cause contaminants to be transported into the electrodes where they can be removed. Alternatively, contaminants are stabilised/immobilised or degraded within the contaminated media. Several patents have been issued that deal with using electrochemical remediation in different creative ways. When water alone is used at the electrodes the process is known as *unenhanced electrochemical remediation*. When enhancement strategies (i.e. use of conditioning solutions and ion exchange membranes at the electrodes) are used, the process is known as *enhanced electrochemical remediation*.

Electrodialytic remediation (EDR), one of the enhanced electrochemical remediation techniques, is developed at the Technical University of Denmark in the early 1990s and aims at removal of heavy metals from contaminated soils (Ottosen, 1995). The main purpose for using ion exchange membranes is that ions are hindered in entering the soil from the electrode compartments. Therefore no current is wasted for carrying ions from one electrode compartment to the other (Ottosen, 1997).

Generally, ion exchange membranes are classified into anion exchange membranes and cation exchange membranes depending on the type of ionic groups attached to the membrane matrix. Cation exchange membranes contains negatively charged groups, such as $-SO3^-$, $-COO^-$, $-PO3^{2-}$, $-PO_3H^-$, $-C_6H_4O^-$, etc., fixed to the membrane backbone and allow the passage of cations but reject anions. While anion exchange membranes contains positively charged groups, such as $-NH3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$, $-SR_2^+$, (R $= -NHCOO(CH_2CH_2O)_nCONH-$) etc., fixed to the membrane backbone and allow the passage of anions but reject cations (Xu, 2005). According to the connection way of charge groups to the matrix or their chemical structure, ion exchange membranes can be further classified into homogenous and heterogeneous membranes, in which the

charged groups are chemically bonded to or physically mixed with the membrane matrix, respectively. However, most of the practical ion exchange membranes are rather homogenous and composed of either hydrocarbon or fluorocarbon polymer films hosting the ionic groups (Xu, 2005). The principle of laboratory EDR cells is shown in Figure 2.
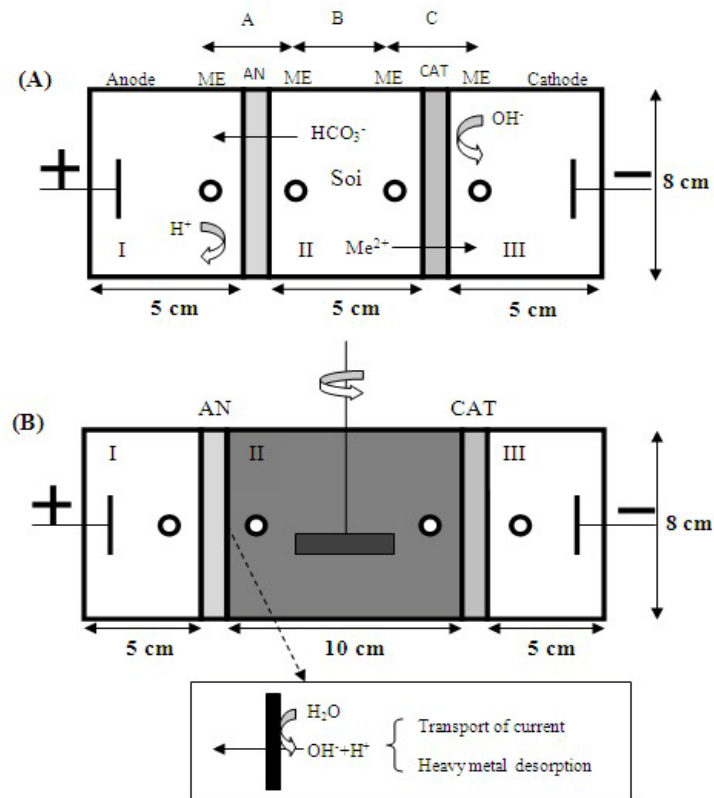
Figure 2. Schematic diagram of the laboratory cells for electrodialytic soil remediation (CAT=cation exchange membrane, AN=anion exchange membrane, ME=monitoring electrode, and letters A, B and C represent the potential drop of different parts). Water dissociation happens at the surface of AN both in stationary and suspend EDR.

1.2 Application of EDR

The EDR technique has been applied for decontamination of mine tailing, harbor sediment, fly ash, and soil (Pedersen et al., 2003; Jensen et al., 2007; Kirkelund et al., 2009; Ottosen et al., 2009).

In previous works including both lab and pilot scale experiments, this technique has demonstrated effective removal of heavy metals from the contaminated materials.

Mine tailing. Metal sulfide-based mining produces huge amounts of solid waste, where the most concerning are the mine tailings. Copper mine tailings have been treated by EDR methods in laboratory scale by different investigators (Kim and Kim, 2001; Hansen et al., 2005). Hansen et al. (2007) found that produced tailings were much more difficult to remediate than tailings deposited more than 30 years ago. The important difference between the two tailing samples was the pH: the fresh tailings are approximately neutral, while the old deposited tailings are acidic. This is due to the oxidation of pyrite, the main residual mineral in sulfide tailings, which releases protons due to the overall reaction (Kontopoulus et al., 1995):

$$4FeS_2(s) + 15O_2 + 14H_2O \rightarrow Fe(OH)_3(s) + 8SO_4^{2-} + 16H^+ \qquad (1)$$
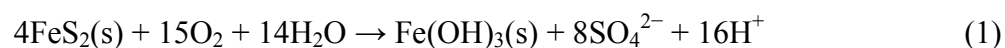
In the old tailings, copper was removed easily from the tailings due to the dissolution of the copper sulfides. This corresponds well with the findings from the sequential analysis of these tailings (Hansen et al., 2005), where the mobility of copper in old tailings was found to be highest. On the other hand, fresh tailings seemed to be difficult to treat without lowering the pH. Both sulfuric and citric acids were tested, and the complexing effect of citric acid seemed to enhance the process slightly. Hansen et al. (2008) evaluated an enhancement system, including an airlift stirring of suspended fresh tailings in dilute sulfuric acid. The tailings were remediated more efficiently in suspended EDR than in stationary EDR. Eighty percent of the copper was removed when suspending the tailings by airlift during EDR. In contrast, only 15% was removed in stationary EDR with similar operation conditions. Initial experiments showed that pH did not seem to be the most important parameter for copper removal in suspended tailings. The liquid-to-solid ratio (L/S ratio) was analyzed, and in the case of copper mine tailings, a suitable L/S ratio seems to be around 6-9 ml/g. Furthermore, if no stirring was applied, maintaining the same L/S ratios, no copper removal

was observed, indicating that the electric current passes in the stagnant liquid above the settled particles.

Harbor sediment. EDR was tested for remediation of harbor sediments in a number of works (Nystrom et al., 2003, 2005; Nystrom et al., 2005a,b; Nystrom et al., 2006; Ottosen et al. 2007), in which the potential was documented (Nystrom et al., 2003). Like for soils, remediation was shown to be faster for noncalcareous sediments compared to calcareous ones (Nystrom et al., 2005). Furthermore, remediation of sediment in suspension was more efficient than remediation of sediment in a solid column (Nystrom et al., 2005). It was also shown that the addition of HCl, lactic acid, citric acid, NaCl, and ammonium citrate reduced remediation efficiency. The highest removals obtained were 67%-87% Cu, 79%-98% Cd, 90%-97% Zn, and 91%-96% Pb regardless of the initial heavy metal concentration (Nystrom et al., 2005b). Recently, the potential of using electrochemical methods for treatment of freshwater sediments was documented in an electrochemical cell, where the metals were transported from the acidified sediment in which carbon rod anodes were placed directly, and into the catholyte separated from the sediment by a cellulose filter (Matsumoto et al., 2007). Removal percentages of 18, 21, 53, 81, 86, and 98 for Pb, Cu, Ni, Cr, and Zn, respectively, were obtained after 10 days of treatment at 2.9 mA/cm^2. Another work proved that Cu can be removed (up to 85% after 14 days with 0.15 mA/cm^2) from artificially contaminated lake sediments, and that the use of nylon membranes and cation exchange membranes as barriers between sediment and cathode improves the treatment (Virkutyte and Sillanpaa, 2007). By means of the electrodialytic method also used for treatment of harbor sediments, it was shown that removal of Pb, Zn, Cu, Cr, and Ni could be obtained from industrially contaminated millpond sediment, with removals of approximately 95%, 85%, 75%, 65%, and 55%, respectively, after 14 days of treatment at 0.8 mA/cm^2 (Jensen et al., 2007).

Fly ash. A serious drawback of MSWI is the production of chemically unstable flue gas purification products that are rich in heavy metals. It has been evaluated whether EDR can be used for treatment of different fly ashes (Pedersen et al., 2003; Ferreira et al., 2005a; Ferreira et al., 2005; Christensen et al., 2006). However, even though the two fly ashes seem comparable overall, there are many differences of importance when it comes to EDR. The major difference is that the ashes contain a high water soluble fraction (mainly salts), which makes it difficult to treat fly ash in the traditional cell. Hansen, Ottosen, and Villumsen (2004) found that about 2/3 wt% straw ash was dissolved during electrodialytic treatment, and thus the transference number of the pollutants was very low and the process to control was difficult due to the significantly decreasing volume of the ash. It proved beneficial to prewash the ash in water to remove the soluble parts before treatment (Pedersen, 2003). The advantage is that less current is wasted on the removal of harmless ions and the volume loss during treatment is less. Furthermore, by prewashing the residues, the production of chlorine gas at the anode was reduced. For the optimization of the process, it was also found to be highly beneficial to treat the ash in a stirred suspension as compared with its treatment as water-saturated matrix (Pedersen, 2003).

Soil. The electrodialytic removal of Cu from soil polluted from wood preservation industry in unenhanced laboratory scale has shown successful (unenhanced here means no addition of enhancement solutions to the soil but utilization of the acidic front developing from the anode to aid the heavy metal desorption). The best removal percentages reached are 98% from a Danish wood preservation soil (Ottosen et al., 1997) and 82% from a Portuguese soil (Ribeiro and Mexia, 1997), both obtained with an electrodialytic setup. On the other hand, the success with electrodialytic removal of As from soil polluted from wood preservation in un-enhanced systems has been limited, e.g. removal of 35% As was obtained in only 1.5 cm in an experiment that lasted for 42 days (Ottosen et al., 2000) and 51% As was removed from a Portuguese soil during 35 days (Ribeiro et

al., 1998). Desorption of As is highly dependent on both redox potential and pH. The primary forms of As in soils are arsenate As(V) and arsenite As(III), and under moderately reducing conditions, As(III) is the predominant form whereas at higher redox levels the predominant form is As(V). The experiments made so far were conducted in closed laboratory cells and As(III) is expected to be the primary form and the main stable species in an reducing environment at neutral to acidic pH is the uncharged (H_3AsO_3) (Cullen and Reimer, 1989) and since it is uncharged it is not mobile with electromigration, which may be the major problem in relation to the inefficient As removal. Pb was easily dissolved by the acidification resulting from water splitting at the anion exchange membrane (Jensen et al., 2007). 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. It was also 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.

Electric energy consumption is an important factor for the application of electrochemically based remediation techniques. Beyond bench and pilot scale setup, this aspect is very important. Power requirement is directly related to the size of the treatment area. Table 1 shows a summary of energy consumption of reported pilot-scale electrokinetic experiments. It can be seen that because of the difference among soil types and concentrations of metals as well as treatment period, the electric energy consumption and removal percentage of soil metals vary significantly from 38 to 2760 kWh m^{-3} (Table 1).

Table 1. Summary of energy consumption of reported pilot-scale electrokinetic experiments.

Reference	Soil	Volume (m^3)	Pollutant ($mg\ kg^{-1}$)	Voltage drop ($V\ m^{-1}$)	Current ($A\ m^{-2}$)	Energy ($kWh\ m^{-3}$)	Duration (h)	Removal percentage (%)
Lageman (1993)	Peat soil	210	Pb: 300–5000 Cu: 500–1000	–	–	38–65	430	Pb:>70 Cu: 80
	Clay soil	90	Zn: 2410	20–40	8	160 kWh t^{-1}	1344	32.8
	Heavy clay soil	200	As: 400–500	20–40	4	–	1560	93
Acar and Alshawabkeh (1996)	Kaolinite	0.46	Pb: 856	4.3–193	1.33	220	1300	–
	Kaolinite	0.46	Pb: 1533	18–262	1.33	700	2950	80–90
	Kaolinite: sand (1:1)	0.46	Pb: 5322	5.9–193	1.33	700	2500	–
Marceau et al. (1999)	Clayey medium	2.7	Cd: 882	9–44.5	3	159	3259	98.5
Gent et al. (2004)	–	125	Cr: 180–1100 Cd: 5–20	10–13.5	9.7–18	208	4800	Cr: 78 Cd: 70
Alshawabkeh et al. (2005)	Sandy and clayed soil	0.6	Pb: 1187–3041	70–120	2.6	1620	9 months	70–85
		1.2	Pb: 1187–3041	90–170	1.3	2760	11 months	70–85
Zhou et al. (2006)	Red soil	0.56	Cu: 829	80	1.68–3.0	244	1680	76

The overall objectives of this PhD study are to investigate the effect of pulsed electric field on energy saving and removal of heavy metals during soil electrodialytic remediation, and discuss its mechanism from the viewpoints of interaction between transport and surface reaction and re-equilibrium process at relaxation period.

1.3 Basic transport processes in soil under electric fields

Soil is a system consisted of solid, liquid, and gas phase. More than 90% of the solid phase is soil minerals. Further, these minerals can be generally divided into coarse (>2mm), sand (0.05mm<Ø<2mm), silt (0.002mm<Ø<0.05mm), and clay (<0.002mm) by grain size. The clay

minerals determine soil behavior and carry the significant surface charge. The surface charge of clay is either a permanent charge caused by ionic substitution in crystal lattice or variable charges determined by soil pH (Sposito, 1989). The charged surfaces are counter-balanced by ions of opposite sign in the diffuse electric double layer. Ions in the solution with the same sign as the charged surface are co-ions and they are represented to a much lesser extent in the electric double layers than the counter-ions. Charge balance is always maintained throughout the system at all times, and the overall system with porous media and electrolyte must be electrically neutral. Charges cannot be added to, formed in, or removed from the system without addition, formation or removal of an equal number of the opposite charge.

Significant material transport processes in soil during application of electric fields are electromigration, electroosmosis, and electrophoresis, which are more or less all related to the surface charge and the electric double layer in vicinity. Diffusion is also important since the concentration gradient is built up by material transport. These transport processes are briefly described below.

Electromigration is the movement of ions and ionic complexes in both electric double layers at soil surface and soil solution in an applied electric field. The ions move towards the electrode of opposite charge: anions towards the anode and cations towards the cathode. Unlike in solutions, the ions in the compacted soil matrix cannot electromigratie directly to the opposite pole by the shortest route. Instead, they have to find their way along the tortuous pores and around the particles or air filled voids that block the direct path. Moreover, the ions can be transported only in continuous pores, but not in closed ones and ions are only transported in the liquid phase (Ottosen et al., 2008). Electromigration is the most important transport mechanisms for ions in porous media and the electromigration flux is dependent on the ionic mobility, tortuosity factor, porosity of the material, and charge of ions (Acar and Alshawabkeh, 1993).

Electroosmosis is the movement of water in a porous media towards the positive or negative electrode dependent on the overall surface charge of the porous material. Both counter- and co-ions will move towards the electrode of opposite charge. Since the counter-ions are in excess to the co-ions in the soil electric double layer, a net-flow of ions across the electrode of opposite sign compared to the surfaces of the porous material will occur, and water molecules are pushed or dragged towards the electrode together with the counter-ions. Electroosmotic flow differs from flow caused by a hydraulic gradient because electroosmotic flow is mainly dependent on the porosity and zeta potential of the soil, rather than pore size distribution and macropores. Therefore, the electroosmosis is efficient in fine-grained soils (Acar and Alshawabkeh, 1993). However, the electroosmotic mobility is generally 10 times lower than the ion mobility during electromigration (Lageman et al., 1989).

Diffusion is the movement of the ionic species in soil solution caused by concentration gradient. Due to the electrically induced mass transport in the porous material the concentration gradients are formed. Estimates of the ionic mobilities (the transport rate of ionic species under unit electric strength) from the diffusion coefficients using the Nernst–Einsetin relation indicates that ionic mobility of a charged species is much higher than the diffusion coefficient (about 40 times the product of its charge and the electrical potential gradient) (Reddy and Cameselle, 2009). Therefore, diffusive transport is often neglected.

Electrophoresis is the opposite of electromigration and is transport of charged particles in an applied electric field. It can include all electrically charged particles (e.g. colloids, clay particles, and organic particles). Electrophoresis is generally of limited importance in compacted soil system (Probstein and Renaud, 1987), but can be significant if an electric field is applied to a slurry (Acar and Alshawabkeh, 1993).
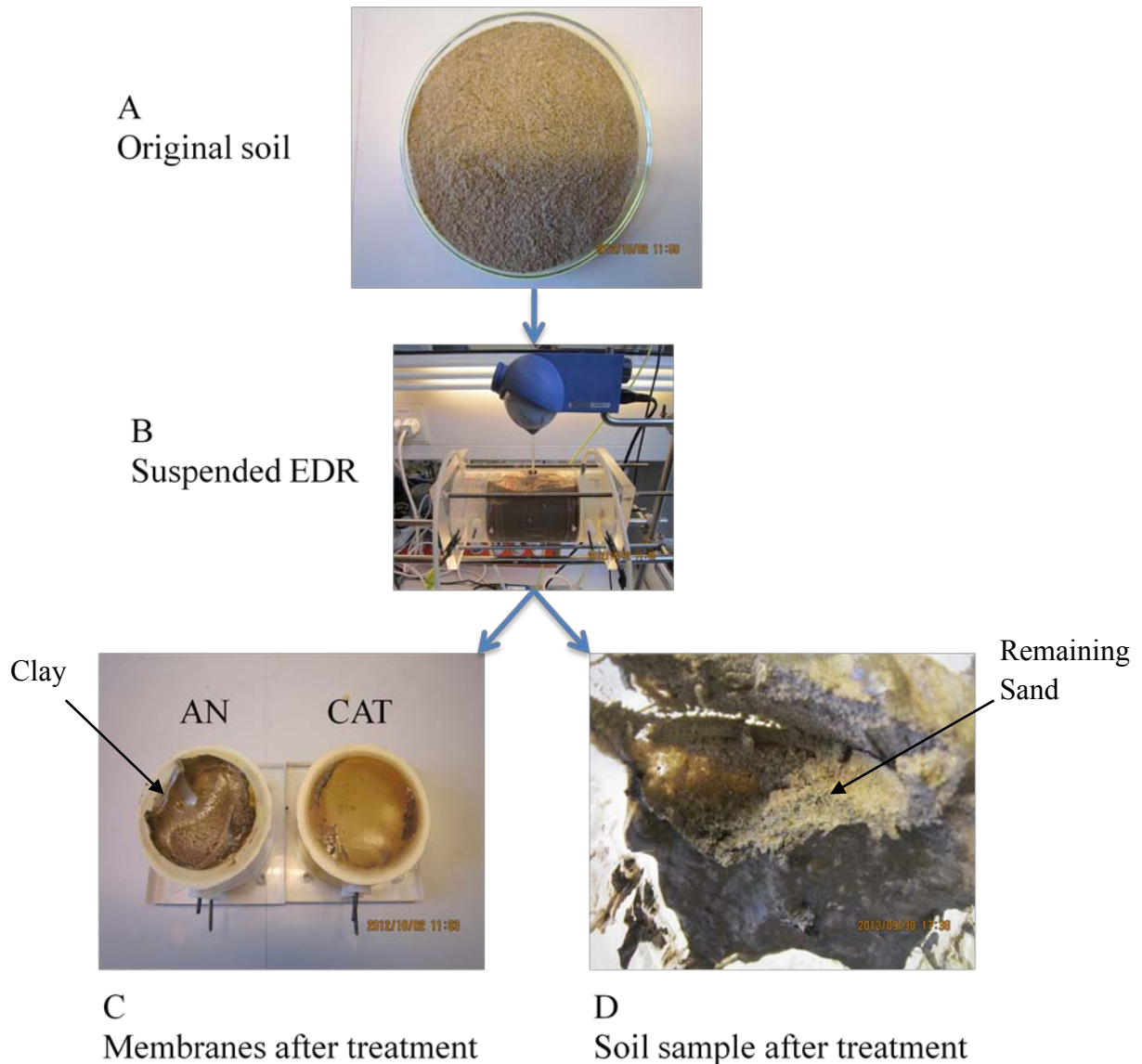
Figure 3. The electrophoresis of clay particles after suspended EDR treatment (AN=anion exchange membrane and CAT=cation exchange membrane, the applied current was 30 mA and L/S=2.5).

It can be seen from Figure 3 that after treatment most clay particles were transported to the anion exchange membrane side and attached on it (Figure 3C). Only sand or other uncharged particles remained in the soil samples (Figure 3D). The most important aspect of this electrophoresis phenomenon is the induced fouling of anion exchange membrane which results in a high voltage drop across the membrane (~30 V) and waste of energy.

1.4 Acidification processes in EDR

In general, the pH in soil samples decreased during EDR treatment and the decreasing pH is an important factor influencing the mobility of heavy metals by dissolution and desorption. The H^+ ions causing the acidification process come from water splitting at the bipolar interface between anion exchange membrane and clay particles, and transport towards the cathode by carrying the current (Mani, 1991; Ottosen et al., 2000a). As illustrated in Figure 4 that due to the negatively charged clay particles, a bipolar interface between anion exchange membrane and clay particles was formed, which depleted the ionic species rapidly in this region.

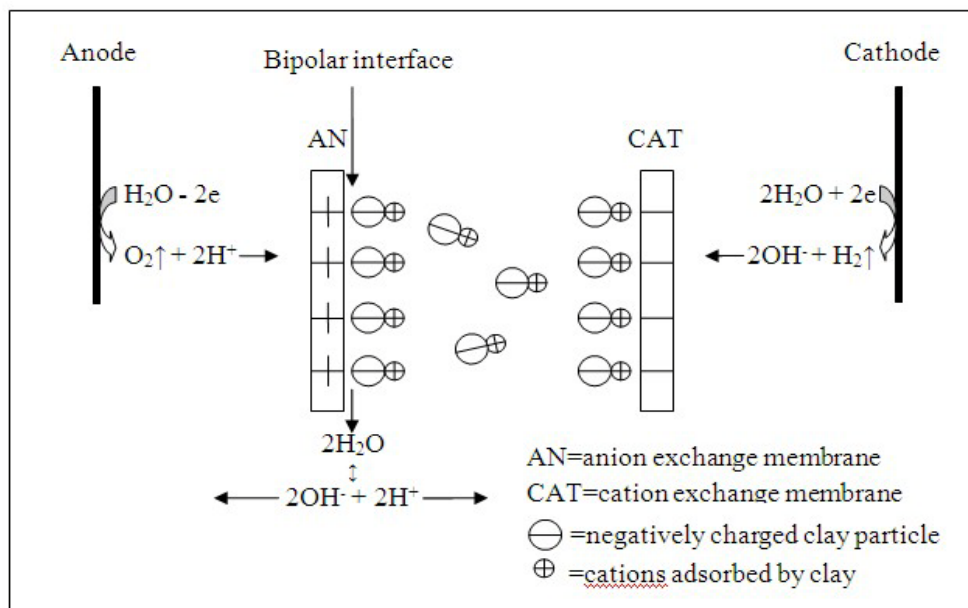Figure 4. Description of the bipolar interface and the following water splitting process between anion exchange membrane and clay particles.

Water splitting can also take place at the cation exchange membrane, and can hinder the remediation process, as it results in an increased soil pH and the re-precipitation of the heavy metals in the area near cation exchange membrane. Ottosen et al. (2000a) found the limiting current

density for the cation exchange membrane to be between 0.3 and 0.5 (mA/cm^2) for the actual soil of their experiments. No water splitting was detected near the cation exchange membrane as the soil pH was not higher than initial value in all experiments conducted in this study.
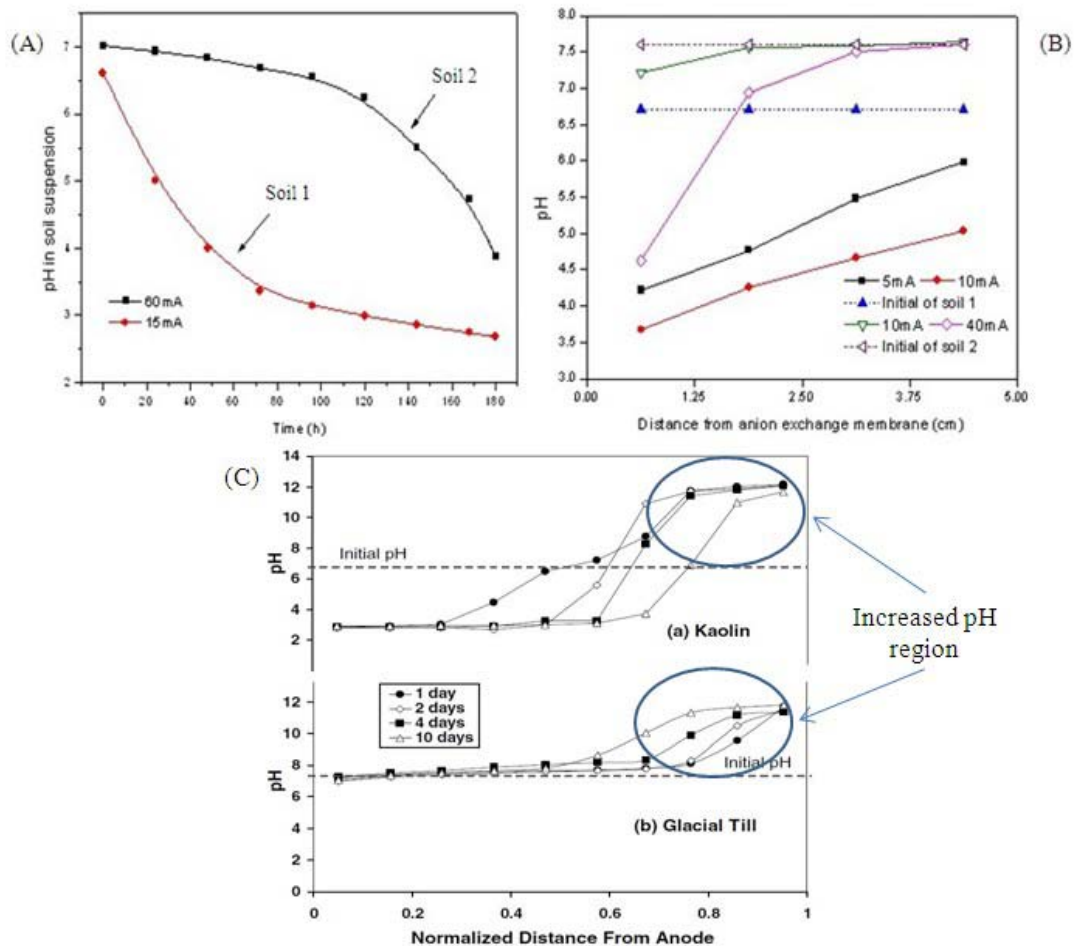
Figure 5. Examples of acidification processes in suspended EDR (A), stationary EDR (B), and EKR (C) cited from (Al-Hamdan and Reddy, 2008).

Figure 5 is the example of acidification processes in suspended EDR (A), stationary EDR (B), and EKR (C). Due to the different buffering capacity of experimental soils 1 (lower buffering capacity) and 2 (higher buffering capacity), the acidification pattern differed. It can be seen from Figure 5A, for soil 2, a "lag-period" was observed before a fast decrease in pH, during which the acidification overcame the buffering capacity of soil, whereas a continuous drop of the pH after

applying the current was seen for soil 1. From Figure 5B, it is obvious that the acidification starts at the anion exchange membrane due to water dissociation, and the acidic front is moving in the soil slice by slice toward the cathode. The extent of acidification is higher in experiments with higher applied current than that with lower applied current. Figure 5C is the pH profile after EKR treatment cited from (Al-Hamdan and Reddy, 2008). The major difference between stationary EDR (Figure 5B) and EKR (Figure 5C) is the pH variation at cathode side. Due to the cation exchange membrane which impedes the transport of OH^- ions from catholyte to soil column, the pH at cathode side in EDR would not higher than the initial value, but in EKR the pH values higher than initial are obtained at cathode side. This region with increased pH will result in a re-precipitation of mobilized heavy metal (transported from anode side) and influence the removal efficiency.

1.5 Mobility of heavy metals

Once the adequate acidification process occurs, heavy metals are desorbed and removed from the soil under the driving force of the electric potential difference, as most heavy metal cations are dissolved in acidic conditions (Alloway, 1995).

Acid front development, as well as heavy metal desorption/dissolution, depends on many factors and the extent to which the factors have influence on the remediation action are dependent on the soil type and the heavy metal itself. The pH and redox conditions in the soil are both important factors affecting heavy metal retention, and a change of these parameters may be beneficial to the remediation. Soil pH affects both the adsorption of heavy metals in exchange sites, the specific adsorption of heavy metals, as well as many dissolution processes. Some heavy metals are removed at higher pH (i.e. slightly acidic) than others. The order of removal of different heavy metals in the acidic front has been reported as follows: $Ni \approx Zn > Cu > Cr$ in a soil polluted from a chlor-alkali

factory (Suer et al., 2003) and Zn > Cu > Pb or Cd > Zn > Cu > Pb > Ni in different industrial polluted soils (Ottosen et al., 2001; Jensen, 2005).

The chemical speciation of heavy metals in soil influences the removal efficiency by determining the mobilization extent of heavy metals. Five fractions (Tessier et al., 1979) are generally used to estimate the speciation of heavy metals, (I) exchangeable, (II) bound to carbonates, (III) bound to Fe-Mn oxides, (IV) bound to organic matter, and (V) residual. Carbonate and exchangeable fraction are easy to mobilize according to previous researches (Ottosen et al., 2009), and followed by fraction (III) to (V). Brief descriptions of different fractions are listed below:

I. Loosely held contaminants, including the exchangeable and soluble forms, that can be readily extracted (extraction procedure represents mild extracting conditions).

II. Tightly adsorbed contaminants and those associated or co-precipitated with carbonates. This fraction would be susceptible to changes of pH.

III. Additional soluble metal oxides/hydroxides under slightly acidic pH as well as contaminants that are associated with Fe-Mn oxides.

IV. Contaminants associated with easily oxidizable solids or compounds, including organic matter.

V. Contaminants present at the crystal structure of clay minerals and as consolidated oxides and strongly held complexes (e.g. metal sulfides).

Unless the transport of the acid front is retarded by the buffering capacity of the soil, the chemistry across the specimen will be dominated by the transport of the hydrogen ion. The carbonate content, organic matter, clay content, as well as cation exchange capacity (CEC) of the mineral that may react with the acid would increase the buffering capacity of the soil (Acar and Alshawabkeh, 1993). Kaolinite clays show much lower buffering capacity because of lower CEC compared with other clay minerals, such as montmorillonite or illite. The carbonate content is more susceptible than other indicators (i.e. CEC, clay content, and organic matter) since during the

acidification process, the calcium carbonate will react with H^+ ions first and with a higher extent. A research reported in (Ottosen et al., 2009) indicated that the acid demand for acidification of the experimental soils correlates well with the carbonate content.

For cationic species Cu, Zn, Pb, Cd, and Ni, it was found that the slice closest to anion exchange membrane that was remediated first and the transport direction was towards the cathode. For Cu, good removal percentages of up to 99% Cu was obtained in unenhanced systems; however, the duration of the successful experiments was very long. In general, the best results are obtained after a long period of applied current of more than 1 month of treatment. Enhancement in the case of Cu is mainly focused on a faster acidification of the soil, and thus remediation. Citric acid showed good results. The acid demand for soils with high buffer capacity is high, and in such soils the enhancement may be the addition of a complex binder for Cu so the remediation can occur at neutral to alkaline pH. An example of this is ammonia (Ottosen et al., 2000). For Zn, remediation results between 17% and 99% have been obtained. Most results are good, with >70% removal. The low removals were obtained in experiments of either short duration (Kim and Kim, 2001) or with calcareous soils (Maini et al., 2000; Ottosen et al., 2005; Wieczorek et al., 2005). This corresponds well to Zn being among the easiest heavy metals to mobilize by EKR (Ottosen et al., 2001; Suer et al., 2003). For Pb, some really low remediation percentages (0% – 10%) were obtained in studies of calcareous soil (Maini et al., 2000) and tailing soil (Kim and Kim, 2001), whereas around 50% removal was obtained in studies of different sludges (Khan and Alam, 1994; Kim et al., 2005). Highly successful removals (92%–98%) were obtained in full scale, as well as in a study of non-calcareous soil (Clarke et al., 1996; Ottosen et al., 2005). Apart from confirming the fact that acidification, and thus buffer capacity, is a determinant of remediation success, it is difficult to deduct any conclusions from the results since Clarke et al. (1996) give no detailed information about remediation conditions. However, it seems that long remediation times are necessary for

successful removal (Ottosen et al., 2005). For Cd, both high and low remediation efficiencies have been reported for unenhanced treatment. It seems that the removal success is highly dependent on site and speciation. Low pH in the soil clearly favors the removal. For Ni, general low removal efficiency without any enhancement even for 2 months' processing. Only Clarke, Lageman, and Smedley (1997) showed that a high removal efficiency could be achieved but remediation time and conditions were not mentioned, so it could not be evaluated if the remediation was enhanced or not.

By contrast to the cationic species, it was found that As accumulated in the anolyte as a compound with negative charges (probably $H_2AsO_3^-$) not as ionic species precipitated on the surface of anode, which was against the direction of acidic front. Previous results with stationary EDR (Ottosen et al., 2000) showed that the As was immobile (as non-charged $As(OH)_3$ or H_3AsO_3) under acidic and neutral conditions, but good removal was obtained by addition of either ammonia or hydroxide to maintain the alkaline conditions (pH>9), suggesting that the As (III) was the dominating species in those soils. But in suspended EDR the oxygen and carbon dioxide concentrations could be assumed to be in equilibrium with atmosphere, which should allow for oxidation of As (III) to moveable species $H_2AsO_4^-$ or $HAsO_4^{2-}$ and facilitated the removal of As in a large range of pH (Jensen, 2005).

1.6 Energy consumption in EDR cells

The energy consumption of electrochemically based remediation techniques is an important factor influencing costs and thus the applicability. For an application of these techniques beyond bench and pilot scale setups, this aspect is very important. Generally, in an electrodialytic cell, the applied electrical potential is sufficient to overcome the ohmic resistance, the potential drop across the membranes, the dialysate and concentrate compartments drop due to concentration gradients

(diffusion potential), potential drop at working electrodes, and the potential drop at the membrane-solution interfaces (Donnan potential) (Belfort and Guter, 1968; Tanaka, 2003). In electrodialytic remediation, the potential drop at electrodes and in the anolyte and catholyte could be assumed negligible compared to the value of other parts, especially when the electrolytes are circulated (Bard and Faulkner, 2001). Further, as most fine grained soils have a negative charged surface like a cation exchanger, and the positive ions removed from the soil are in excess of the negative ions, the removal processes are briefly controlled by two steps: (a) the transport in the contaminated soil and (b) the transport across the cation exchange membrane, which are also expected to be the main energy consumption steps.

1.7 Polarization processes in EDR cells

Polarization, as an inevitable process, is responsible for the nonproductive energy consumption. In the EDR system, it includes the polarization of electrodes, membranes and clay particles in the soil.

The electrode polarization is controlled by electrochemical polarization and/or concentration polarization, depending on the different rates of the electrode reactions and mass transport processes (Bard and Faulkner, 2001). Electrochemical polarization is due to the slower rate of electrode reaction compared to the mass transport process which results in an accumulation of net charges between the electrode and electrolyte interface. On the contrary, concentration polarization is due to the slower rate of mass transport process compared to the electrode reaction which causes the decreasing of electrolyte concentration at the vicinity of electrode and deviation of electrode potential from its equilibrium value. However, in EDR the electrodes are placed in compartments

separated from the soil by ion exchange membranes and electrolytes are circulated in the electrode compartments, which reduce the electrode polarization.

Concentration polarization occurs in all membrane separation processes. In electrodialysis it is the result of differences in the transport numbers of ions in the solution and in the membrane. The net result of the difference is a reduction of the electrolyte concentration in the solution at the surface of the membrane, and a concentration gradient is established in the solution between the membrane surface and the bulk solution. This concentration gradient results in a diffusive electrolyte transport. A steady state is obtained when the additional ions, that are needed to balance those removed from the interface due to the faster transport rate in the membrane, are supplied by the diffusive transport. When the applied current density reaches the limiting current density of the membrane, water splitting ($H_2O \rightarrow H^+ + OH^-$) will happen at the interface between membrane and solution as a consequence of the concentration polarization (Tanaka, 2007; Strathmann, 2010). The optimum current for electrodialytic soil remediation is when the limiting current of the anion-exchange membrane is exceeded while that for the cation-exchange membrane is not (Ottosen et al., 2000a). The limiting current density of an anion exchange membrane in EDR is much lower than that of a cation exchange membrane because there are fewer anions than cations in soil solution. Further, next to the anion exchange membrane is the negatively charged soil surface, and a bipolar interface depleting ions rapidly is formed in between. This interface can be compared to a bipolar membrane, which is a membrane that consists of a layered ion-exchange structure composed of a cation selective layer (with negative fixed charges) and an anion selective layer (with positive fixed charges) (Xu, 2002). The water splitting of the anion exchange membrane is of crucial importance for development of an acidic front through the soil in which heavy metals mobilized. The acidic front will cause a rise in potential drop at the bipolar area. At the cation exchange membrane, at sublimiting current density (current density under the limiting value), the concentration polarization

will induce the increase in resistance at the boundary layer, both of which can increase the potential drop of membrane.

In a compacted soil system, the most active part interacting with the external electric field is the clay particles (Sposito, 1989). It is hypothesized that the polarization processes of the clay particles mainly include polarization of the diffused double layer (Figure 6A) and induced polarization (Figure 6B). Due to the nonconductive bulk of clay particles, the diffused layer will move towards the opposite pole under applied electric field and give rise to a characteristic dipole moment, similar to the dielectric polarization (Derjaguin et al., 1980; Kornilovich et al., 2005). The polarization results in an induced electric field at the vicinity of clay particles, which is opposite and counteracted to the applied electric field thus impedes the transport of ions. In other words, more energy will be consumed to maintain an identical charge transport of cations compared to a non-polarized clay matrix. However, this polarization effect could be considered as negligible small in a real soil. The above discussion of double layer polarization concerns an individual particle, but particles are in physical contact in a compacted soil. As the distance between particles decreases, the polarization weakens. The reason is that lines of electric force of the local fields of polarization charges close not on a particle's own surface like shown in Figure 6A, but on the nearby polarization charges of the neighboring particles. As a result, instead of a dipole with a particle size in the first case, dipoles with inter-particle distance size are formed. At the same time, not only the length of the dipole decreases but the amount of polarization charges themselves declines (Kornilovich et al., 2005).

The induced polarization in the clay pore fluid (Figure 6B) plays more important role at increasing the energy consumption in EDR than double layer polarization at clay surface. Two mechanisms are possible explanations for induced polarization (Sumner, 1976; USEPA, 2003). (1) Charges accumulate at both sides of pore space which narrow to within several boundary layer

thicknesses when an electric field is applied. Result is a net charge dipole which adds to any voltage measured at the surface. (2) Due to the incompatibility between the conductivity of the clay particles with low surface conductivity and the surrounding electrolyte solution (i.e. pore fluid) with high ionic conductivity (Pamukcu et al., 2004), induced space charge will probably occur with a potential difference across the interface layer, similar to the charging of the ionic double layer at the electrode-electrolyte solution interface.
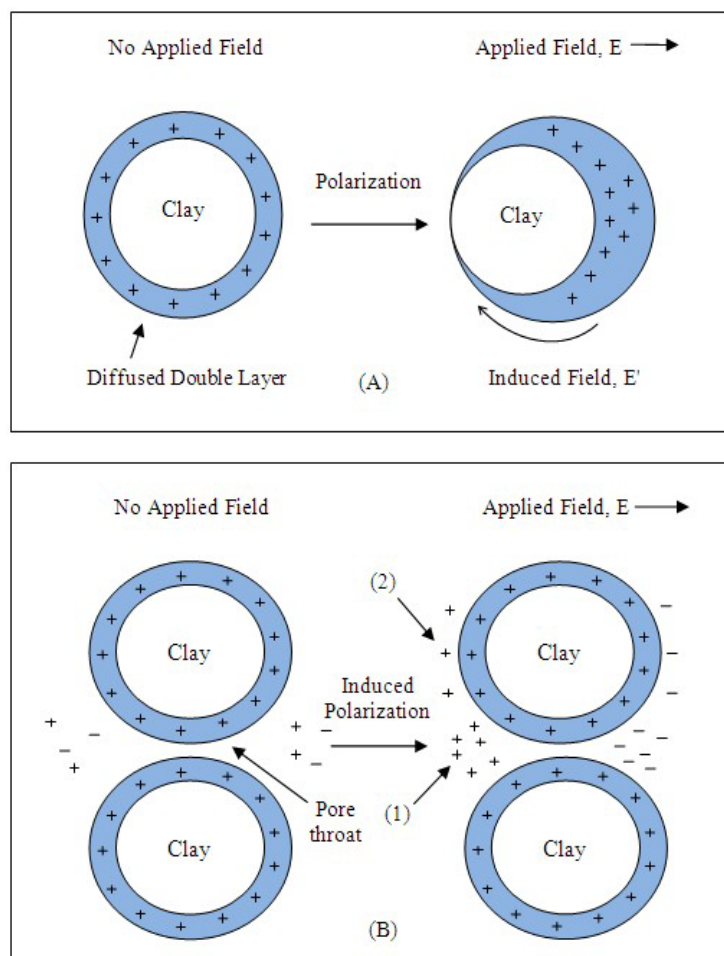

Figure 6. Schematic description of the polarization processes in clay matrix with (A) polarization of the diffused double layer and (B) induced polarization.

Considering the connection between clay particles and pore fluid as in series, the total potential drop (V_t) between two monitoring electrodes across the soil compartment in the EDR system under an external applied electric field can be expressed as:

$$V_t = (V_{eq} + V_R) + \eta \tag{2}$$

according to the expression of the potential drop in the electrolysis between anode and cathode (Bard and Faulkner, 2001), where V_{eq} is the potential drop under equilibrium state, V_R is the ohmic potential drop induced by the pore fluid, and η is the overpotential.

1.8 Applications of pulsed electric field

It has previously been reported that the application of a pulsed electric fields can give substantial improvements in the performance of pressure-driven membrane processes by reduction of concentration polarization, control of membrane fouling and increase in the membrane selectivity (Mishchuk et al., 2001; Lee et al., 2002). However, the fouling phenomenon has merely been observed in EDR soil cells. The transference number of the membranes and perm-selectivity did not change after being used in electrodialytic soil remediation experiments (Hansen et al., 1999). The positive result gained by application of pulsed current for EDR may mainly be a diminishing of the effect from polarization gradients and thus requirement for a lower potential to supply the same current. At electrokinetic remediation, researchers have also investigated application of a pulsed electric filed to improve the remediation process. A summary of experiments and results when applying a pulsed electric field in electrokinetic and electrodialytic soil remediation is shown in Table 2. It can be seen that the pulsed electric filed improve the remediation process by means of increasing the removal efficiency of heavy metals and/or decreasing the energy input for remediation.

Table 2. Summary of pulsed electric field application in electrokinetic and electrodialytic soil remediation.

Experimental setup	Power supply	Pulse mode (ON time/OFF time)	Frequency (cycles/h)	Enhancing effect
EKR (Kornilovich et al., 2005)	Constant voltage 1-10 V/cm	5s/5s 10s/10s 15s/15s 0.1-0.9s/0.9-0.1s	360 180 120 3600	The use of pulse voltage changes the distribution of contaminations in soil and allows decreasing power inputs.
EKR (Ryu et al., 2009)	Constant voltage 1-3 V/cm	1s/1s 1s/1s 2s/1s 1s/2s 1s/2s	1800 1800 1200 1200 1200	A high pulse frequency enhanced the removal efficiency of the heavy metals compared to a low pulse frequency at a supplied voltage gradient of 1 V/cm.
EKR (Jo et al., 2012)	Constant voltage 1 V/cm	15min/15min 30min/30min 60min/60min 120min/120min 240min/240min	2 1 0.5 0.25 0.125	The pulsed electrokinetic process lowered the electrical energy consumption to 42% of that of the conventional process, while producing a similar decrease in salinity.
EKR (Reddy and Saichek, 2004)	Constant voltage 1-2 V/cm	5days/2days	0.006	Considerable contaminant removal can be achieved by employing a high voltage gradient along with a periodic mode of voltage application.
EKR (Cérémonie et al., 2008)	Constant voltage 0-6 kV/cm	-/~5ms	-	A significant increase of 330% of the total heterotrophic culturable bacteria 2 days after soil samples was found resulting from pulsed electric current injections.
EKR (Rojo et al., 2012)	Constant voltage 15-22.8 V	20s/1s 2000s/100s 3000s/200s 2500s/100s	171 1.7 1.1 1.3	Pulses in a sinusoidal electric field improve the EKR process, especially when the pulses and a polarity inversion in the sinusoidal electric field are present simultaneously, since both phenomena reduce polarization during the process.
EDR (Hansen and Rojo, 2007)	Constant voltage 20 V	100min/5min 50min/2.5min 25min/1.25min	0.6 1.2 2.3	Applying pulsed electric fields in EDR, it was found that the remediation time decreased compared to dc EDR. Increasing the pulse frequency, the copper removal in the anode side is improved, and in the cathode side an accumulation is observed.

Identification of knowledge gaps based on Table 2:

A. All these reported works were performed using pulse voltage; there was no information about the effect of pulse current on the remediation process.

B. The chosen of applied pulse frequency seemed random and the reasons for using these frequencies were not given, therefore there is a need for a method to determine the optimal frequency.

C. The mechanism of the enhancement on remediation induced by pulsed electric field was not clarified.

In the present PhD study, these gaps were filled out.

Generally the pulse mode is determined by the ratio of current "ON" time to current "OFF" time. A relatively low pulse frequency (e.g. 30 cycles per day) should be applied when the pulsed electric field is introduced to improve the EDR process. The pulse mode in stationary EDR can be expressed as $t_{ON}/t_{OFF}=a/x$, with "a" indicating the fixed current "ON" time and "x" indicates that the "OFF" time is a variable and determines the effectiveness of applied pulse mode.

In suspended EDR the pulse mode is $t_{ON}/t_{OFF}=x/a$, with the "ON" time as variable based on the different transport process of H^+ ions between stationary and suspended EDR. For example, in stationary EDR, the effective mobility of H^+ ions in the soil pore fluid is 760×10^{-6} cm^2 V^{-1} s^{-1}. In suspended EDR, the ionic mobility of H^+ ions could be approximately estimated as its value in aqueous solution, which is 3625×10^{-6} cm^2 V^{-1} s^{-1} (Acar and Alshawabkeh 1993). So the time for the transport of H^+ ions from the anion exchange membrane to the cation exchange membrane in stationary EDR is around 3.7 h under unit electric field strength and assuming the distance from the anion exchange membrane to the cation exchange membrane is 10 cm, but in suspended EDR it will only take 0.8 h for the same transport process. This means that there is a much longer time for the contact between H^+ ions and soil particles in stationary EDR than that in suspended EDR. The use

of x/a mode is not only because of the higher ionic mobility of H^+ ions in suspended EDR, but also because of the fast reaction rate during the "OFF" time since the stirring system highly increases the contact between H^+ ions and soil particles and thus increases the reaction rate. Therefore, the variation of "OFF" time in suspended EDR will hardly influence the efficacy of the pulse regime.

2. Research methodology

Two types of soils contaminated with different heavy metals were chosen for this study. The NORD soil was sampled from a wood preservation site and contaminated by Cu and As, and the KMC soil was sampled from a pile of excavated soil and contaminated by Cu and Cd. Information about experimental setup (EDR cells), analysis of soil characteristics, experimental design, and sample collection and data analysis after experiment are given in e.g. Appendixes I. The title, aim, and relation of the appendixes to the knowledge gaps are listed in Table 3.

Table 3. List of Appendixes with title, aim, and relation to the knowledge gap.

Appendix	Title	Aim	Relation to knowledge gap
I	Effects of pulse current on energy consumption and removal of heavy metals during electrodialytic soil remediation	The aims of this paper were to investigate the possibility for energy saving when using a pulsed electric field during electrodialytic soil remediation (EDR) and the effect of the pulsed current on removal of heavy metals.	A
II	Effect of pulse current on acidification process and removal of heavy metals during suspended electrodialytic soil remediation	The effect of pulse current on acidification process and removal of heavy metals during suspended electrodialytic soil remediation was investigated in this work.	C

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III	Pulse current enhanced electrodialytic soil remediation – Comparison of different pulse frequencies	This work is focused on the comparison of energy saving effect at different pulse frequencies. Based on the restoration of equilibrium, the relaxation process of the soil–water system was investigated by chronopotentiometric analysis to find the optimal relaxation time for energy saving.	B
IV	Electrodialytic soil remediation enhanced by low frequency pulse current – Overall chronopotentiometric measurement	The effect of low frequency pulse current on decreasing the polarization and energy consumption during the process of electrodialytic soil remediation was investigated in the present work.	C
V	Reduction of hexavalent chromium in contaminated clay by direct current transported ferrous iron: Kinetics, energy consumption, and application of pulse current	The effect of pulse current on reduction of hexavalent chromium in contaminated clay was investigated in this work.	A, C
VI	Electrodialytic remediation of suspended soil – Comparison of two different soil Fractions	The present paper focused on the processing parameters for remediation of a soil polluted with Cu and As from wood preservation.	—
VII	The effect of pulse current on energy saving during electrochemical chloride extraction (ECE) in concrete	This paper investigated the possibility for energy saving when using a pulsed electric field during ECE and the effect of the pulsed current on removal of chloride.	—

Characteristics of the used membranes reported in (Xu, 2005; Tanaka, 2007) and by the supplier are listed in Table 4.

Table 4. Characteristics of the ion exchange membranes used in this study.

Company	Product	Name	Type	Thickness (mm)	IEC (mol/g)	Electric resistance (Ω/cm^2)	Ionic transport number	Bursting strength (kg/cm^2)	Features
Ionics	Nepton	AR204 SZRA B02249C	AN	0.57	2.3-2.7	3	0.95	7.0	Desalination
		CR67 HUY N12116B	CAT	0.58	2.1-2.45	2	0.89	7.0	Desalination

Note: AN=anion exchange membrane, CAT=cation exchange membrane, and IEC=ion exchange capacity.

Figure 7 show the set-up for the pre-chronopotentiometric measurement of the transition time of membranes, which was conducted by automatic record of the potential drop between the saturated calomel electrodes inserted on both sides of the membranes. The potential drop was recorded by a datalogger (Agilent 34970A) with a rate of once per 5 s.
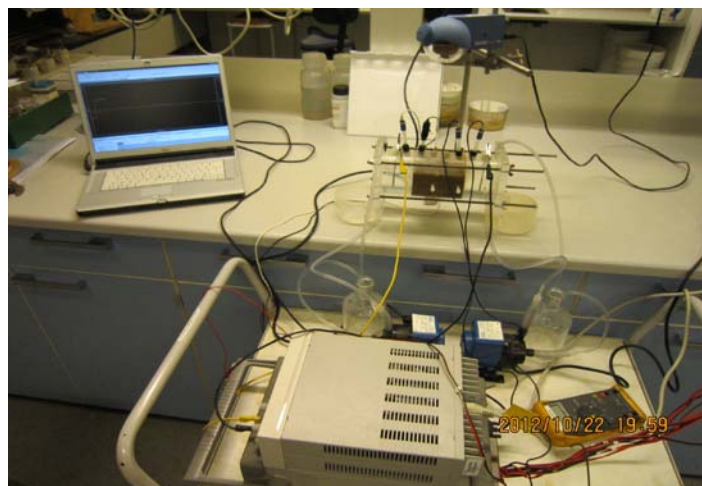

Figure 7. Photograph of the pre-chronopotentiometric measurement of membranes.

3. Major findings from the experimental work

3.1 Energy distribution in EDR cells

In all experiments a constant current was applied, and therefore the variation in potential is an indicator for the energy consumption. The distribution of potential drop over the cell with soil during stationary EDR is shown in Figure 8 (from Appendix IV). It can be seen that the total potential drop increases over time. The increase is fastest in beginning of the experiment. The potential drop is lowest in the electrolyte solutions in the anolyte and the catholyte compartments during the whole experiment. This is due to the circulation systems and that pH was controlled

around 2 during the experiment, so the conductivity of the solution was high. The potential drop

over the cation exchange membrane including interphases to soil and catholyte (part c in Figure 8)

was significantly higher than over the anion exchange membrane and related interphases (part a)

and over the soil (part b) after 12 h working time and increasing with time. This is seen from the

slopes of part c. The part with cation exchange membrane was thus the most energy consuming part.

In other words, when constant voltage was applied, the step transporting cations through the cation

exchange membrane was the rate controlling step, by which the kinetics of the whole EDR process

was determined. The increased potential drop at part c was probably due to the re-precipitation and

crystallization of dissolved metal ions at the surface of cation exchange membrane (Figure 9)

caused by the higher pH in the soil solution near cation exchange membrane. It can be seen from

Figure 9 that many solid deposits unevenly distributed at the surface of cation exchange membrane

after experiment, but not at the surface of anion exchange membrane. SEM-EDX mapping revealed

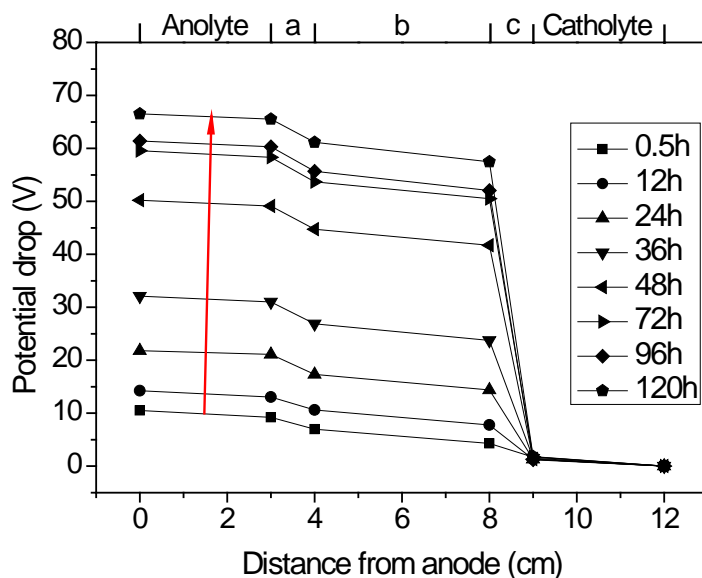that these solids are a mixture of aluminum and calcium oxides.

Figure 8. Distribution of potential drops across the stationary EDR cell, with "a", "b", and "c" indicates anion exchange membrane, soil compartment, and cation exchange membrane, respectively.
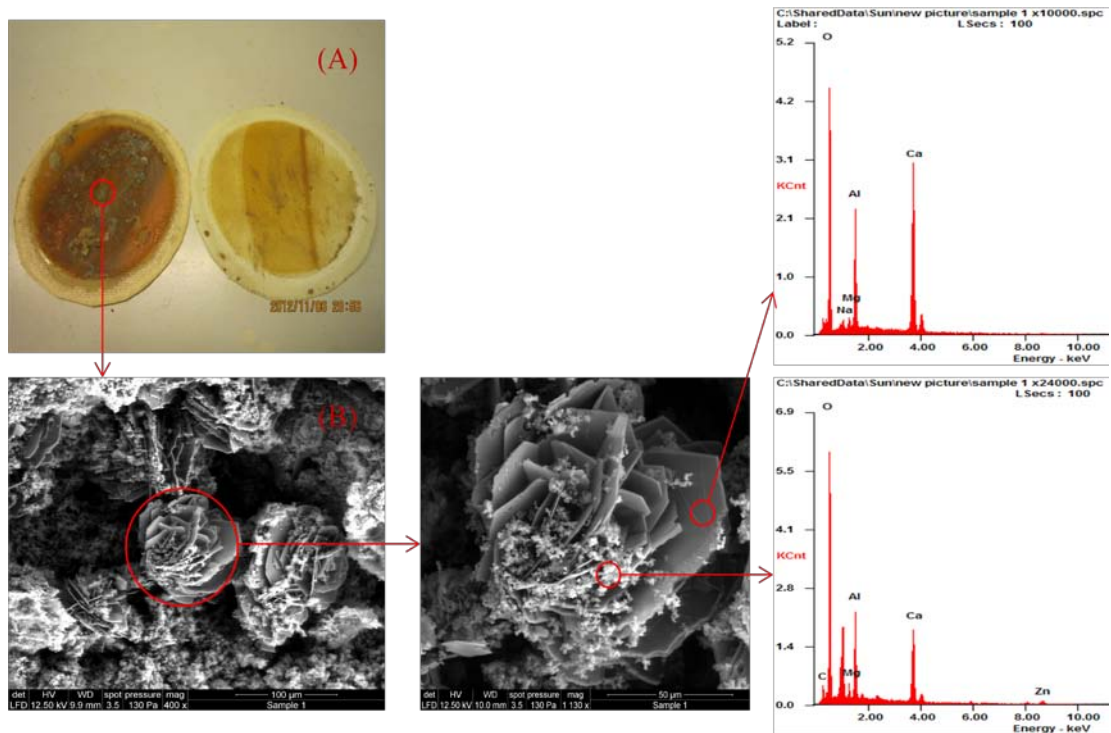
Figure 9. Photograph of anion exchange membrane (right) and cation exchange membrane (left) after experiment (A) and the SEM-EDX mapping of the solids on cation exchange membrane (B).

Unlike stationary EDR with highest energy consumption over the cation exchange membrane, the major energy consumption in suspended EDR was in the soil compartment as shown in Figure 10. In the soil suspension, both the amount of frees ions and the electric mobility of the ionic species are higher than that in stationary EDR, so less energy was needed for transport of ionic species across the membranes. But at the same time the depletion of free ions caused an increasing of resistance in the soil suspension which gave rise to higher energy consumption in the soil compartment.
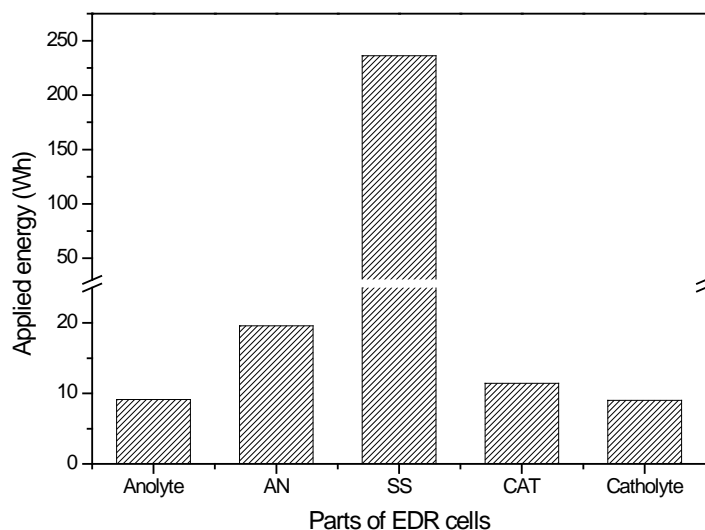
Figure 10. Energy consumption at different parts of suspended EDR cell (AN=anion exchange membrane, SS=soil suspension, and CAT=cation exchange membrane).

3.2 Effect of pulse current on energy consumption and heavy metal removal

In the present PhD study it was demonstrated that the pulse current had positive effects on energy savings and improvement of heavy metal removal during EDR treatment by enhancing the acidification process, increasing the electric conductivity in soil pore fluid, and diminishing the polarization process of membranes and soil particles (Appendix I-V). Basically, all these effects are due to the additional proceeding of chemical dissolution in the relaxation period when the current was switched off, which improves the effectiveness of H^+ ions in dissolution ad desorption reactions rather than to carrying of current. When the current is applied again, there are more target ions and less H^+ to maintain the mass transport process in soil-water system. The efficacy of the pulse current was found dependent on the applied current density, soil buffering capacity, and applied pulse frequency.

3.2.1 Effect of applied current density on pulsed EDR

The effect of the pulse current was tested for different applied current densities (Appendix I). Results showed that at a current density of 0.1 mA/cm^2 in the NORD soil and 0.2 mA/cm^2 in the KMC soil, there was no difference in energy consumption and removal of heavy metals between pulse current and constant current experiments. At higher current densities though, i.e. 0.2 mA/cm^2 in NORD soil and 0.8 mA/cm^2 in KMC soil, energy was saved 67% and 60% and the removal of heavy metals was increased 17-76% and 31-51% by pulse current in NORD soil and KMC soil, respectively.

3.2.2 Effect of soil buffering capacity on pulsed EDR

The effect of pulse current on EDR of the KMC soil (with high buffering capacity) and the NORD soil (with low buffering capacity) were investigated in Appendix II. The buffering system existed in soil is the first mechanism reacting with the produced H$^+$ ions and impeding the heavy metal mobilization. The H$^+$ ions are produced ($P_H{}^+$) by water dissociation at anion exchange membrane surface under over-limiting current density. Afterwards, part of them will be current carrier ($I_H{}^+$) since the ionic mobility of H$^+$ ions are much higher than other ions and a high transference number could be expected. $I_H{}^+$ is the amount of H$^+$ ions transported into the cathode side from anion exchange membrane, passing through soil suspension and cation exchange membrane. The other part will release the heavy metals from soil particles and is defined as reactive H$^+$ ions ($R_H{}^+$). This part includes (I) the amount of H$^+$ ions conquering the soil buffering capacity (e.g. carbonate content and organic matter), (II) desorption (i.e. cation exchange) of non-specific adsorbed heavy metals, (III) dissolution of co-precipitated heavy metals, and (IV) mobilization of

specific adsorbed heavy metals from soil minerals combined with destroy of mineral lattice by H^+ ions. Simplified expression by equation is $P_H{}^+ = I_H{}^+ + R_H{}^+$. To improve the efficiency of EDR is actually to increase the ratio of $R_H{}^+/P_H{}^+$.

The results showed that pulse current improved the acidification process by supplying more reactive H^+ ions. The molar ratio of reactive H^+ ions to total produced H^+ ions ($R_H{}^+/P_H{}^+$) was higher in pulse current experiments than constant experiments. Correspondingly, the removal efficiencies of heavy metals were also improved. However, the effect of improvement on the acidification process and the removal of heavy metals were more significant in the KMC soil than in the NORD soil. The positive effect from energy saving caused by pulse current was clearly shown experimentally since both the total energy consumption and the energy consumption per removed milligram heavy metals were lower in pulse current experiments than in constant current experiment in both soils. Moreover, the decrease in total energy consumption was higher in the KMC soil (up to 33%) than that in the NORD soil (up to 11%), which is anticipated related to the higher carbonate content in the KMC soil because in the soil with higher buffering capacity, more ions would be released after a pulse than that in the soil with low buffering capacity under a similar condition of acidification; therefore higher extent of energy saving was achieved.

3.2.3   Effect of applied pulse frequency on pulsed EDR

A comparison of energy saving effects at different pulse frequencies in stationary EDR is given in Appendix III. The applied pulse program was 60 min "ON" in every experiment, and 5, 15, or 30 min "OFF", which means the frequency was approximately 22, 19 or 16 cycles per day. Finding the optimal relaxation time is important since it determines both of the lowering of energy consumption by the pulse current and the duration of the treatment. It must on one hand be long enough to

complete the relaxation and on the other hand as short as possible to minimize the treatment time. The optimum duration of the relaxation period ("OFF") is thus the time for restoration of equilibrium state.
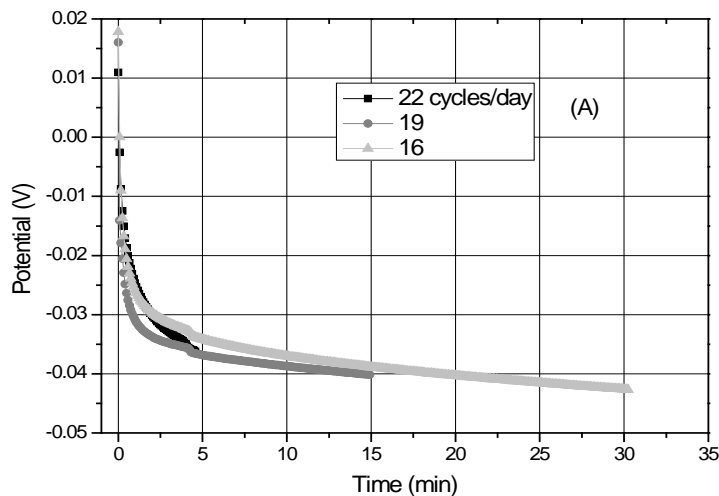
The relaxation process of the soil-water system was investigated experimentally by chronopotentiometric analysis to find the optimal relaxation time for energy savings. The results showed that the pulse current decreased the energy consumption to varying extent depending on the pulse frequency. The experiment conducted with a frequency of 16 cycles per day showed the best restoration of equilibrium (i.e. re-equilibrium processes) and lowest energy consumption.

The re-equilibrium processes at the relaxation period found by the chronopotentiometric analysis are given in Figure 11 with (A) for the initial stage i.e. in the beginning of the experiment, (B) for the middle stage, and (C) for the late stage. At the initial stage (Figure 10A), a similar relaxation trend was obtained in different pulse experiments. The experiment with frequency of 16 cycles per day showed the best condition approaching the equilibrium which can be seen from its relatively stable potential difference at relaxation period, followed by the experiment with 19 cycles per day, and the experiment with 22 cycles per day was far from equilibrium. It was hypothesized that The re-equilibrium process was determined by (1) the discharging of soil double layers driving by the electrostatic force, which was indicated by the sharp decrease in the potential after switching off the current; and (2) concentration gradients are built during the period with applied current and in this phase of the relaxation, these concentration gradients are leveled out by diffusion, which was indicated by the slow decrease in Figure 11A. In the middle stage (Figure 11B); the slight increase in potential after the initial drop in all pulse current experiments was probably due to a diffusion potential. Diffusion potential occurs when two solutions of different concentrations are in contact with each other. The more concentrated solution will have a tendency to diffuse into the comparatively less concentrated one. The rate of diffusion of each ion will be roughly proportional

to its speed in an electric field. If the anion diffuses more rapidly than the cation, it will diffuse ahead into the dilute solution, leaving the latter negatively charged and the concentrated solution positively charged. So a potential difference will be produced at the junction of the two solutions. In a simple case with two same kind of electrolytes (1:1) but different concentration ($a_{i,1} < a_{i,2}$), the diffusion potential could be expressed as:

$$E = -\frac{RT}{zF}(2t_+ - 1)\ln\frac{a_{\pm,2}}{a_{\pm,1}}$$ (3)

where t_+ is the transference number of cations, $a_\pm$ is the average activity of electrolyte. There is no simplified equation to quantitatively express the diffusion potential in a soil-water system. However, the pH and ionic strength are considered as the most important factors influencing the diffusion potential by changing the ionic mobility and the activity coefficient (Yu and Ji, 1993). The H^+ ions produced by water dissociation near the anion exchange membrane and transported towards the cathode causes acidification resulting in dissolution process within the soil, which can give rise to huge difference in pH and ionic strength even over short distances in the soil, thus the diffusion potential increases.
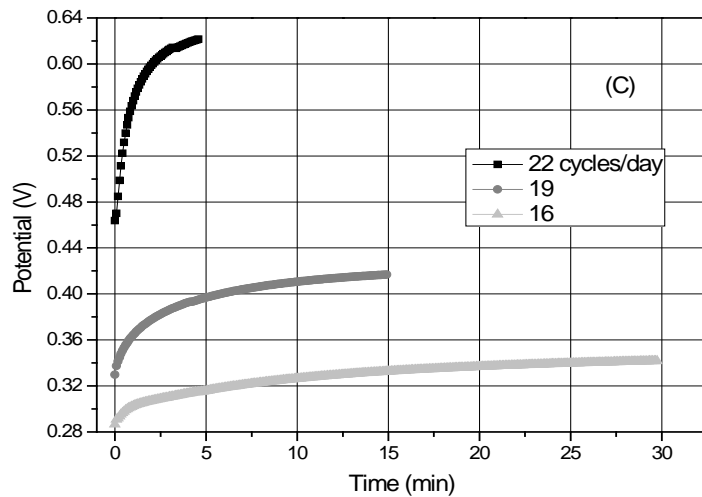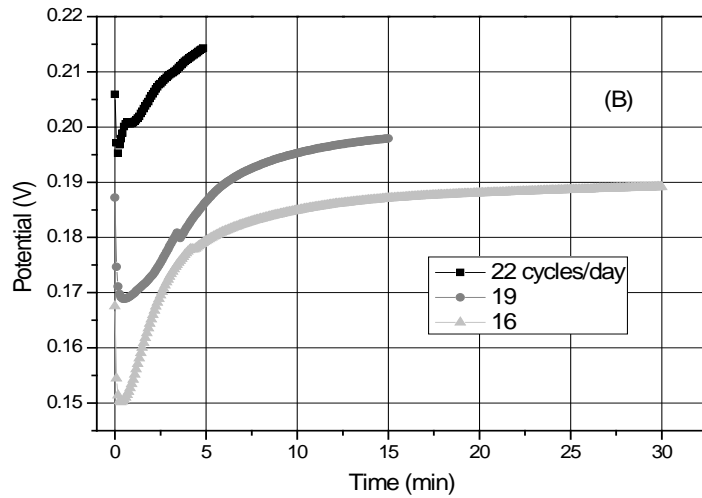
Figure 11. Selected chronopotentiometric measurements (form Appendix III) of the relaxation processes within the soil compartment. The initial, middle and late stages of the experimental duration are represented by (A)-(C), respectively.

In the late stage (Figure 11C); the discharging processes, which was seen in the two former stages, cannot be identified in any of the experiments. This does not necessarily mean that this discharging process is not occurring but the process was possibly masked by the high diffusion potential. The potential range (0.16, 0.09, and 0.06 V for experiment with pulse frequency 22, 19, and 16 cycles/day, respectively) in this stage may be an indicator for the deviation of the system

from the equilibrium state after the remediation process. From Figure 11C, it can be seen that the experiment with 22 cycles/day had the largest deviation from the equilibrium state, while it for the experiment with 16 cycles/day was smallest. Therefore, it can be concluded that the suitable relaxation time for the present experimental soil was between 15 to 30 min from the viewpoint of both energy consumption and remediation time.

As mentioned earlier (Chapter 1.8), the efficacy of pulse current on suspended EDR is determined by the current "ON" time rather than on relaxation ("OFF") time as in stationary EDR. Therefore, in suspended EDR, another factor the so-called transition time becomes important. The transition time is the time from application of current till the concentration at the membrane surface decreases to zero. The occurrence of a transition time indicates that an overlimiting current density has been applied over the anion exchange membrane. An overlimiting current here is enhanzing the remediation as it results in water dissociation at the anion exchange membrane, acidification of the soil suspension by the produced H^+ ions following mobilization of heavy metals. It can be seen from Figure 12 that the transition time decreased with the increase in applied current density. Due to the lower concentration of ionic species (shown by the conductivity data) in the solution with the NORD soil compared to the solution with the KMC soil, the transition time was shorter for the NORD soil than for the KMC soil under the same current density. In principal, water dissociation will occur as long as the experimental time is longer than the transition time, no matter what constant current density is applied to the EDR. In the EDR cells with pulse current, the transition time is highly important since it gives the highest limit of the pulse frequency. For example, at the applied current density of 1.2 mA/cm^2 for the KMC soil and 0.3 mA/cm^2 for the NORD soil (Appendix xx) the transition time was 1.4 and 0.9 min respectively. Therefore, the current "ON" time must not be shorter than these values at the actual current densities; otherwise the water

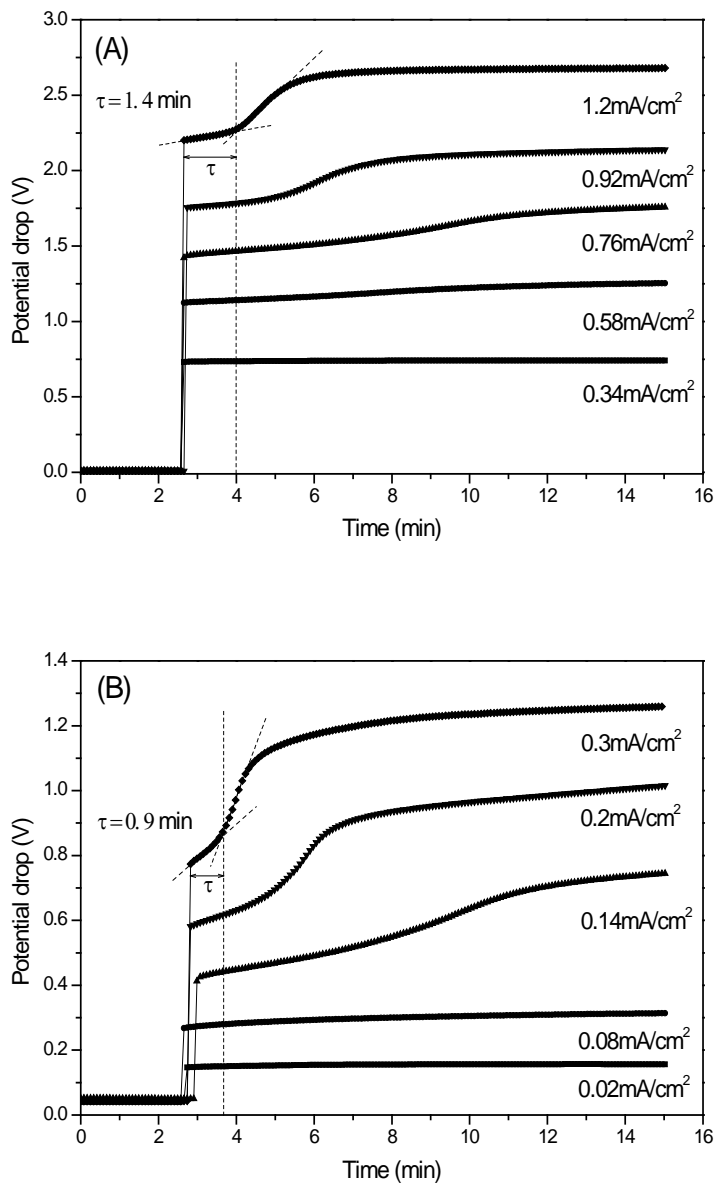dissociation will be diminished by diffusion of anionic species towards the anion exchange membrane.

Figure 12. Chronopotentiogram of anion exchange membrane with (A) for KMC soil and (B) for NORD soil.

4. Overall conclusions

This PhD study investigated the effect of pulse current (in low pulse frequency) for reducing the energy consumption and increasing the removal efficiency of heavy metals during the EDR process. Results showed that the pulse current had positive effects both on energy saving aspect by increasing the electric conductivity in soil pore fluid and diminishing the polarization process of membranes and soil particles, and improvement of removal of heavy metals by enhancing the acidification process.

Applied current density, soil buffering capacity, and applied pulse frequency were found as the major important factors to determine the efficacy of pulse current. In stationary EDR, the efficacy of pulse current was more significant at higher current density, higher buffering capacity, and lower pulse frequency (i.e. adequate relaxation time with respect to the current "ON" time). Moreover, a re-equilibrium (i.e. the restoration of the soil-water system to its equilibrium state after the passing of current) mechanism at relaxation period was proposed to determine the optimal pulse frequency for its application. On the contrary, in suspended EDR, higher pulse frequencies were preferred due to the different transport process of H^+ ions soil in pore fluid of stationary EDR and soil suspension of suspended EDR.

The major part of the supplied energy was consumed by transport of cations through the cation exchange membrane in stationary EDR, whereas major energy consumption was in the soil suspension in suspended EDR. Applying pulse current to the two types of cells, result in higher energy savings in stationary EDR (maximum 70% energy savings), compared to suspended EDR (maximum 33% energy saving).

It has been demonstrated the pulse current is a possible way to decrease the energy consumption and increase the removal efficiency of heavy metals during EDR processes, however, long-term tests are still needed in future studies to evaluate the possible efficacy decay of pulse current as a function of remediation time. Although the influences of applied current density and soil buffering

capacity on pulse current were investigated, the test range of current density and buffering capacity was narrow; therefore more experiments are needed for future study to make the conclusion more general. Moreover, clarification on the redistribution of ionic species in soil pore fluid and interaction between ions and soil particles at the relaxation period are also needed for better understanding the mechanism of pulse current in a microscopic viewpoint.

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Appendixes I-VII

Appendix I

Effects of pulse current on energy consumption and removal of heavy metals

during electrodialytic soil remediation

(Published in Electrochimica Acta)

Effects of pulse current on energy consumption and removal of heavy metals during electrodialytic soil remediation

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ABSTRACT

The aims of this paper were to investigate the possibility for energy saving when using a pulsed electric field during electrodialytic soil remediation (EDR) and the effect of the pulsed current on removal of heavy metals. Eight experiments with constant and pulse current in the different industrially polluted soils were performed. At a current density of $0.1 \, mA/cm^2$ in soil 1 and $0.2 \, mA/cm^2$ in soil 2, there was no difference on energy consumption and removal of heavy metals between pulse current and constant current experiments, but at higher current experiments (i.e., $0.2 \, mA/cm^2$ in soil 1 and $0.8 \, mA/cm^2$ in soil 2) the energy was saved 67% and 60% and the removal of heavy metals was increased 17–76% and 31–51% by pulse current in soil 1 and soil 2, respectively. When comparing the voltage drop at different parts of EDR cells, it was found that the voltage drop of the area across cation exchange membrane was the major contributor of energy consumption, and the pulse current could decrease the voltage drop of this part effectively. The overall removal of heavy metals in soil 1 (6–54%) was much higher than soil 2 (1–17%) due to the different acidification process and chemical speciation of heavy metals reflected by sequential extraction analysis. Among all experiments, the highest removal efficiency occurred in pulse current experiment of soil 1, where 54% of Cu and 30% of As were removed.

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1. Introduction

Electrodialytic remediation (EDR) is a method developed for removal of heavy metals from soils. The method is closely connected to electrokinetic remediation since the cleaning agent of both methods is application of a direct current to the soil. The electrodialytic remediation method differs from electrokinetic remediation in the use of ion exchange membranes for separation of the soil and the solution in the electrode compartments. The main purpose for using ion-exchange membranes is that ions are hindered in entering the soil from the electrode compartments. Therefore no current is wasted for carrying ions from one electrode compartment to the other [1]. The EDR technique has been applied for decontamination of e.g. soil, fly ash, and harbor sediment [2–5]. In previous works including both lab and pilot scale experiments, this technique has demonstrated effective removal of heavy metals from the contaminated materials. In the present work, the focus turns to energy saving aspect of EDR.

Generally, in an electrodialytic cell, the applied electrical potential should be sufficient to overcome the ohmic resistance, the potential drop across the membranes, the dialysate and concentrate compartments drop due to concentration gradients (diffusion potential), potential drop at working electrodes, and the potential drop at the membrane–solution interfaces (Donnan potential) [6,7]. However, in cases of electrodialytic remediation, the potential drop at electrodes and in the anolyte and catholyte could be assumed negligible compared to the value of other parts especially when the electrolytes are circulated [8]. Further, as most fine grained soils have a negative charged surface like a cation exchanger, and the positive ions removed from the soil are in excess of the negative ions, the removal processes are briefly controlled by two steps: (a) the transport in the contaminated soil and (b) the transport across the cation exchange membrane, which are also expected to be the main energy consumption steps. Concentration polarization occurs in all membrane separation processes. In electrodialysis it is the result of differences in the transport numbers of ions in the solution and in the membrane. The net result of the difference is a reduction of the electrolyte concentration in the solution at the surface of the membrane, and a concentration gradient is established in the solution between the membrane surface and the bulk solution. This concentration gradient results in a diffusive electrolyte transport. A steady state is obtained when the additional ions, that are needed to balance those removed from the interface due to the faster transport rate in the membrane, are supplied by the diffusive transport. When the applied current density reaches the limiting current density of the membrane, water splitting will happen at the interface between membrane and solution as a consequence of concentration polarization [9,10]. The optimum current for

Table 1
Characteristics of experimental soils.

	Soil 1	Soil 2	Limiting values of heavy metals
Cu (mg kg^{-1})	1502	1117	500
As (mg kg^{-1})	212	–	20
Cd (mg kg^{-1})	–	16	0.5
Organic matter (%)	2.1	6.5	
Carbonate content (%)	0.4	7.1	
pH	6.7	7.6	
Electric conductivity (mS cm^{-1})	0.4	2.1	
Clay (<0.002 mm)	5%	15%	
Silt (0.002–0.06 mm)	21%	61%	
Sand (0.06–2 mm)	72%	24%	

electrodialytic soil remediation occurs when the limiting current of the anion-exchange membrane is exceeded while that for the cation-exchange membrane is not [11]. The limiting current density of anion exchange membrane is supposed to be much lower than that of cation exchange membrane because there are fewer anions than cations in soil solution. Further, next to the anion exchange membrane is the negatively charged soil surface which forms a bipolar interface depleting ions rapidly. The water splitting of the anion exchange membrane is of great importance for development of an acidic front through the soil in which heavy metals mobilized. The acidic front will cause a rise in potential drop at this area. At the cation exchange membrane, under subliminal current density, the concentration polarization will induce the increase in resistance at the boundary layer, both of which can increase the potential drop of membrane.

It has been reported that the application of pulsed electric fields could give substantial improvements in the performance of pressure-driven membrane processes by reduction of concentration polarization, control of membrane fouling and increase in the membrane selectivity [12,13]. However, the fouling phenomenon has merely been observed in EDR soil cells. The transference number of the membranes and permselectivity did not change after being used in electrodialytic soil remediation experiments [14]. Thus use of pulsed current for EDR may diminish the effect of building up polarization gradients and thus require a lower potential to supply the same current. At electrokinetic remediation, researchers have also attempted to change the electric field to improve the remediation process. For example, Kornilovich et al. [15] indicated that pulse voltage changes the distribution of contaminations in soil and allows decreasing power inputs during electrokinetic remediation. Ryu et al. [16] found that pulsed electrokinetics could improve the removal efficiency of heavy metals and decrease the energy consumption at different extent depending on the pulse frequency. Therefore, the objectives of this paper are to investigate the possibility of pulsed electric field on energy saving of soil electrodialytic remediation and the effect on removal of heavy metals.

2. Experimental

2.1. Experimental soil

Two types of soils contaminated by different heavy metals were chosen for this study. Soil 1 was sampled from a wood preservation site, and soil 2 was sampled from the top layer on an industrial site. The soils were air-dried and passed through 2 mm mesh sieve. Some characteristics of the soils are shown in Table 1.

2.2. Analysis of soil characteristics

Concentrations of heavy metals were determined after pretreatment of the soil according to Danish Standard method DS259 [17]

where 1.0 g of dry soil and 20.0 mL (1:1) HNO$_3$ were heated at 200 kPa (120 °C) for 30 min. The liquid was separated from the solid particles by vacuum through a 0.45 mm filter and diluted to 100 mL. The Cu and Cd concentrations were measured with AAS. The As concentration was measured with ICP. Soil pH was measured by suspending 10.0 g dry soil in 25 mL distilled water. After 1 h of shaking, pH was measured using a Radiometer pH electrode. The content of organic matter was found as a loss of ignition after 1 h at 550 °C. The carbonate content was determined volumetrically by the Scheibler-method when reacting 3 g of soil with 20 mL of 10% HCl. The amount was calculated assuming that all carbonate is present as calcium-carbonate. Grain-size distribution was determined by wet-sieving approximately 100 g natural wet soil with 0.002 M Na$_4$P$_2$O$_7$ through a 0.063 mm 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 micrometritics® SEDIGRAPH 5100.

2.3. Desorption of heavy metals as a function of pH

To examine the pH dependent desorption of Cu, Cd and As from the soils, the following procedure was used: 5.0 g dry soil (dried at 105 °C for 24 h) and 25 mL HNO$_3$ in various concentrations (from 0.01 M to 1 M) were suspended for 1 week. The suspensions were filtered (0.45 mm) and the Cu and Cd concentrations in the liquid phase were measured with AAS and As with ICP. Extractions in distilled water were made as a reference.

2.4. Sequential extraction of heavy metals

Sequential extraction was performed according to the method described in the Standards, Measurements and Testing Program of the European Union [18]: 0.5 g of dry, crushed soil was treated in four steps as follows: (1) extraction with 20.0 mL 0.11 M acetic acid pH 3 for 16 h, (2) extraction with 20.0 mL 0.1 M NH$_2$OH·HCl pH 2 for 16 h, (3) extraction with 5.0 mL 8.8 M H$_2$O$_2$ for 1 h and heating to 85 °C for 1 h with a lid followed by evaporation of the liquid at 85 °C until it became almost dry by removal of the lid. After cooling down, 25.0 mL 1 M NH$_4$OOCCH$_3$ pH 2 was added, and extraction took place for 16 h. (4) Digestion according to DS 259 [17] was made for identification of the residual fraction (this step is an addition to the standard). All extractions were performed at room temperature, and samples in each step were made in triplicate.

2.5. Electrodialytic setup and experimental design

A laboratory cell for electrodialytic remediation is seen in Fig. 1. In compartment II, is the contaminated soil. Compartment II is separated from the electrolyte compartments I (anolyte) and III (catholyte) by ion exchange membranes (anion exchange membrane and cation exchange membrane, respectively). The electrodialytic cells were made from polymethyl methacrylate. Each cell had an internal diameter of 8 cm. The length of each cell compartment was 5 cm. The ion exchange membranes were commercial membranes from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum coated electrodes from Permascand were used. Between the two working electrodes, four monitoring electrodes (platinum coated electrodes) were used to monitor the voltage drop of different parts. A power supply (Agilent E3612A) was used to maintain a constant current. The pulse current was accomplished by a power supply timer instrument (Joel TE102), and the program was 1 h "on", 0.5 h "off". In each of the electrode compartments 500 mL 0.01 M NaNO$_3$ adjusted to pH 2 with HNO$_3$ was circulated. Due to the electrode processes, pH-changes occurred in the electrolytes. The pH in the electrolytes was manually measured
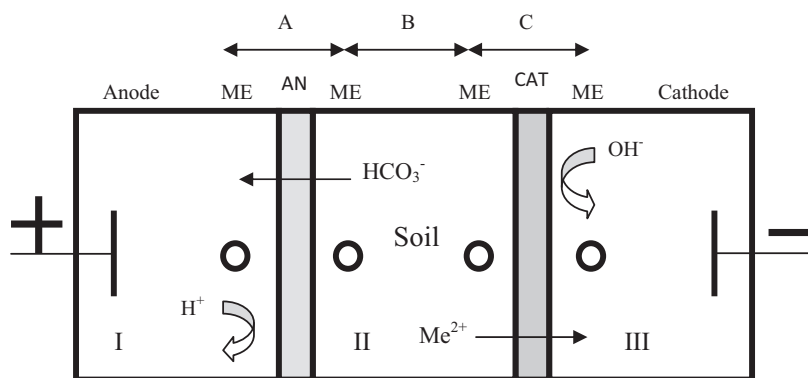
Fig. 1. Schematic diagram of the laboratory cell for electrodialytic soil remediation (CAT = cation exchange membrane, AN = anion exchange membrane, ME = monitoring electrode).

every 12 h and kept between 1 and 2 by addition of 1:1 HNO₃ and 5 M NaOH. At the end of the experiments, the contents of heavy metals in the different parts of the cell (membranes, soil, solutions, and electrodes) were measured. The soil samples were segmented to four slices, dried and crushed lightly in a mortar by hand before the measurement of heavy metal concentrations (three samples) and pH (three samples). The contents of heavy metals in the membranes were measured after extraction in 1 M HNO₃ and rinsing of the electrodes prior to measurement was done in 5 M HNO₃.

Eight electrodialytic experiments were performed as listed in Table 2. In all experiments, 370 g soil with 18% water content was in the central compartment. The duration was designed to maintain the identical working time between constant and pulse current experiments under the same current. A constant current was applied and the voltage was recorded by a multimeter.

The power consumption (E) was calculated as:

$$E = \int VI\, dt$$

where E is the power consumption (Wh); V is the voltage between working electrodes (V); I is the current (A); t is the duration (h).

The mass balance of an element was defined as the relation between the sum of mass found in the different parts of the cell at the end of the experiment and the initial mass calculated on basis of the mean initial concentration. The removal efficiency for each element was calculated as mass of the actual heavy metal at the parts of electrodes, electrolyte, and membranes, divided by the total mass found in all parts of the cell at the end of the experiment.

3. Results and discussion

3.1. Characteristics of heavy metals in soil

The experimental soil 1 was polluted by Cu and As, and the soil 2 was polluted by Cu and Cd. Also the Danish limiting values of heavy metals for sensitive land use are listed in Table 1.

Fig. 2 shows the concentrations of Cu, As and Cd extracted from soil 1 (A) and soil 2 (B) at different pH values. It is seen that desorption of the heavy metals increases with the decrease in pH from both soil 1 and 2. For Cu, the desorption pattern was quite similar between soil 1 and soil 2, which started between pH 5 and 6 and approached 100% at approximately pH 1. As in soil 1 was not desorbed before pH was below about 2. From soil 2, on the other hand, Cd already desorbed before pH 6 and 7. Below pH 1 complete desorption was reached for all heavy metals. A little As was extracted at higher pH; this was not necessarily mobile in the soil before the sampling. Mobile As is expected to be washed out to deeper soil layers, and the aeration of the soil sample between sampling and treatment may likely have influenced the mobility of As.

The distribution pattern of heavy metals in the two soils found from the sequential extraction is shown in Fig. 3. Generally, the carbonate and exchangeable part of heavy metals in soil is more removable than other parts, and the exchangeable part could be considered directly mobile by electromigration according to previous research [19]. As it was shown in Table 1, the carbonate content in soil 1 is much lower than that in soil 2. This probably means that the exchangeable fraction of heavy metals in soil 1 is more than that in soil 2. Combined with the residual part which is the most difficult part to remove, the removal order was expected to be Cu > As in soil 1 and Cd > Cu in soil 2. Moreover, through the comparison of Cu in soil 1 and soil 2, it can be seen that the residual fraction of Cu in soil 1 is much lower than that in soil 2, but the carbonate and exchangeable fraction is much higher. This probably indicates that a higher removal efficiency of Cu in soil 1 could be expected compared with soil 2.

3.2. Acidification process

The profile of pH in soil at the end of experiments is shown in Fig. 4. The decreasing pH is an important factor influencing the mobility of heavy metals by dissolution and desorption. The pH was lower than the initial value after EDR treatment which means that acidification occurred in all experiments though the extent was
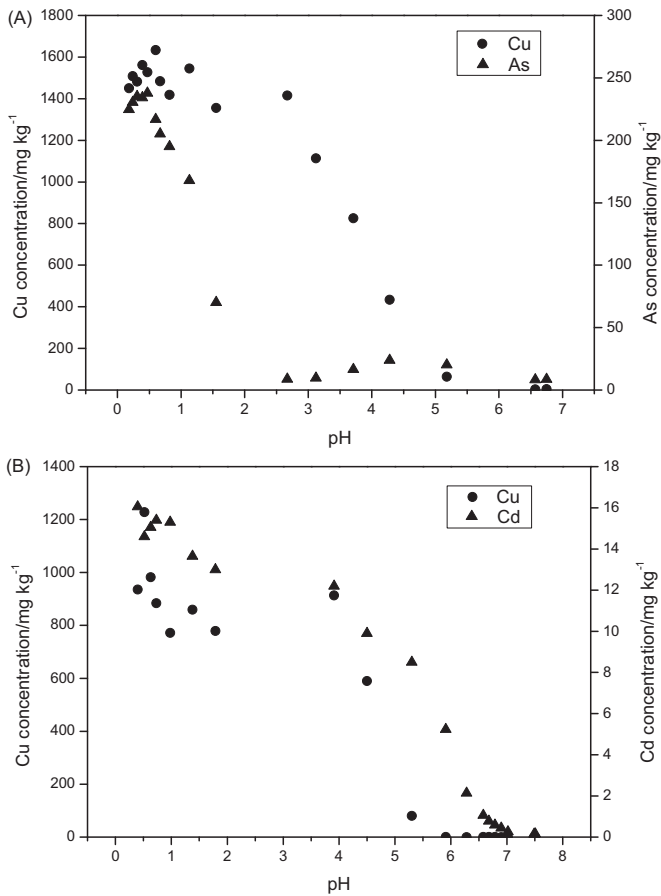
Table 2
Experimental design.

Experiments	Soil type	Current density (mA/cm⁻²)	Current type	Duration (working hours)
1C	Soil 1	0.1	Constant	240
1P	Soil 1	0.1	Pulse	240
2C	Soil 1	0.2	Constant	240
2P	Soil 1	0.2	Pulse	240
3C	Soil 2	0.2	Constant	240
3P	Soil 2	0.2	Pulse	240
4C	Soil 2	0.8	Constant	240
4P	Soil 2	0.8	Pulse	240

(A)

Fig. 2. pH dependent extraction of Cu, As and Cd from the soil 1 (A) and soil 2 (B).

Fig. 4. Profiles of soil pH developed after application of current.

different. The H+ ions causing the acidification process come from water splitting near the anion exchange membrane and transports toward the cathode by electromigration [1,11]. Water splitting can also take place at the cation exchange membrane, and can hinder the remediation process, as it results in an increased soil pH and the reprecipitation of the heavy metals in this area. Using a similar experimental setup, Ottosen et al. [11] found the limiting current density for the cation exchange membrane to be between 0.3 and 0.5 mA/cm^2 for the actual soil of their experiments. The soil in [11] was sampled at the same site as soil 1 in the present work.

A maximum 0.2 mA/cm^2 of current density was applied to the soil 1, so water splitting near cation exchange membrane was not expected. The soil 2 was applied up to 0.8 mA/cm^2 of current density, which was higher than the limiting current density mentioned above, but no water splitting was detected near the cation exchange membrane as the soil pH was not higher than initial value. The higher limiting current density at the cation exchange membrane is probably due to the higher conductivity in this soil (Table 1).

The acidic front passed through all soil slices in soil 1, but only a little in slice 1 in the 0.2 mA/cm^2 experiments and partly in slice 2 in the 0.8 mA/cm^2 experiments in soil 2. This difference was a result of different buffering capacity of the two soils. The buffering capacity of the soil (including the cation exchange capacity, available organic species and carbonate content) [20] will neutralize the acidification process during EDR treatment. In the present work, the carbonate content was chosen as a qualitative indicator of soil buffering capacity since it is more susceptible than other indicators [21]. The variation of the carbonate content in soil slices after experiments is shown in Fig. 5. After experiments, the decrease of carbonate content was more than the decrease of pH, which directly demonstrated the interaction between H+ ions and the buffering capacity. Additionally, the original organic matter and clay content of soil 2 were higher than soil 1, which also supported the higher buffering capacity in soil 2.
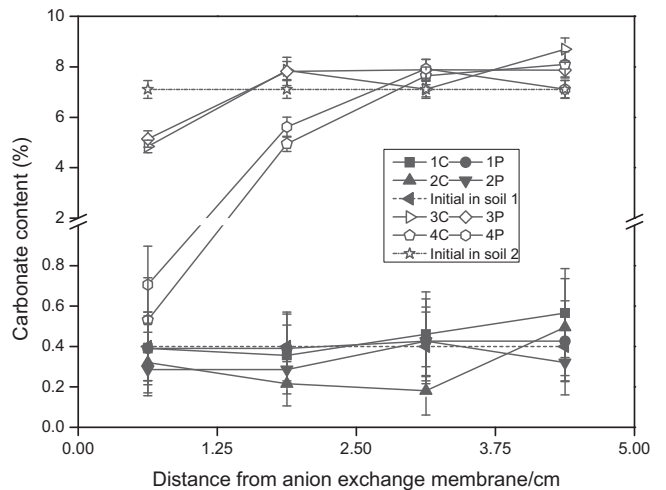

Fig. 3. Sequential extraction of Cu, Cd and As in soil 1 and soil 2.

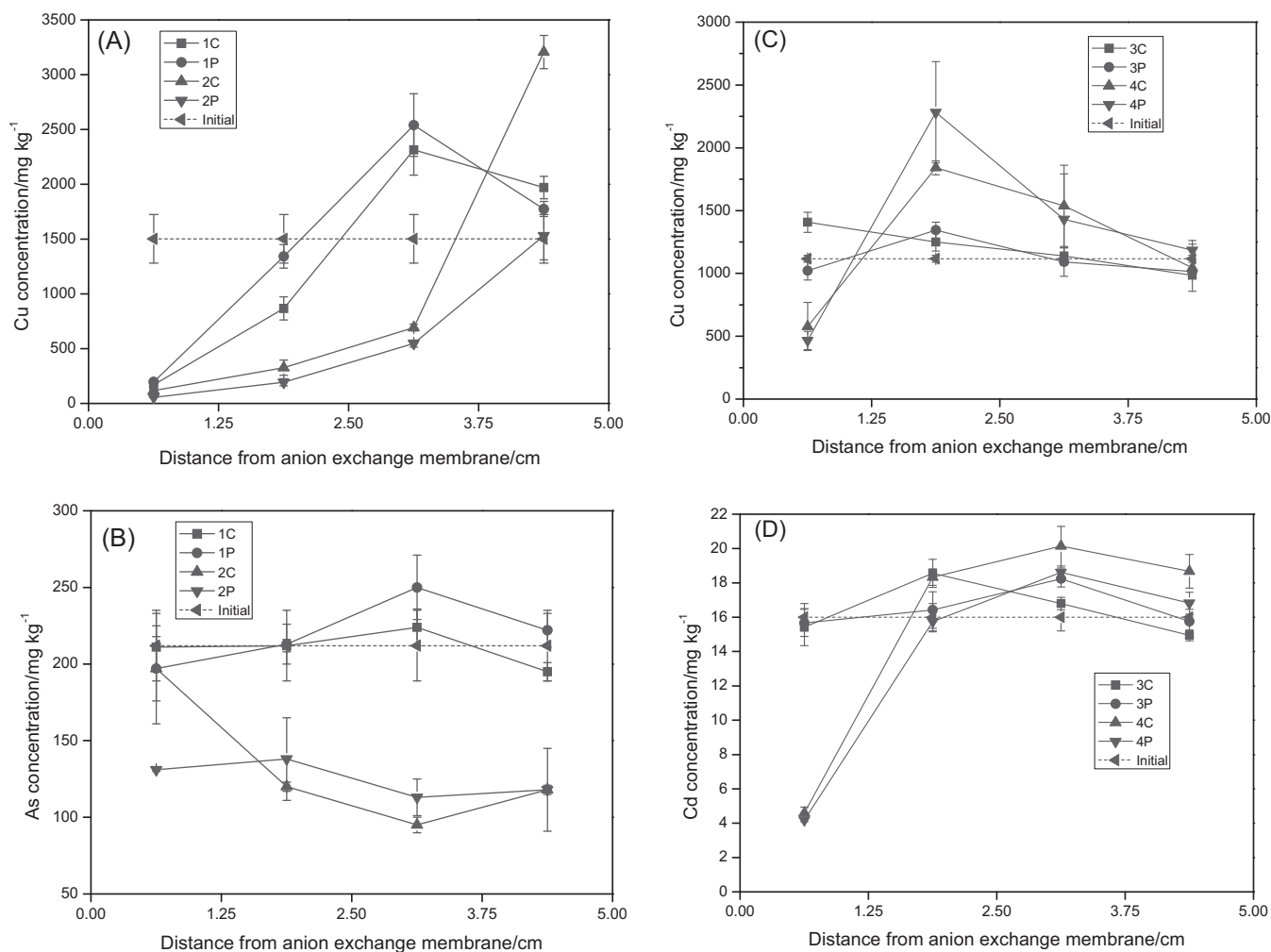**Fig. 5.** Profiles of soil carbonate content developed after application of current.

Fig. 6. Final profiles of heavy metals in the soil. (A) Cu in soil 1, (B) As in soil 1, (C) Cu in soil 2, and (D) Cd in soil 2.

3.3. Mobility of heavy metals

Fig. 6(A)–(D) shows the residual concentration of heavy metals in soil slices after treatment. The release of heavy metals and the following accumulation process from one slice to another are determined by pH [1].

In soil 1, Cu was mobilized as cation, because it was the slice closest to anion exchange membrane that was remediated first and the transport direction was toward the cathode. Cu accumulated in slice 3 in experiments 1C and 1P and in slice 4 in the experiments 2C and 2P (Fig. 6(A)). Arsenic was mainly found as uncharged species at the condition of low pH and moderate oxidation state [22], which means the more acidic the less mobile As for electromigration in soil with no access to air. At the end of the present experiments, it was found that As accumulated in the anolyte as a compound with negative charges (probably $H_2AsO_3{}^-$) not as ionic species precipitated on the surface of anode, which was against the direction of acidic front (Fig. 6(B)).

In soil 2, the 0.2 mA/cm² current density was too low and the duration of the experiments was too short to remove the heavy metals due to the high buffering capacity as discussed. The soil pH was more than 7 in all slices by the end of experiments 3C and 3P and at this pH neither Cu nor Cd were expected mobile in accordance to (Fig. 2(B)). In the two experiments with 0.8 mA/cm² current, both Cu and Cd were removed from slice 1 (i.e., at pH below 4.5), and accumulated at pH above 6.7 (slices 2 and 3) (Fig. 6(C) and (D)). The Cu accumulation was though most steep, which

corresponds well to Cd being mobile at a higher pH (Fig. 2(B)). It can be concluded that once the adequate acidification process occurs, heavy metals are desorbed and removed from the soil slice by slice under the driving force of electric field.

3.4. Energy consumption

In all experiments current was constant when applied, therefore the variation of voltage is an indicator of the energy consumption. Fig. 7 shows the variation of voltage (between working electrodes) in soil 1 (A) and soil 2 (B), respectively. The pulse pattern was not shown in the figures; because the data of voltage was recorded at the working (current on) time every 24 h in both the constant and the pulse current experiments. The voltage in the low current density experiments was not influenced by the pulse as experiments 1C and 1P as well as 3C and 3P were comparable. This is probably because the free ions in the soil solution are sufficient for low current transport. For the higher current density, as 0.2 mA/cm² in soil 1 and 0.8 mA/cm² in soil 2, the difference in voltage between constant and pulse experiments was significant. The pulse current experiments had much lower voltage. Furthermore the voltage in the pulse current experiments decreased with time, which means that the pulse current showed effective for energy saving in these experiments. When considering the comparison between soil 1 and soil 2 with the same current density (0.2 mA/cm²), the voltage was much lower in soil 2 than in soil 1 which is because of the higher conductivity in soil 2 than soil 1 (Table 1).

Table 3
Overall results of electrodialytic remediation.

Experiments	Mass balance (%) Cu/As/Cd	Removal efficiency (%) Cu/As/Cd	Energy consumption (Wh)	Energy consumption per removed Cu/As/Cd (Wh mg^{-1})
1C	95/113/–	6/14/–	12	0.4/1/–
1P	100/114/–	6/9/–	9	0.3/1.2/–
2C	85/94/–	13/25/–	128	2.1/7.1/–
2P	112/89/–	54/30/–	42	0.1/2/–
3C	110/–/109	1/–/7	10	2.6/–/22
3P	99/–/113	1/–/8	10	3.2/–/19
4C	117/–/130	1/–/8	382	73/–/588
4P	123/–/102	2/–/17	151	19/–/151

The voltage during experiments in the different parts of cell is shown in Fig. 8. Fig. 8(A) is the part across the anion exchange membrane measured between electrodes in the anolyte and in the soil, (B) is the part in soil compartment between, and (C) is the part across cation exchange membrane between soil and in the catholyte.

In the (A) part, the voltage increased first and obtained the maximum value after a period, then decreased or kept constant in all experiments. The increasing voltage was probably caused by the depletion of ions at the surface of anion exchange membrane due to concentration polarization. Afterward, water splitting supplied sufficient anions and cations to decrease the voltage drop and the produced H$^+$ ions initiated desorption and dissolution process resulting in increased conductivity. The variation in voltage in

the (A) part could verify the difference in acidification among the experiments (Figs. 4 and 5).

The voltage in the (B) part reflected the mass transport of ionic species in the soil–water system. In the soil–water system, the soil colloids and clay particles have fully developed diffuse double layers (DDL). When the ionic concentration in the pore solution where the current is passing is high, the ions within DDL diffuse and accumulate toward the clay surface, giving rise to concentration polarization. When the current pass through the system, potential variation in a certain extent can be used to describe the electrotransport and electrochemical transformation processes of ionic species in the soil solution and at the particle surfaces. In the soil solution, the driving force for the transport of ion comes from electromigration and electroosmosis, while at electrochemical surfaces, such as soil colloid or clay particles, double layer charging, redox reactions, and surface conduction can take place simultaneously [23]. Results showed that the voltage in part (B) in the pulse current experiments was lower than that in the constant current experiments. The lower voltage drop of the pulse current experiments at this part could be explained by diffusion that occurred in the pause time of pulse current experiments which probably decreased the overpotential caused by concentration polarization of DDL. Also, the charging and discharging cycles within DDL in the pulse current experiment could possibly decrease the electrochemical overpotential at the soil colloid surfaces.

Finally, the voltage in the (C) part (Fig. 8(C)) has a highly similar pattern and value compared to the voltage applied to the working electrodes (Fig. 7) in all experiments. This means the highest voltage drop occurred in the part across the cation exchange membrane, and that this part was the mainly contributor of energy consumption. However, the voltage in this part in the pulse current experiments was lower than that in the constant current experiments and decreased during the experiments. This indicated that the energy saving effect caused by pulse current in the whole EDR system was expressed by the energy saving in (C) part. The reason for this phenomenon was probably primarily the diffusion of ions at the pause periods in the pulse current experiments, which diminished the concentration polarization and increased the conductivity within and in the vicinity of the cation exchange membrane determined by Donnan equilibrium.

3.5. Electrodialytic experiments—overall results

The overall results from the EDR experiments are given in Table 3. As seen, the mass balances were between 85% and 130%, which is an acceptable range for inhomogenous industrially polluted soil. The removal efficiency of heavy metals in soil 1 (6–54%) was much higher than in soil 2 (1–17%) due to the differences in acidification level and heavy metal mobilization. The pulse current showed the possibility of energy saving from the viewpoint of lower voltage; however the efficacy on the removal of heavy metals also should be considered. The energy consumption per removed
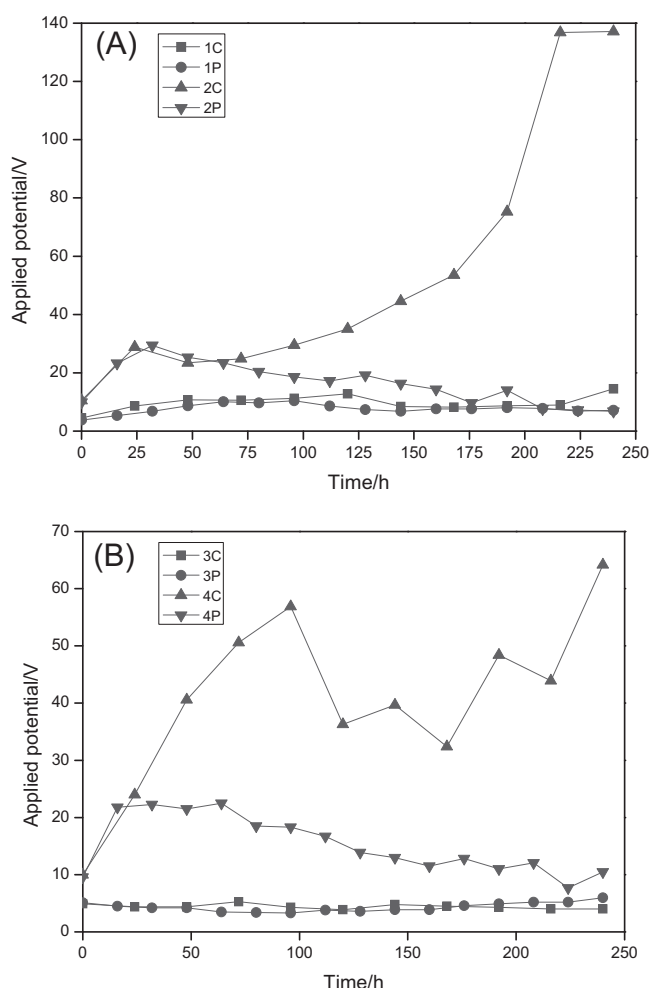
Fig. 7. Variation of voltage between working electrodes in soil 1 (A) and soil 2 (B).
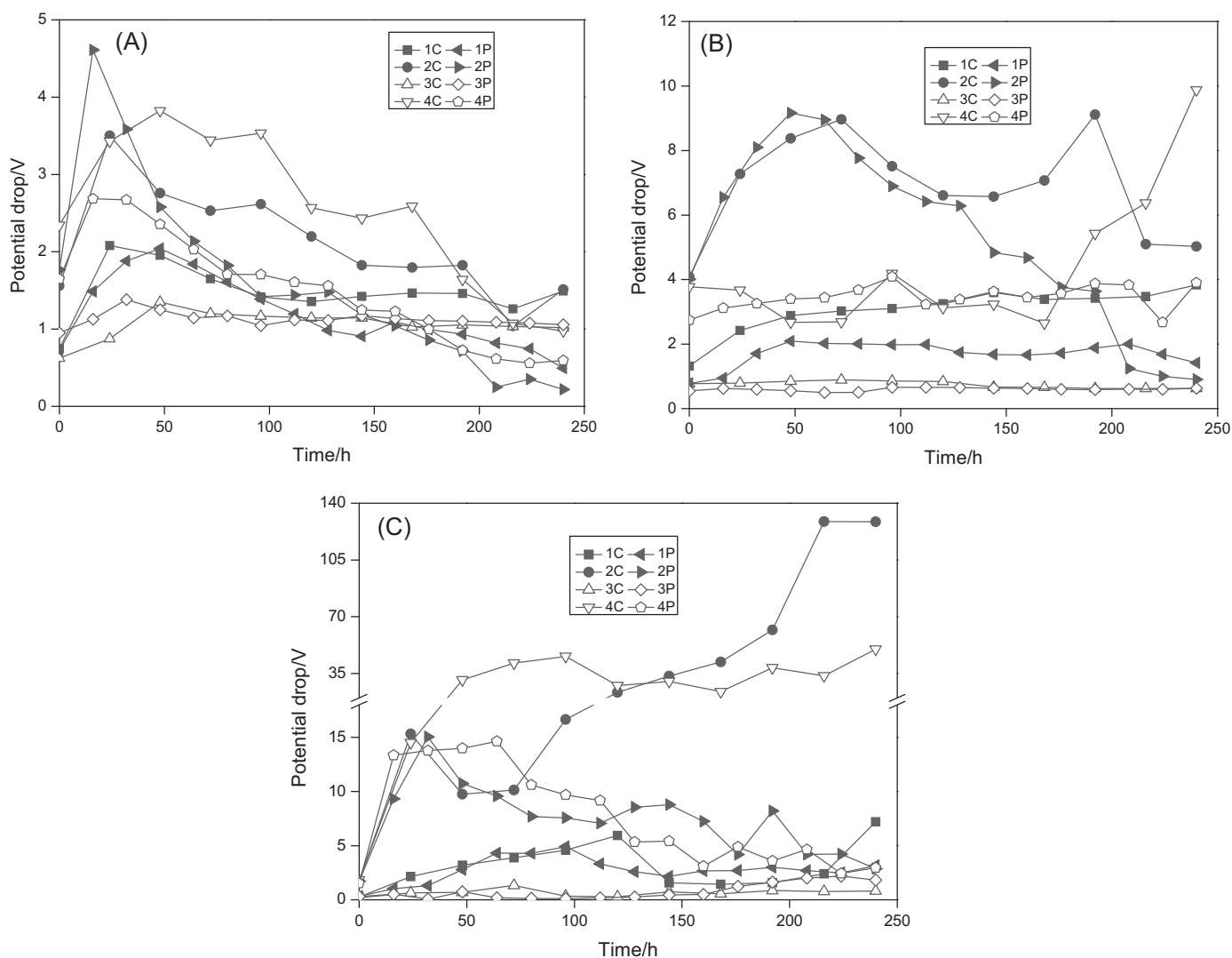
Fig. 8. Variation of voltage at different parts of EDR cells. (A) is the part across the anion exchange membrane with two monitoring electrodes one in anolyte and one in soil, (B) is the part in soil compartment with two monitoring electrodes both inside, and (C) is the part across cation exchange membrane with two monitoring electrodes one in soil and one in catholyte.

milligram heavy metals was much lower in soil 1 (0.4–7.1 Wh/mg) than soil 2 (2.6–588 Wh/mg), which meant the DC field was more effective in soil 1 compared to soil 2. This phenomenon was obviously demonstrated by the direct comparison of soil 1 (2C and 2P) and soil 2 (3C and 3P) with the same charge transfer. The Cu had higher removal efficiency than As in soil 1 and the Cd had higher removal efficiency than Cu in soil 2, which corresponds to their speciation in the soils (Fig. 3). At the lower current density applied (0.1 mA/cm^2 in soil 1 and 0.2 mA/cm^2 in soil 2) there was no difference in energy consumption and removal of heavy metals between the pulse current and the constant current experiments. At the experiments with higher current density (0.2 mA/cm^2 in soil 1 and 0.8 mA/cm^2 in soil 2) the energy consumption was saved 67% and 60% by pulse current in soil 1 and soil 2, respectively. The removal of Cu and As was increased by 76% and 17% in soil 1 and the removal of Cu and Cd was increased by 31% and 53% in soil 2 by the pulse current. The percentages were calculated as the difference of the energy consumption and removal efficiency value between the constant and the pulse current experiments divided by the values of the constant current experiments. The increased removal was probably because the rate of dissolution caused by H$^+$ ions was slow compared to the rate of transport of ionic species when the current was "on". A period when the current was "off" then allowed

the system to precede the chemical mechanisms of dissolution, and the species concentration in solution increased. When the current started again, there would be more targeted ions instead of H$^+$ to maintain the mass transport process in soil–water system.

4. Conclusions

The possibility for application of pulsed electric current for energy saving during electrodialytic remediation and the effect on removal of heavy metals were investigated. Comparing the voltage drop at different parts of EDR cells, the voltage drop of the area across cation exchange membrane was the major contributor of energy consumption, and the pulse current could decrease the voltage drop of this part effectively. The removal of heavy metals in soil 1 (6–54%) was much higher than soil 2 (1–17%) due to (1) the difference in acidification caused by a higher buffering capacity in soil 2, and (2) the different chemical speciation of the heavy metals in the two soils reflected by the sequential extraction analysis. Between the direct comparison of soil 1 and soil 2 with the same current density, the removal of heavy metals in soil 1 was much higher but the energy consumption per removed heavy metals was lower than for soil 2, which means that the DC field was more effective in soil 1 compared with soil 2. Among all experiments, the

highest removal efficiency occurred in the pulse current experiment of soil 1, where 54% of Cu and 30% of As were removed. Overall, at relatively lower current density there was no difference on energy consumption and removal of heavy metals between pulse current and constant current experiments, but at higher current density the energy was saved 67% and 60% and the removal of heavy metals were increased 17–76% and 31–51% by pulse current in soil 1 and soil 2, respectively.

Acknowledgment

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Appendix II

Effect of pulse current on acidification and removal of Cu, Cd, and As during suspended electrodialytic soil remediation

(Submitted)

Effect of pulse current on acidification and removal of Cu, Cd, and As during suspended electrodialytic soil remediation

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Abstract

The effect of pulse current on the acidification process and the removal of heavy metals during suspended electrodialytic soil remediation were investigated in this work. Eight experiments with constant and pulse current in two polluted soils were conducted. Soil 1 was sampled from a pile of excavated soil at a site with mixed industrial pollution (Cu and Cd), and soil 2 was sampled from the top layer of a wood preservation site (Cu and As). Results showed that pulse current improved the acidification by supplying more reactive H^+ ions (defined as the H^+ ions causing release of heavy metals from soil particles). The molar ratio of reactive H^+ ions to total produced H^+ ions (R_H^+/P_H^+) was higher in every pulse current experiment than in the corresponding constant current experiment. In addition the removal efficiencies of heavy metals were also improved. The carbonate buffering system in a soil is the first mechanism reacting with the produced H^+ ions and impeding the heavy metal mobilization. It was found that the effect of improvement on both the acidification process and the removal of heavy metals were more significant in the soil with highest buffering capacity than the soil with low. Energy distribution analysis demonstrated that most energy was consumed by the transport of ionic species through the soil suspension, and then followed by membranes and electrolytes. The pulse current decreased the energy consumption to different extent depending on the pulse frequency. The lowest energy consumption was obtained in the experiment with the highest pulse frequency (96 cycles per day) for both soils.

Key words: Suspended electrodialytic remediation; Pulse current; Acidification; Heavy metals; Soil buffering capacity

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1. Introduction

Electrodialytic soil remediation (EDR) is one of a group of electrochemically based soil remediation methods with the purpose of removing heavy metals from polluted soil. EDR was originally applied to soil that was moist and consolidated in attempts at in-situ treatment (i.e. stationary EDR) [1]. A faster and continuous process was then developed, which can be used ex-situ [2-4]: the soil is suspended in a solution (most often water) during such treatment (i.e. suspended EDR). The overall idea is to combine the method with soil washing and develop a continuous process for heavy metal removal from the fine fraction. Larger debris or soil particles are separated out by the washing procedure, leaving only a highly contaminated sludge for EDR. In the soil matrixes of stationary EDR, the ionic species are not able to move by electromigration directly to the opposite pole by the shortest route. Instead, they have to find their way along the tortuous pores and around the particles or air filled voids that block the direct path. By contrast, in the soil suspension of suspended EDR, the electromigration of released ions is more similar to that in aqueous solution. The stirring system in suspended EDR could increase the redox potential in soil solution by aeration, but in stationary EDR, slower oxygen transport gives a relatively reductive environment, which could influence the speciation of some heavy metals (e.g. As, Cr) susceptible to the redox condition and their removal.

It has been reported for both electrokinetic remediation (EKR) and stationary EDR that the utilization of pulsed electric field instead of constant electric field is a potential way to improve the removal of heavy metals and reduce the energy consumption of remediation processes [5-10]. The major difference between suspended EDR and stationary EDR is the transport and distribution of H^+ ions in soil, which is the key factor determining the efficacy of electrochemically based remediation techniques by aiding the mobilization of heavy metals, as most heavy metal cations are dissolved in acidic conditions [11]. For example, in stationary EDR, the effective mobility of H^+

ions in the soil pore fluid is 760×10^{-6} cm^2 V^{-1} s^{-1}. In suspended EDR, the ionic mobility of H$^+$ ions could be approximately estimated as its value in aqueous solution, which is 3625×10^{-6} cm^2 V^{-1} s^{-1} [12]. So the time for the transport of H$^+$ ions from the anion exchange membrane (AN) to the cation ion exchange membrane (CAT) in stationary EDR is around 3.7 h under unit electric field strength and assuming the distance from AN to CAT is 10 cm, but in suspended EDR it will only take 0.8 h for the same transport process. This means that there is a much longer time for the contact between H$^+$ ions and soil particles in stationary EDR than that in suspended EDR. Therefore, a different pulse mode should be applied in suspended EDR.

Generally the pulse mode is determined by the ratio of current "ON" time to current "OFF" time. In EKR, the most reported time ratio is $t_{ON}/t_{OFF}\approx1$ and the applied pulse frequency is high, e.g. 1500 cycles per hour [5,8]. But the high frequency is expected to impede the acidification process in EDR by influencing the water dissociation at AN [13]. Therefore, a relatively low pulse frequency (e.g. 30 cycles per day) should be applied when the pulsed electric field is introduced to improve the EDR process. The pulse mode in stationary EDR can be expressed as $t_{ON}/t_{OFF}=a/x$, with "a" indicates the fixed current "ON" time and "x" indicates the "OFF" time is a variable and determines the effectiveness of applied pulse mode on remediation. However, the pulse mode in suspended EDR is expected to be $t_{ON}/t_{OFF}=x/a$, with the "ON" time as variable based on the different transport process of H$^+$ ions between stationary and suspended EDR. The use of x/a mode is not only because of the higher ionic mobility of H$^+$ ions in suspended EDR, but also because of the fast reaction rate during the "OFF" time since the stirring system highly increases the contact probability between H$^+$ ions (produced during the "ON" time) and soil particles thus increases the reaction rate. Therefore, the variation of "OFF" time in suspended EDR will hardly influence the efficacy of the pulse regime.

As depicted in Fig. 1, the H^+ ions are produced (P_H^+) by water dissociation at AN surface under over-limiting current density. The value of P_H^+ (mmol H^+ g^{-1} soil) is approximately calculated by Eq. (1) according to the Faraday's law,

$$P_{H^+} = \frac{It}{Fm} \times 1000 \qquad (1)$$

where I is current (A), t is working time (s), F is the Faraday constant, and m is the mass of soil samples (g). The calculation of P_H^+ is based on the assumption that all passage of current over the AN was related to water dissociation after transition time when the electrolyte concentration at AN surface decreases to zero. Afterwards, part of them will be current carrier (I_H^+) since the ionic mobility of H^+ ions are much higher than other ions and a high transference number could be expected. I_H^+ is the amount of H^+ ions transported into the cathode side from AN, passing through soil suspension and CAT. The other part will release the heavy metals from soil particles and is defined as reactive H^+ ions (R_H^+). This part includes (I) the amount of H^+ ions conquering the soil buffering capacity, (II) desorption (i.e. cation exchange) of non-specific adsorbed heavy metals, (III) dissolution of co-precipitated heavy metals, and (IV) mobilization of specific adsorbed heavy metals from soil minerals combined with destroy of mineral lattice by H^+ ions. Simplified expression by equation is $P_H^+=I_H^++R_H^+$. To improve the efficiency of suspended EDR is actually to increase the ratio of R_H^+/P_H^+. Therefore, the objectives of the present work are to (1) test the effect of pulse current on the ratio of R_H^+/P_H^+, and (2) investigate the energy saving effect caused by pulse current in suspended EDR.

2. Experimental

2.1. Experimental soil

Two types of soils contaminated by different heavy metals were chosen for this study. Soil 1 was sampled from the top layer on an industrial site, and soil 2 was sampled from a wood preservation

site. The soils were air-dried and passed through 1 mm mesh sieve. Some characteristics of the soils are shown in Table 1.

2.2. Analysis of soil characteristics

Concentrations of heavy metals were determined after pretreatment of the soil according to Danish Standard method DS259 [14] where 1.0 g of dry soil and 20.0 mL (1:1) HNO_3 were heated at 200 kPa (120 ºC) for 30 minutes. The liquid was separated from the solid particles by vacuum through a 0.45 mm filter and diluted to 100 mL. The Cu and Cd concentrations were measured with AAS. The As concentration was measured with ICP. Soil pH was measured by suspending 10.0 g dry soil in 25 mL distilled water. After 1 hour of shaking, pH was measured using a Radiometer pH electrode. The content of organic matter was found as a loss of ignition after 1 hour at 550 ºC. The carbonate content was determined volumetrically by the Scheibler-method when reacting 3 g of soil with 20 mL of 10% HCl. The amount was calculated assuming that all carbonate is present as calcium-carbonate. Grain-size distribution was determined by wet-sieving approximately 100 g natural wet soil with 0.002 M $Na_4P_2O_7$ through a 0.063 mm 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 micrometritics® SEDIGRAPH 5100.

2.3. Desorption of heavy metals as a function of pH

To examine the pH dependent desorption of Cu, Cd and As from the soils before the EDR treatment, the following procedure was used: 5.0 g dry soil (dried at 105 ºC for 24 hours) and 25 mL HNO_3 in various concentrations (from 0.01 M to 1 M) were suspended and put on a shaking table for 1 week. Afterwards, the suspensions were filtered (0.45 mm) and the Cu and Cd concentrations in the liquid phase were measured with AAS and As with ICP. Extractions in distilled water were made as a reference.

2.4. Electrodialytic setup and experimental design

A laboratory cell for electrodialytic remediation is seen in Fig. 1. In compartment II, is the suspended soil. Compartment II is separated from the electrolyte compartments I (anolyte) and III (catholyte) by ion exchange membranes (anion exchange membrane and cation exchange membrane, respectively). The electrodialytic cells were made from polymethyl methacrylate. The ion exchange membranes were commercial membranes from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum coated electrodes (8 cm length, 0.2 cm diameter for each) from Permascand were used as working electrode in compartment I and III. Between the two working electrodes, four monitoring electrodes (platinum coated electrodes) were used to monitor the potential drop of different parts during the experiment. A power supply (Agilent E3612A) was used to maintain a constant current. The applied current was 60 and 15 mA for soil 1 and soil 2, respectively; therefore the current density was 1.2 and 0.3 mA cm^{-2} orthogonal cross-sectional area of soil suspension (50 cm^2). In each of the electrode compartments, 500 mL of 0.01 M $NaNO_3$ adjusted to pH 2 with HNO_3 was circulated. The soil was kept suspended during the experiments by constant stirring with a plastic-flap attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). Due to the electrode processes, pH-changes occurred in anolyte and catholyte. The pH in these electrolytes was manually measured every 12 hours and kept between 1 and 2 by addition of 1:1 HNO_3 and 5 M NaOH. By the end of the electrodialytic experiments, the contents of Cu and As in the different parts of the cell (membranes, soil, solutions, and electrodes) were measured. The suspension from the central compartment was filtered. The sediment was dried and crushed lightly in a mortar by hand before the heavy metal concentrations and pH were measured. The contents of Cu and As in membranes and at the electrodes were measured after extraction in 1 M HNO_3 and 5 M HNO_3, respectively.

The pulse current was accomplished by a power supply timer instrument (Joel TE102), and the program was 30, 20, or 10 min "ON", and 5 min "OFF", so the frequency was approximately 41, 58 or 96 cycles per day, respectively. The pre-chronopotentiometric measurement of membranes was conducted by automatic record of the potential drop between the saturated calomel electrodes (SCEs) inserted into both sides of the membranes. The potential drop was recorded by a datalogger (Agilent 34970A) with a rate of once per 5 s. In all experiments, the duration was designed to maintain the identical total charge transfer between constant and pulse current experiments under the same current. As it was shown in Table 2, the total duration was different among the experiments, but the working time was kept the same. The liquid to solid ratio (L/S) was designed as 5, i.e. 100 g soil suspended in 500 ml distilled water, to be consistent with the desorption experiments and previous studies.

The energy consumption (E) was calculated as:

$$E = \int VIdt \tag{2}$$

where E is the energy consumption (Wh), V is the potential drop between working or monitoring electrodes (V), I is the current (A), and t is the duration (h).

The mass balance of an element was defined as the relation between the sum of mass found in the different parts of the cell at the end of the experiment and the initial mass calculated on basis of the mean initial concentration. The removal efficiency for each element was calculated as mass of the actual heavy metal at the parts of electrodes, electrolyte, and membranes, divided by the total mass found in all parts of the cell at the end of the experiment.

3. Results and discussion

3.1. Characteristics of heavy metals in soil

The experimental soil 1 was polluted by Cu and Cd, and the soil 2 was polluted by Cu and As. Large amount of carbonate content, organic matter, and clay content were measured in soil 1, which implied a higher buffering capacity than soil 2. The higher conductivity in soil 1 indicated a possibility for applying a higher current density for treatment compared to soil 2.

Fig. 2 shows the concentrations of Cu, Cd and As extracted from soils and pH variation at different addition of H^+ ions. It is seen that desorption of the heavy metals increases with the decrease in pH from both soil 1 and 2. For Cu, the desorption pattern was quite similar between soil 1 and soil 2, which started between pH 5 and 6 and approached 100% at approximately pH 1. As in soil 2 was not desorbed before pH was below about 2. From soil 1, on the other hand, Cd already desorbed before pH 6 and 7. Below pH 1 complete desorption was reached for all heavy metals. A little As was extracted at higher pH; this was not necessarily mobile in the soil before the sampling. Mobile As is expected to be washed out to deeper soil layers, and the aeration of the soil sample between sampling and treatment may likely have influenced the mobility of As. The C/C_0 was higher than 1 in few case. Industrially polluted soils as used in this study are very inhomogeneous. In addition due to the destructive measuring method, the measured concentration of heavy metals in soil after experiments cannot match the initial value precisely. It also can be seen from Fig. 2 that all the heavy metals were mobilized when the pH was low enough, no matter the speciation of heavy metals in the soil.

3.2. Chronopotentiometric analysis of AN and CAT

The chronopotentiometric curves for anion exchange membranes of soil 1 and soil 2 are shown in Fig. 3A and 3B, respectively. The potential drop was measured by two SCEs (1 and 2) between anion exchange membranes as shown in Fig. 1. The detailed description of the chronopotentiometric curves has been given in previous reports [15-17]. The most important parameter obtained from the curves is the transition time indicating the concentration at the vicinity

of membrane surface decreases to zero. The transition time (τ) as a function of applied current density is derived from Fick's second law and given by:

$$\tau = \frac{\pi D}{4} \left(\frac{C_i^0 z_i F}{T_i - t_i} \right)^2 \frac{1}{i^2} \tag{3}$$

where D is the diffusion coefficient of the electrolyte in the soil suspension, C_i^0 and z_i are the initial concentration of the electrolyte in the soil suspension and the charge of the counter-ion, respectively, T_i and t_i are the transference numbers of the counter-ion in the membrane and soil suspension, respectively, i is the current density, and F is the Faraday constant. Eq. (3) is equivalent to the Sand equation frequently used in studies of electrode systems [18]. The occurrence of transition time indicated that an overlimiting current density has been applied to the anion exchange membrane. This results in water dissociation and acidification of the soil suspension as described, and subsequent mobilization of heavy metals could be expected [15]. It can be seen that the transition time decreased with increase in the applied current density, which is a highly agreement with Eq. (3) as the current density is inversely proportional to the transition time. The transition time was lower in soil 2 than that of soil 1 under the same current density, which could be due to the lower concentration (here simplified by the conductivity data in Table 1) of ionic species in the solution of soil 2 compared to soil 1. In principle when applying a constant current, water dissociation will occur as long as the experimental time is longer than the transition time, no matter what current density is applied. But in the EDR cells with pulse current, the transition time is important since it determines the limit for the highest applied pulse frequency. The applied current density was 1.2 mA cm^{-2} for soil 1 and 0.3 mA cm^{-2} for soil 2 in the present work (the reasons to choose these two current densities were based on previous studies [2,19]). The applied current density must on one hand be high enough to obtain a short transition time, and on the other hand low enough to ensure a continuous remediation process and prevent a too fast acidification which results in a low

transference number for the heavy metals as most current is carried by H^+ ions. The optimal current density depends on soil type, composition, and liquid to solid ratio. The transition time of soils 1 and 2 was 1.4 and 0.9 min respectively at the chosen current density (Fig. 3). Therefore, the current "ON" time must not be shorter than these values; otherwise the water dissociation will be diminished by diffusion of anionic species towards the anion exchange membrane.

The transition state was not seen for the cation exchange membrane (measured by SCE 3 and 4, data not shown). This means that current density applied was sublimiting for the cation exchange membrane, which is the requirement during EDR. The limiting current density of anion exchange membrane was lower than that of cation exchange membrane, probably because there were fewer anions than cations in the electric double layer of the clay particles. The limiting current density is expected to be determined by clay fraction, type of clay mineral in soil solid phase, and ionic concentration in soil solution. Further, next to the anion exchange membrane is the negatively charged soil surface which forms a bipolar interface depleting ions rapidly [20], even though the concentration of anionic species could be increased in bulk soil solution by acidification.

3.3. Acidification process and removal of heavy metals

The pH changes in the soil suspensions in soils 1 and 2 during the experiments are shown in Fig. 4. In general, the pH in suspension of all experiments decreased over time and the decreasing pH is an important factor influencing the mobility of heavy metals by dissolution and desorption. The H^+ ions causing the acidification process come from water dissociation near the anion exchange membrane and transports towards the cathode by electromigration as discussed above. Due to the different buffering capacity of experimental soils 1 and 2 (Table 1), the acidification pattern differed. It can be seen for soil 1, a "lag-period" was observed before a fast decrease in pH, during which the acidification overcame the buffering capacity of soil, whereas a continuous drop of the pH after applying the current was seen for soil 2. Among the experiments in soil 1 (EXP.1-4), both

the lowest pH value and highest acidification rate (expressed by slope) were obtained in EXP.4 (pulse current, 10 min on and 5 min off) then followed by EXP.3 and 2, the highest pH during and after experiments occurred in EXP.1 (constant current). This corresponds to the order in R_H^+/P_H^+ ratios which are listed in Table 3. The value of reactive H^+ ions (R_H^+, mmol H^+ g^{-1} soil) was obtained by polynomial fitting of pH data in Fig. 2 and matched with the pH value after each experiment shown in Fig. 4. The consumed H^+ ions in Fig. 2 is also the total amount of reactive H^+ ions (the summation of that in I-IV processes as mentioned in Introduction), so a direct comparison between R_H^+ and the consumption of H^+ ions in pre-desorption experiments is possible. The maximum increase of R_H^+/P_H^+ ratios was 0.14 units from EXP.1 to EXP.4, which indicated that pulse current improved the acidification process by supplying more reactive H^+ ions (R_H^+). Similar trend was shown for soil 2 (EXP.5-8) but with a slow decrease in pH after certain time and approaching to the same value at the end of experiments probably due to the H^+ ions were major contributor to the transport of current at this period (I_H^+). Therefore, the maximum increase of R_H^+/P_H^+ ratios was lower (0.04 units) in soil 2 than that of soil 1, which means the improvement caused by pulse current was more significant in the soil with higher buffering capacity than the soil with low.

In present work, the carbonate content was chosen as a qualitative indicator to estimate the soil buffering capacity variation since it is more susceptible than other indicators, like organic matter or CEC [21]. The residual carbonate contents in soil after different experiments were shown in Table 3. It can be seen that in soil 1 the carbonate content decreased from EXP.1 to EXP.4, corresponding to its acidification process. In soil 2, there is no significant difference between experiments, and actually the carbonate contents after treatments were below the limit of the test method. This means there was almost no buffering capacity left after treatments, which also supplied a possible explanation to the decreased acidification rate at the late stage and levelling out the slope.

Fig. 5A and 5B show the distribution of Cu, Cd and As in the EDR cells at the end of the experiments. In all experiments the major part of the Cu and Cd were found either at the cathode side or in the soil, which means Cu and Cd were mobilized as cations, while for As the major part was distributed either in the anode side or in the soil, so the As was removed as anions. The stirring process in suspended EDR could increase the redox potential in soil solution by aeration. But in stationary EDR, slower oxygen transport gives a relatively reductive environment. Based on the Eh-pH diagram [22], in stationary EDR, the non-charged $AsOH_3$ is expected in the low pH region near anion exchange membrane, which impedes the As removal. This has been demonstrated in study [23,24] that As (III) is the dominating species, and by addition of alkaline reagents, the As removal could be significantly improved. By contrast, in suspended EDR, due to the aeration, oxidation of As (III) to moveable species $H_2AsO_4^-$ or $HAsO_4^{2-}$ facilitates the removal of As in a large range of pH. The removal of Cu, Cd and As were all improved (although with different extent) by pulse current since their concentration in the cathode side increased and the residual concentration in soil decreased both in soil 1 and soil 2. Combined with the pH profile, it can be concluded that the positive effect of pulse current on removal of heavy metals mainly caused by the enhanced acidification process. Comparing soil 1 and soil 2, a major difference was the certain concentration of residual heavy metals observed in soil 1's suspension, which probably due to the releasing of ionic species during the conquering of buffering capacities. The released ionic species acted as supporting electrolyte and decreased the transference number of dissolved heavy metals. The SEM-EDX mapping of the electrode deposition shown in Fig. 6 confirmed that large amount of Ca existed at soil 1's cathode, whereas only small amount of Ca showed up compared to Cu at soil 2's cathode. The elements Al, Si, and Fe were released from clay minerals. Among the experiments in soil 1, it can be seen that the concentration of both Cu and Cd in soil suspension decreased from EXP.1 to EXP.4, which implied an increased transference number in pulse current experiments.

3.4. Electrodialytic remediation—Overall results

The overall results from the EDR experiments are given in Table 3. As seen, the mass balances were between 88% and 111%, which is an acceptable range for inhomogeneous industrially polluted soil. The removal efficiency was increased by pulse current both in soil 1 and soil 2, increase in pulse frequency, the removal efficiency improved. However, the increased extent was higher in soil 1 (up to 32% for Cu and 20% for Cd) than that in soil 2 (up to 10% for Cu and 5% for As), which was probably due to the decreased acidification rate at the late stage of soil 2 (Figure 3). At the beginning, the acidification rate was highest in EXP.8 and followed by EXP.7, 6 and 5, therefore the same order of heavy metals removal rate could be expected. After the pH dropped to around 3.2, the acidification leveled out. The time for this decreased from EXP.5 to 8, so during the period from 48 to 72 h, more heavy metals were dissolved in EXP.5 and followed by EXP.6, 7 and 8. Also the absence of large amount support electrolyte in soil 2's suspension (compared to soil 1) and low buffering capacity lead to a similar transference number of heavy metals among EXP.5-8. Further, the removal efficiency of Cd (62-82%) was significantly higher than that of Cu (24-57%) in soil 1 and the removal efficiency of Cu (72-82%) was higher than that of As (53-58%), which were corresponding to the expectations from the pH desorption pattern (Fig. 2) with different desorption characteristics for different heavy metals.

The positive effect of energy saving caused by pulse current was shown in Table 3 since the total energy consumption and the energy consumption per removed milligram heavy metals were lower in pulse current experiments than that in constant current experiment both in soil 1 (with lowest value in EXP.4) and soil 2 (with lowest value in EXP.8). Between soil 1 and soil 2, the decrease extent of total energy consumption was higher in soil 1 (up to 33%) than that in soil 2 (up to 11%). Based on previous studies [7], the possible mechanism of decreased energy consumption in pulse current experiments is the additional proceeding of chemical dissolution at the relaxation period

when the current is switched off, which induces increased species concentration in solution. In the soil with higher buffering capacity, more ions would be released after a pulse than that in the soil with low buffering capacity under a similar condition of acidification; therefore higher extent of energy saving was achieved. Compared with stationary EDR (maximum 70% energy saving) [9,25], less energy was saved (maximum 33% energy saving in present work) in suspended EDR even with higher applied current densities. The possible explanation is the more effective dissolution or desorption process (especially when the current is "ON") caused by continuous stirring in suspended EDR, while in stationary EDR this process is dominated by classic Nernst-Planck mass transport. Unlike stationary EDR with highest energy consumption occurred at cation exchange membrane [9,25], the major energy consumption in suspended EDR occurred at the soil compartment as shown in Fig. 7. In soil suspension, both the amount of frees ions and the electric mobility of ionic species are higher than that in stationary EDR, so less energy was needed for transport of ionic species across the membranes. But at the same time the depletion of free ions caused an increase in resistance and gave rise to higher energy consumption in the soil compartment.

4. Conclusions

This paper focused on the investigation of possible enhancement caused by pulse current during suspended EDR. After 180 h experiments, the results demonstrated that the pulse current improved the acidification process by supplying more reactive H^+ ions since the molar ratio of reactive H^+ ions to total produced H^+ ions ($R_H{}^+/P_H{}^+$) was higher in the pulse current experiments than in constant current experiments. The highest ratio occurred in a pulse current experiment with the frequency of 96 cycles per day (the highest pulse frequency in the investigation) for both soils. As a result of the enhanced acidification process, the removal efficiencies of heavy metals were also improved. The effect of improvement on either acidification process or removal of heavy metals

was more significant in the soil with higher buffering capacity than the soil with low, which was supported by the higher increase extent in R_H^+/P_H^+ (0.14 unit) and removal efficiency of heavy metals (~32%) in soil1 than that in soil 2 (0.04 unit and ~10%, respectively). Increasing the pulse frequency further would probably not improve the efficiency as the highest applicable pulse frequency was limited by transition time of anion exchange membrane. The energy distribution analysis demonstrated that most energy was consumed for the transport of ionic species through the soil suspension, followed by membranes and electrolytes. The pulse current decreased the energy consumption to different extent depending on the pulse frequency.

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Table 1
Characteristics of experimental soils.

Items	Soil 1	Soil 2
Cu (mg kg^{-1})	1064	1196
As (mg kg^{-1})	-	3334
Cd (mg kg^{-1})	16	-
Organic matter (%)	6.5	3.6
Carbonate content (%)	7.1	0.6
pH	7.2	6.7
Electric conductivity (mS cm^{-1})	2.6	0.8
Clay (< 0.002 mm)	15%	8%
Silt (0.002-0.06 mm)	61%	26%
Sand (0.06-2 mm)	24%	66%

Table 2
Experimental design.

	Experiments	Current density (mA cm^{-2})	Current type	Frequency (cycles day^{-1})	L/S	Total duration (h)	Working time (h)
Soil 1	EXP.1	1.2	Constant	-	5	180	180
	EXP.2	1.2	Pulse 30minON/5minOFF	41	5	210	180
	EXP.3	1.2	Pulse 20minON/5minOFF	58	5	225	180
	EXP.4	1.2	Pulse 10minON/5minOFF	96	5	270	180
Soil 2	EXP.5	0.3	Constant	-	5	180	180
	EXP.6	0.3	Pulse 30minON/5minOFF	41	5	210	180
	EXP.7	0.3	Pulse 20minON/5minOFF	58	5	225	180
	EXP.8	0.3	Pulse 10minON/5minOFF	96	5	270	180

Table 3
Overall results of electrodialytic remediation.

Experiments	Mass balance Cu/Cd/As (%)	Removal efficiency Cu/Cd/As (%)	R_H^+/P_H^+	Final carbonate content (%)	Energy consumption (Wh)	Energy consumption per removed Cu/Cd/As (Wh mg^{-1})
EXP.1	106/95/-	24/62/-	0.44	1.3±0.04	285	11/303/-
EXP.2	110/103/-	35/70/-	0.49	0.9±0.03	255	6.1/222/-
EXP.3	105/100/-	45/77/-	0.53	0.5±0.03	227	4.5/182/-
EXP.4	111/110/-	57/82/-	0.58	0.3±0.02	192	2.9/133/-
EXP.5	98/-/91	72/-/53	0.39	0.1±0.01	276	3.3/-/1.7
EXP.6	96/-/89	75/-/54	0.40	0.1±0.03	268	3.1/-/1.7
EXP.7	104/-/88	79/-/57	0.42	0.1±0.02	258	2.6/-/1.6
EXP.8	110/-/88	82/-/58	0.43	0.1±0.01	247	2.3/-/1.4
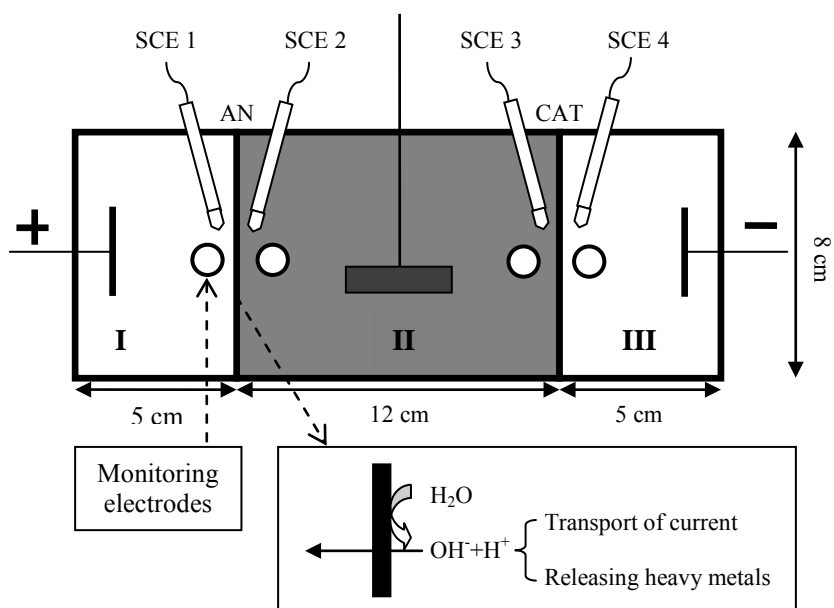
Fig. 1. Schematic diagram of the laboratory cell for electrodialytic soil remediation (AN = anion exchange membrane, CAT = cation exchange membrane, and SCE=saturated calomel electrode). The four monitoring electrodes were used for measuring the potential drop of different parts during the experiment. The SCEs were used for pre-chronopotentiometric measurement of membranes.
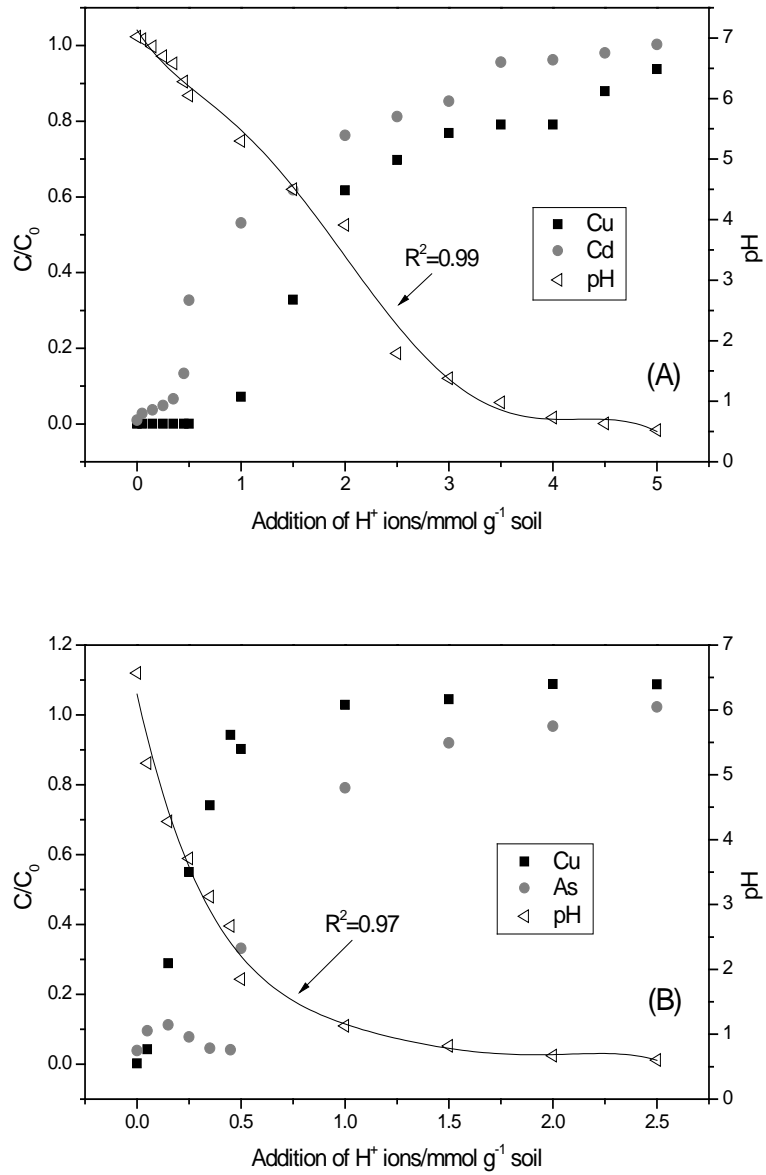
Fig. 2. pH dependent extraction of Cu, Cd, and As from the soil 1 (A) and soil 2 (B). C_0 is the initial concentration of Cu, Cd, and As in soil 1 and 2.
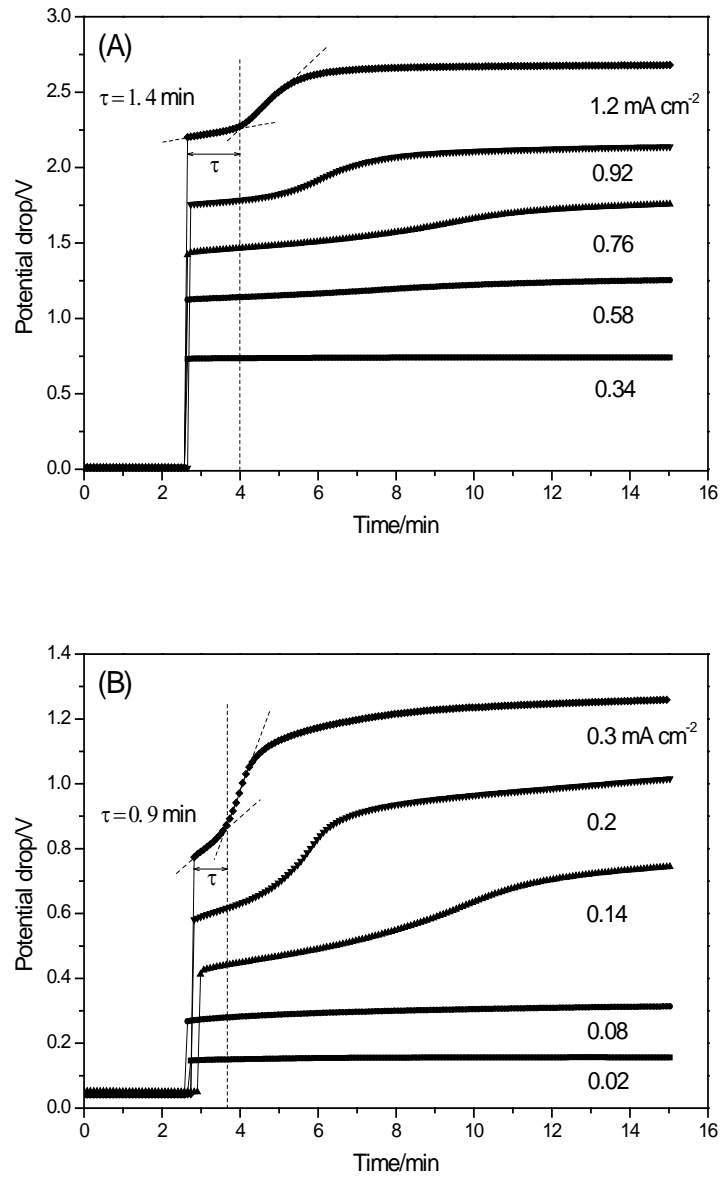
Fig. 3. Chronopotentiogram of anion exchange membrane with (A) for soil 1 and (B) for soil 2. The applied current densities were from 0.34 to 1.2 mA cm^{-2} for soil 1 and from 0.02 to 0.3 mA cm^{-2} for soil 2, respectively. Temperature=25˚C.
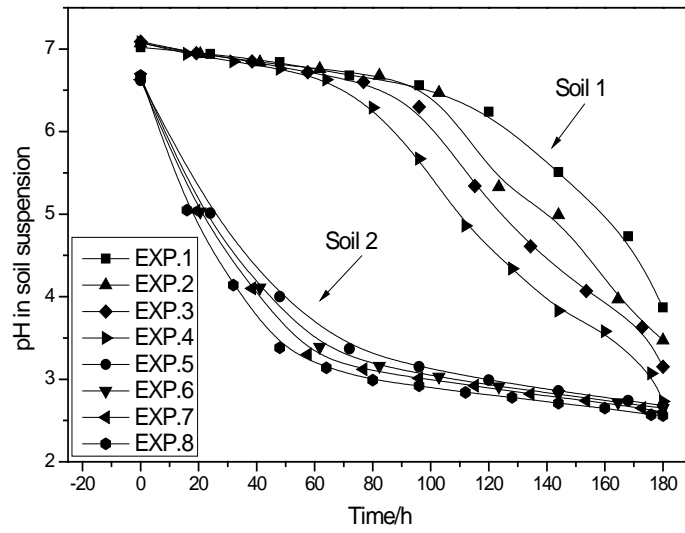
Fig. 4. pH variation in soil suspension during the electrodialytic remediation process. The current densities applied in soil 1 and 2 were 1.2 and 0.3 mA cm^{-2}, respectively. Temperature=25°C.
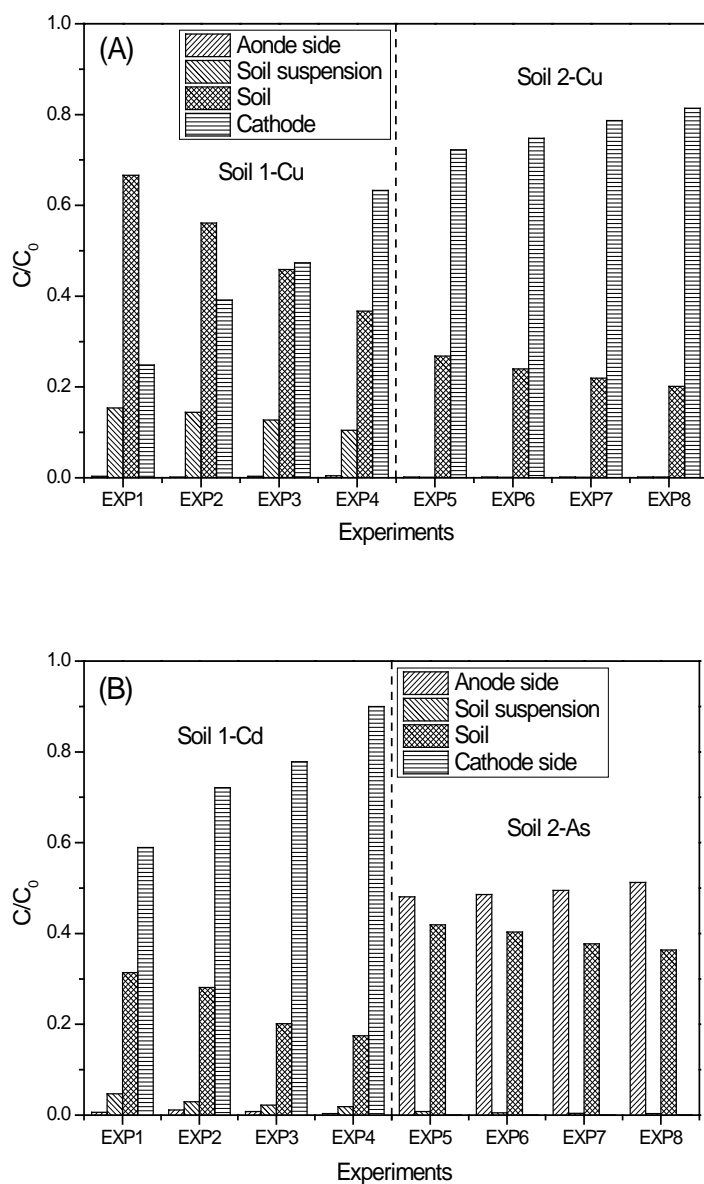
Fig. 5. Distribution of heavy metals in the different parts of the electrodialytic cell at the end of the experiments, with (A) for Cu in both soil 1 and 2, (B) for Cd in soil 1 and As in soil 2. The current densities applied in soil 1 and 2 were 1.2 and 0.3 mA cm^{-2}, respectively. Temperature=25˚C.
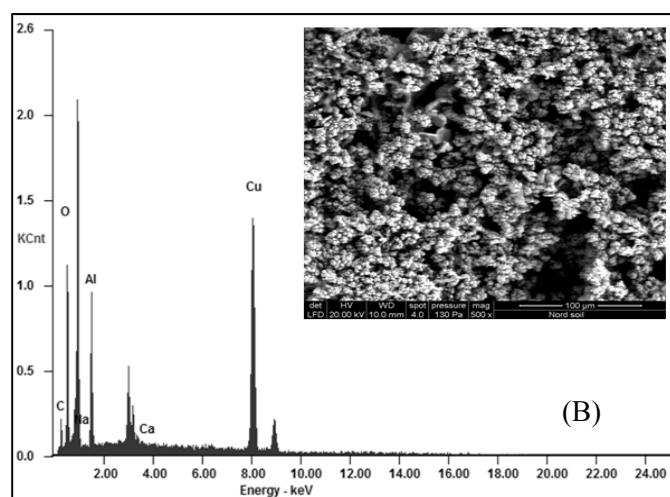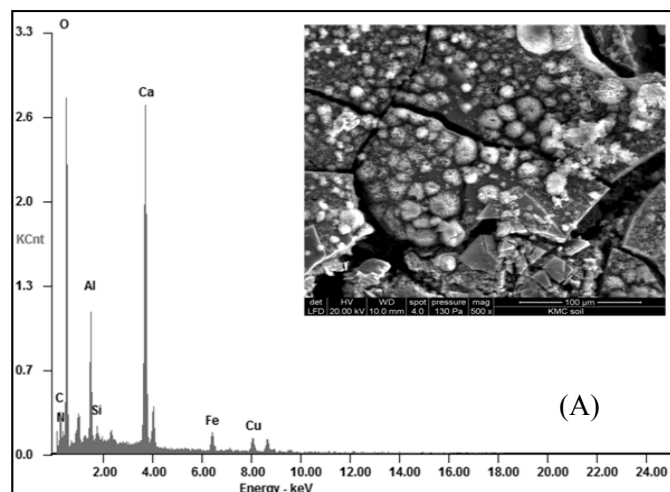
Fig. 6. SEM picture of electrodeposits at cathode and result from EDX mapping, with (A) for soil 1and (B) for soil 2. Samples were collected from constant current experiments for both soils. The current densities applied in soil 1 and 2 were 1.2 and 0.3 mA cm^{-2}, respectively. Temperature=25˚C.
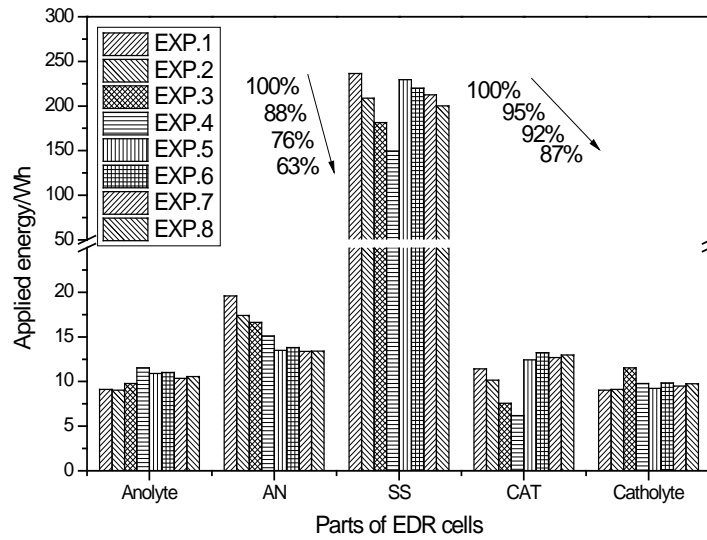
Fig. 7. Distribution of energy consumption at different parts of EDR cells (AN=anion exchange membrane, SS=soil suspension, and CAT=cation exchange membrane). The data indicate the decrease percentage induced by pulse current in soil 1 and 2. The current densities applied in soil 1 and 2 were 1.2 and 0.3 mA cm^{-2}, respectively. Temperature=25˚C.

Appendix III

Pulse current enhanced electrodialytic soil remediation—Comparison of different pulse frequencies

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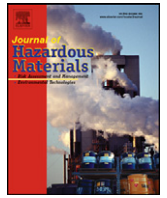
Pulse current enhanced electrodialytic soil remediation—Comparison of different pulse frequencies

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HIGHLIGHTS

▶ The energy consumption could be decreased by pulse current during EDR.
▶ The comparison of different pulse frequencies was made.
▶ The relaxation process of the soil–water system was investigated.
▶ The rate controlling step of the EDR process was determined.
▶ The effect of pulse current on the removal of heavy metals was investigated.

ARTICLE INFO

ABSTRACT

Energy consumption is an important factor influencing the cost of electrodialytic soil remediation (EDR). It has been indicated that the pulse current (in low frequency range) could decrease the energy consumption during EDR. This work is focused on the comparison of energy saving effect at different pulse frequencies. Based on the restoration of equilibrium, the relaxation process of the soil–water system was investigated by chronopotentiometric analysis to find the optimal relaxation time for energy saving. Results showed that the pulse current decreased the energy consumption with different extent depending on the pulse frequency. The experiment with the frequency of 16 cycles per day showed the best restoration of equilibrium and lowest energy consumption. The energy consumption per removed heavy metals was lower in pulse current experiments than constant current and increased with the pulse frequency. It was found that the transportation of cations through the cation exchange membrane was the rate controlling step both in constant and pulse current experiments, thus responsible for the major energy consumption. Substitution of the cation exchange membrane with filter paper resulted in a dramatic decrease in energy consumption, but this change impeded the acidification process and thus the removal of heavy metals decreased significantly.

1. Introduction

Electrodialytic remediation (EDR) is a method developed for removal of heavy metals from soils, which differs from electrokinetic remediation (EKR) in the use of ion exchange membranes for separation of the soil and the solution in the electrode compartments. The main purpose of the ion-exchange membranes is to prevent ions in the electrode compartments from entering the soil, therefore no current is wasted for carrying ions from one electrode compartment to the other [1]. The EDR technique has been applied for decontamination of e.g. soil [2], fly ash [3], and harbor sediment [4]. In previous works including both lab and pilot scale

experiments, this technique has demonstrated effective removal of heavy metals from the contaminated materials.

The energy consumption of the electrochemically based remediation techniques is an important factor influencing costs and thus the applicability. In a conventional electrodialytic cell, the applied electrical potential must be sufficient to overcome the ohmic resistance, the potential drop across the membranes, the dialysate and concentrate compartments drop due to concentration gradients, potential drop at working electrodes, and the potential drop at the membrane–solution interfaces (Donnan potential) [5]. In electrodialytic soil remediation, the potential drop at electrodes and in the anolyte and catholyte can be assumed negligible compared to the value of other parts especially when the electrolytes are circulated [6]. Further, as most fine grained soils have a negative charged surface like a cation exchanger, and the positive ions removed from the soil are in excess of the negative ions, the removal process are briefly controlled by two steps: (a) the transport in moist

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Table 1
Chemical properties of the soil sample.

| Items	Values
Concentration of heavy metals	
Cu/limiting value	1117/500 mg kg^{-1}
Cd/limiting value	16/0.5 mg kg^{-1}
pH	7.6
Conductivity	2.1 mS cm^{-1}
Carbonate content	7.1%
Organic matter	6.5%
Grain size distribution	
Sand	24%
Silt	61%
Clay	15%

Fig. 1. Schematic diagram of the laboratory cell for electrodialytic soil remediation (CAT, cation exchange membrane; AN, anion exchange membrane; ME, monitoring electrode).

pores of the contaminated soil and (b) the transport across the cation exchange membrane, which are also expected to be the main energy consuming steps. Concentration polarization occurs in all membrane separation processes owing to differences in the transport numbers of ions in the solution and in the ion exchange membrane [7]. When an electric current is passed through an ion exchange membrane, ionic concentration on the desalting surface of the membrane is decreased due to concentration polarization, and reduced to zero at the limiting current density. At this point, there are no more ionic species available to carry the current. Thus, the voltage drop across the boundary layer increases drastically resulting in a higher energy consumption and generation of water dissociation.

In pressure-driven membrane processes the application of pulsed electric fields can give substantial improvements in the performance by reduction of the concentration polarization, control of membrane fouling and increase in the membrane selectivity [8,9]. For EKR, researchers have also investigated the effect of a pulsed electric filed to improve the remediation process. For example, Kornilovich et al. [10] indicated that a pulse voltage changes the distribution of heavy metals in the soil and allows decreasing power inputs during electrokinetic remediation. Ryu et al. [11] found that pulsed electrokinetics could improve the removal efficiency of heavy metals and decrease the energy consumption. A high pulse frequency (e.g. 1500 cycles per hour) applied in EKR is expected to impede the acidification process in EDR by influencing the water dissociation at anion exchange membrane. Therefore, a relatively low pulse frequency (e.g. 30 cycles per day) should be applied when the pulsed electric field is introduced to improve the EDR process. It has previously been shown by Hansen et al. [12] that a pulse voltage with low frequencies could enhance the removal efficiency for copper during EDR of mine tailings. Later, Sun et al. [13] demonstrated that the energy consumption could be decreased by low frequency pulse current. However, the effect of pulse frequency on energy consumption during EDR has not been clarified before. Therefore, the present work aims at the comparison of different pulse frequencies on energy consumption and developing a possible method to estimate the effect.

2. Materials and methods

2.1. Experimental soil

The experimental soil contaminated by Cu and Cd was a Danish soil, sampled from a pile of excavated soil. The collected soil was air-dried at room temperature, and gently crashed and passed through a 2 mm mesh sieve before experiment. Some characteristics of the soils are shown in Table 1.

Concentrations of heavy metals were determined after pretreatment of the soil according to Danish Standard 259 [14], where 1.0 g of dry soil and 20.0 mL (1:1) HNO$_3$ were heated at 200 kPa
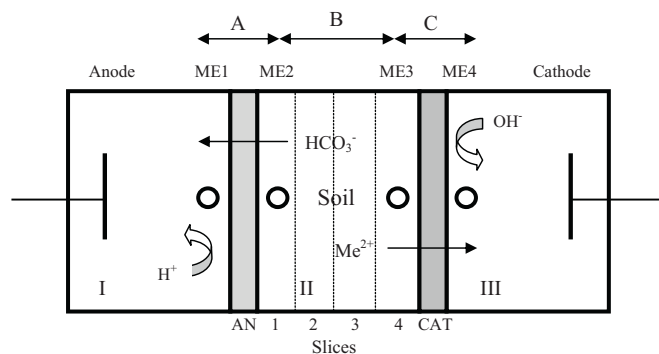
(120 °C) for 30 min. The liquid was separated from the solid particles by vacuum through a 0.45 mm filter and diluted to 100 mL. The concentrations of Cu and Cd were measured with AAS. Soil pH and conductivity were measured by suspending 10.0 g dry soil in 25 mL distilled water. After 1 h of agitation, pH and conductivity were measured using Radiometer pH and conductivity electrodes, respectively. The content of organic matter was found as a loss of ignition after 1 h at 550 °C. The carbonate content was determined volumetrically by the Scheibler-method, which reacted 3 g of soil with 20 mL of 10% HCl. The carbonate content was calculated assumed that all carbonate was present as calcium-carbonate. Grain-size distribution was determined by wet-sieving approximately 100 g natural wet soils with 0.002 M Na$_4$P$_2$O$_7$ through a 0.063 mm sieve. The particles larger than 0.063 mm were dried and sieved, while the solution under 0.063 mm was transferred to an Andreassen-pipette. The weight of each size was recorded.

2.2. Desorption of heavy metals as a function of pH

To examine the pH dependent desorption of Cu and Cd from the soil, the following procedure was used: 5.0 g dry soil (dried at 105 °C for 24 h) and 25 mL HNO$_3$ in various concentrations (from 0.01 M to 1 M) were suspended for 1 week. The suspensions were filtered (0.45 mm) and the Cu and Cd concentrations in the liquid phase were measured with AAS. Extractions in distilled water were made as a reference.

2.3. Sequential extraction of heavy metals

Sequential extraction was performed according to the method described in the Standards, Measurements and Testing Program of the European Union [15]: 0.5 g of dry, crushed soil was treated in four steps as follows: (1) extraction with 20.0 mL 0.11 M acetic acid (pH 3) for 16 h, (2) extraction with 20.0 mL 0.1 M NH$_2$OH·HCl (pH 2) for 16 h, (3) extraction with 5.0 mL 8.8 M H$_2$O$_2$ for 1 h, and (4) digestion according to DS 259 [14] was made for identification of the residual fraction. Samples in each step were taken in triplicate.

2.4. Electrodialytic setup and experimental design

A schematic diagram of the experimental setup is shown in Fig. 1. The electrodialytic cell was made from polymethyl methacrylate. The cell had an internal diameter of 8 cm. The length of each cell compartment was 5 cm. The ion exchange membranes were from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum coated electrodes (8 cm length, 0.2 cm diameter for each) from Permascand were used as working electrode in compartments I and III. Between

Table 2
Experimental design.

Experiments	Current density (mA/cm^2)	Current type	Frequency (cycles per day)	Membrane use	Duration (working hours)
EXP. 1	0.8	Constant	–	AN and CAT	240
EXP. 2	0.8	Pulse 60 min(on)/5 min(off)	22	AN and CAT	240
EXP. 3	0.8	Pulse 60 min(on)/15 min(off)	19	AN and CAT	240
EXP. 4	0.8	Pulse 60 min(on)/30 min(off)	16	AN and CAT	240
EXP. 5	0.8	Constant	–	AN and filter	240

the two working electrodes, four monitoring electrodes (platinum coated electrodes) were used to monitor the voltage drop of different parts. Sieved (passed 2 mm sieve) soil sample (370 g) with water content adjusted to 23% was packed in compartment II. Five electrodialytic experiments were performed as listed in Table 2. The cation exchange membrane was replaced by a filter paper in EXP. 5 for additional comparison. Before switching on the current, in each of the electrode compartments, 500 mL 0.01 M NaNO$_3$ (adjusted to pH 2 by HNO$_3$) was injected and circulated by pumps for 24 h to obtain the equilibrium for the system. Afterwards, a 40 mA constant current (corresponding to 0.8 mA/cm^2) instead of voltage in [12] was applied to maintain a stationary transport of ionic species for all experiments by a power supply (Agilent E3612A). The voltage drop between the anode and the monitoring electrodes inserted in different parts of the EDR cells was recorded automatically by a datalogger (Agilent 34970A).

The pulse current was accomplished by a power supply timer instrument (Joel TE102), and the program was 60 min "on", and 5, 15, or 30 min "off", which means the frequency was approximately 22, 19 or 16 cycles per day. In all experiments, the duration was designed to maintain the identical total charge transfer between constant and pulse current experiments under the same current density. Due to the electrode processes, pH changed in the electrolytes. The pH in the electrolytes was therefore manually maintained between 1 and 2 by addition of HNO$_3$ and NaOH. By the end of the experiments, the contents of heavy metals in the different parts of the cell (membranes, soil, solutions, and electrodes) were measured. The soil samples were segmented to four slices as illustrated in Fig. 1, dried and crushed lightly in a mortar by hand before the measurement of heavy metal concentrations (three samples), pH (three samples) and conductivity (three samples).

The energy consumption (E) was calculated as:

$$E = \int VIdt \qquad (1)$$

where E is the energy consumption (Wh), V is the voltage between working electrodes (V), I is the current (A), and t is the duration (h).

3. Results and discussion

3.1. Characteristics of heavy metals in soil

The soil was polluted by Cu and Cd which have highly exceeded the Danish limiting value for sensitive land use (Table 1). Compared to other polluted soils in Denmark [16,17], large amount of carbonate content, organic matter, and clay content were measured in the present soil which implied a higher buffering capacity thus high energy input is required for treatment. The higher conductivity in soil solution indicated a possibility for applying a higher current density for treatment. Based on these characteristics this soil was chosen as the experimental sample for the present work since it would be more apparent to compare the energy saving effect among different pulse frequencies according to previous research [13]. Fig. 2 shows the concentrations of Cu and Cd desorbed from the soil by chemical extraction in HNO$_3$ at different pH values. It is seen that desorption increased with the decrease in pH as expected. The
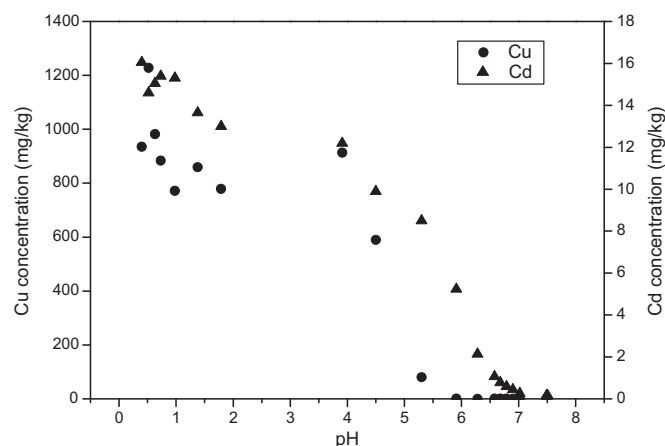

Fig. 2. Desorption dependency on pH of Cu and Cd from the soil sample.

Cu desorption started between pH 5 and 6 while the Cd desorption started from pH 7. Both heavy metals approached 100% desorption at approximately pH 1.

3.2. Acidification process and removal of heavy metals

Soil pH changed during the electrodialytic experiments (Fig. 3). The decreasing pH is an important factor influencing the mobility of heavy metals by desorption as seen from the desorption experiments (Fig. 2). The H$^+$ ions acidifying the soil come mainly from water dissociation near the anion exchange membrane and transport towards the cathode by electromigration [18]. Different acidification process was expected based on the consideration of the different H$^+$ ions transportation caused by the relaxation in the pulse current experiment. But similar acidification pattern among EXP. 1–4 was observed and possibly due to the relatively high buffering capacity (Table 1) of the experimental soil which covered the difference. Further discussion will be given with the
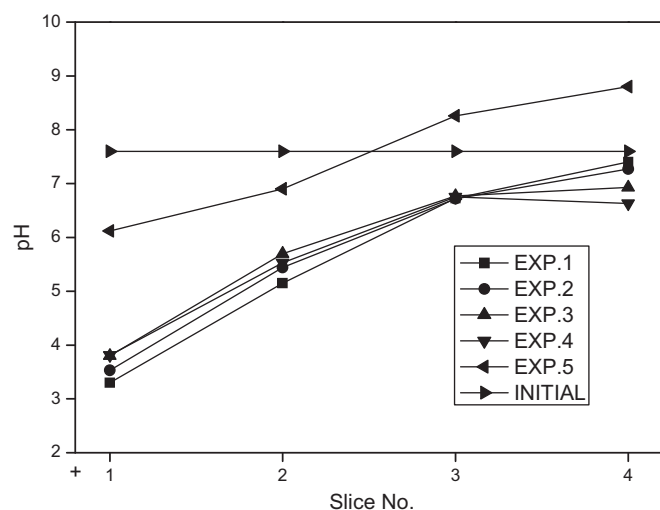

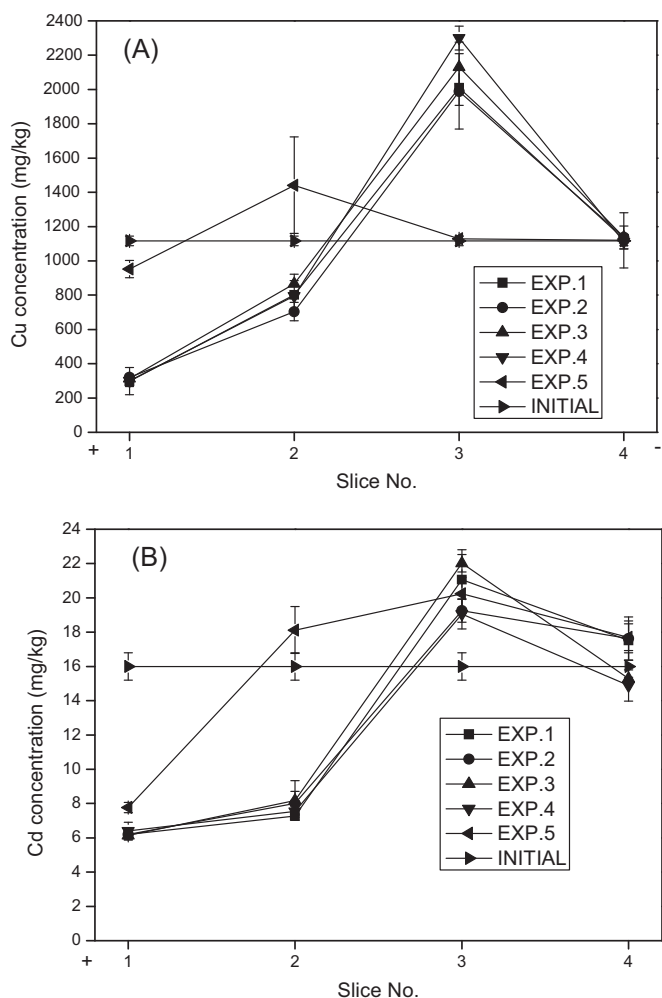**Fig. 3.** Profiles of soil pH developed after application of current.

Fig. 4. Final profiles of heavy metals in the soil. (A) Cu and (B) Cd.

Table 3
Overall results of electrodialytic remediation.

Experiments	Mass balance % Cu/Cd	Removal efficiency % Cu/Cd	Energy consumption (Wh)	Energy consumption per removed Cu/Cd (Wh/mg)
EXP. 1	96/102	1.2/10.5	385	79.8/631
EXP. 2	99/100	1.1/12.0	293	66.9/422
EXP. 3	94/97	1.3/14.5	210	39.2/248
EXP. 4	98/98	1.5/16.3	115	18.9/121
EXP. 5	101/107	0.1/1.6	74	119/797

higher than that of Cu (0.1–1.2%), which was corresponding to the expectations from the pH desorption pattern (Fig. 2) since at pH 7 the Cd started to mobilize whereas the pH was around 5 for Cu. Moreover, from the speciation analysis (Fig. 5), it can be seen that the percentage in the carbonate and exchangeable fraction which is more removable than other fractions [20–22] of Cd is much higher than that of Cu. This is probably another reason for the higher removal efficiency of Cd. For Cu, there was no significant improvement caused by pulse current (EXP. 2–4) compared with constant current (EXP. 1) since the removal efficiency was low for all experiments. By contrast, the removal efficiency of Cd in EXP. 2–4 was higher than that in EXP. 1. The highest removal efficiency of Cd occurred in the experiment with lowest frequency (EXP. 4), and decreased with the increase of the frequency. The removal efficiency of Cu and Cd was much higher in EXP. 1–4 than that in EXP. 5, which means the removal was more effective in the experiments with cation exchange membrane than the experiment with filter paper.

3.3. Energy consumption

In all experiments the current was constant (40 mA) and did not change over the entire duration, therefore the variation of voltage is an indicator of the energy consumption. Fig. 6 shows the variation of voltage (between working electrodes) with the consumption of electrical energy (Wh). The pulse pattern is not shown in the figures in order to allow for a direct comparison. The voltage in EXP. 5 was lower than in the other experiments all through the experiments, and thus this experiment had the lowest energy consumption. The only difference between EXP. 5 and 1–4 was the filter paper instead of the cation exchange membrane applied in experimental setup. This on one hand decreased the resistance and on the other hand allowed more free ions and water to transport into soil compartment, but it was not beneficial for the removal of heavy metals as discussed, and most importantly the energy consumption per removed heavy metals was higher in EXP. 5 than other experiments
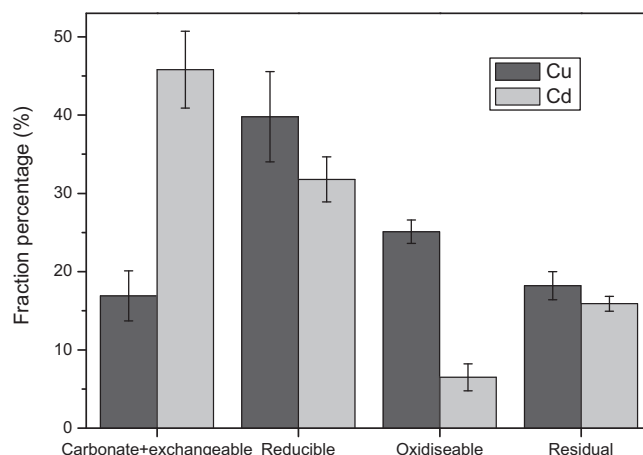
conductivity results in the following text. In these experiments, the pH values were below 5 in slice 1, which indicated that the Cu and Cd started to be mobilized according to Fig. 2. In the pulse current experiments, the slight differences in the pH of the soil parts near cation exchange membrane were possibly caused by the interdiffusion of H^+ ions from cathode compartments and positive ions from soil solution, and the extent was dependent on the relaxation time. In EXP. 5, the relatively high pH was due to the migration of NO_3^- and OH^- ions from cathode compartment (since pH was not strictly kept at 2, it was done manually at every 24 h) which diminished the water dissociation and increased the pH.

The final distribution of Cu and Cd in the soil (Fig. 4) was highly related to the pH profiles since the release of heavy metal ions and the following accumulation from one soil slice to another were determined by pH. It can be seen that Cu and Cd were mobilized in all experiments, and as cations as expected, because it was the slices closest to anion exchange membrane that was remediated first and the transport direction was towards the cathode. Table 3 is the removal efficiency of Cu and Cd after treatments. The removal efficiency was calculated as the mass of the actual heavy metal in the electrode components (membranes, electrolyte, and on electrodes) divided by the total mass found in all parts of the cell at the end of the experiment. The low removal efficiency is probably due to the high buffering capacity as discussed above and the short remediation time operated on the experiments. Further enhancement is probably necessary to obtain high removal efficiency [19]. The removal efficiency of Cd (1.6–16%) was significantly

Fig. 5. Sequential extraction of Cu and Cd in experimental soil.

Fig. 6. Variation of voltage between working electrodes.

Fig. 7. Variation of voltage at different parts of EDR cells. (A), (B), and (C) are the parts between monitoring electrodes 1–2, 2–3, and 3–4, respectively.

(Table 3). The pulse current showed effective reduction in energy consumption compared with constant current, as it could be seen that the voltage was lower in EXP. 2–4 than EXP. 1. Among EXP. 2–4, the energy consumption decreased with the decrease of frequency. Similarly, the energy consumption per removed heavy metals is higher in EXP. 1 than that in EXP. 2–4, and the lowest value was obtained in EXP. 4 (Table 3).

The voltage drop during experiments in the different parts of cell is shown in Fig. 7, in which (A), (B), and (C) are the parts between monitoring electrodes 1–2, 2–3, and 3–4, respectively.

In the (A) part (Fig. 7A), the voltage increased first and reached a maximum value after a period, and then it decreased in EXP. 1–4. The increasing voltage was probably caused by the depletion of ions at the surface of the anion exchange membrane due to concentration polarization. Afterward, water dissociation supplied sufficient ions to decrease the voltage drop, and the produced H^+ ions initiated desorption and dissolution processes in the soil which resulted in an increase of conductivity. In EXP. 5, only a slight increase of the voltage was observed. The concentration polarization near the anion exchange membrane is determined by the applied current density and ionic concentration in the soil pore fluid. Since the current density was identical in all experiments, the reason for the lower voltage in EXP. 5 was the higher ionic concentration. This was probably due to the injection of free ions to the soil compartment by pump at the initial equilibrium period without current.

It can be seen from Fig. 7B that the voltage drop across the soil compartment showed different patterns between the experiments. The EXP. 5 (without the cation exchange membrane) had the lowest voltage drop through the entire duration. The cation exchange membrane is used in order to prevent ions in the cathode compartments from entering the soil, so no current is wasted in carrying ions from one electrode compartment to the other. Meanwhile, this causes a depletion of the free ions in the soil solution like in the desalination compartment in conventional electrodialysis, and thus increases the voltage drop. In EXP. 5, all ions were allowed to pass from the catholyte to the soil, which decreased the voltage drop. However, in this case, the transference number of the heavy metals decreased as well and subsequently the current efficiency. The voltage drop in EXP. 2–4 was lower than that of EXP. 1. The voltage drop between two monitoring electrodes across the soil compartment in the EDR system under an external electric field can be expressed as:

$$V_t = V_{eq} + IR + \eta \tag{2}$$
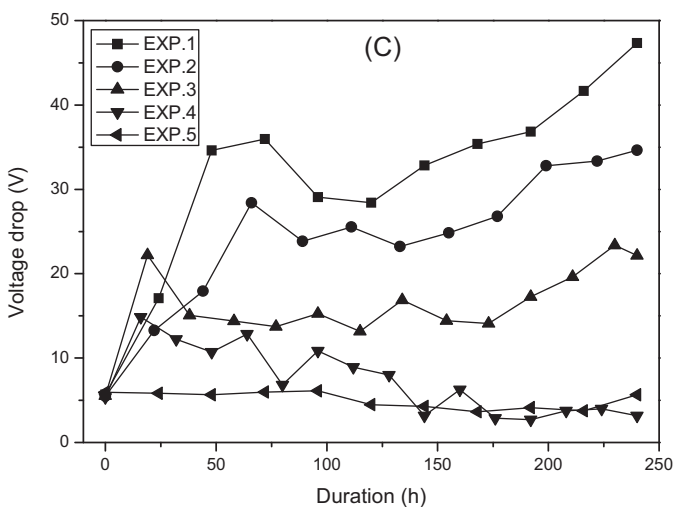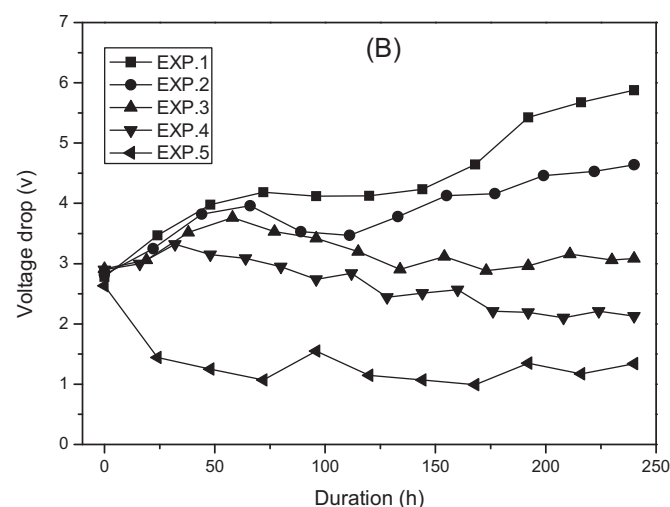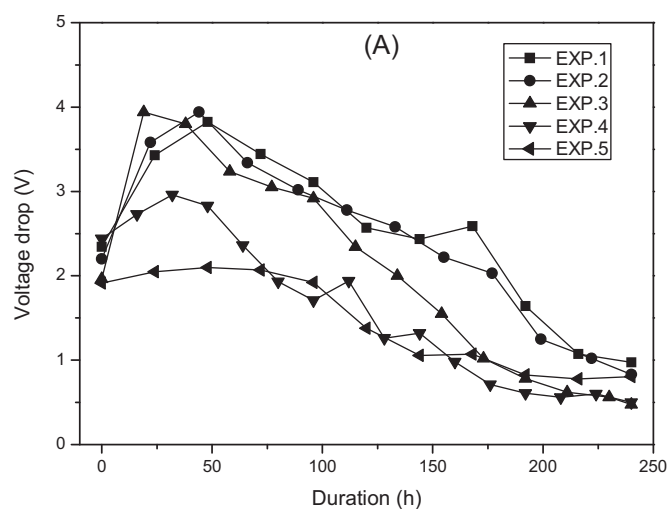
following the expression of the voltage drop in the electrolysis between anode and cathode [6], where V_{eq} is the voltage drop under equilibrium state without applied current, which is the summation of redox potential difference and diffusion potential caused by the inhomogeneity of the experimental soil, IR is the ohmic voltage drop induced by the pore fluid, and η is the overpotential
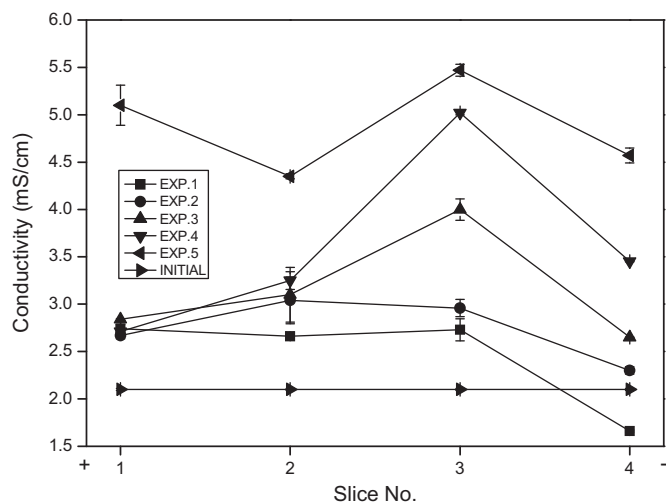
Fig. 8. Final profiles of the conductivity in the soil sample.

caused by the polarization of clay particles. The latter is related to the electrodialysis of the clay particles due to the inherent negatively charged surface and non-conductive bulk. During application of a direct current to the saturated soil system, excess ionic species will be accumulated on one side of the clay particles and depleted on the other, giving rise to a concentration polarization [23,24]. Moreover, an induced space charge will probably occur with a potential difference across the interface layer (i.e. the electric double layer) due to the conductivity difference between the clay particle surface and the surrounding solution, similar to the charging of the ionic double layer at the electrode-electrolyte solution interface [6,25]. However, it has been indicated by previous studies [10,26] that the overpotential caused by the polarization of clay particles is low (at the magnitude of mV); therefore, the pulse current enhanced energy saving effect within the soil compartment is mainly expected as the decreasing of pore fluid resistance.

The variation in electric conductivity measured in a suspension of each soil slice at the end of experiment is shown in Fig. 8. The increased conductivity in EXP. 1–4 was caused by the H+ ions, which enhanced desorption and dissolution processes. But in EXP. 5, the high conductivity was mainly maintained by the electromigration of negative ions and other free ions along with water movement from the cathode compartment. At slice 4 of EXP. 1, the conductivity decreased to a value lower than initial which indicated that there was a barrier impeding the transport of free ions from slices 1–3 to slice 4. This phenomenon was also observed in pulse current experiments (EXP. 2–4) expressed by the accumulation of free ions in slice 3. From the pH profile in Fig. 3, it was deduced that the re-precipitation and crystallization at higher pH region in slice 3 led to the barrier in EXP. 1 and accumulation in EXP. 2–4. Due to the diffusion process from slices 3 to 4 at the relaxation period in pulse current experiments, the conductivity in slice 4 maintained the value higher than the initial. Through the comparison of EXP. 1 and EXP. 2–4, the results demonstrated that the conductivity in the pulse current experiments was higher than that in the constant current experiment, which explained the lower voltage drop at soil compartment shown in Fig. 7B. Among the pulse current experiments, the conductivity increased with the relaxation time. The reason for this is possibly that the rate of dissolution caused by H+ ions is slow compared to the rate of transport of ionic species when the current is "on". A relaxation period when the current is "off" then allows the system to precede the chemical mechanisms of dissolution, and the species concentration in solution increased. The maximum time for the relaxation is the restoration of the equilibrium state.
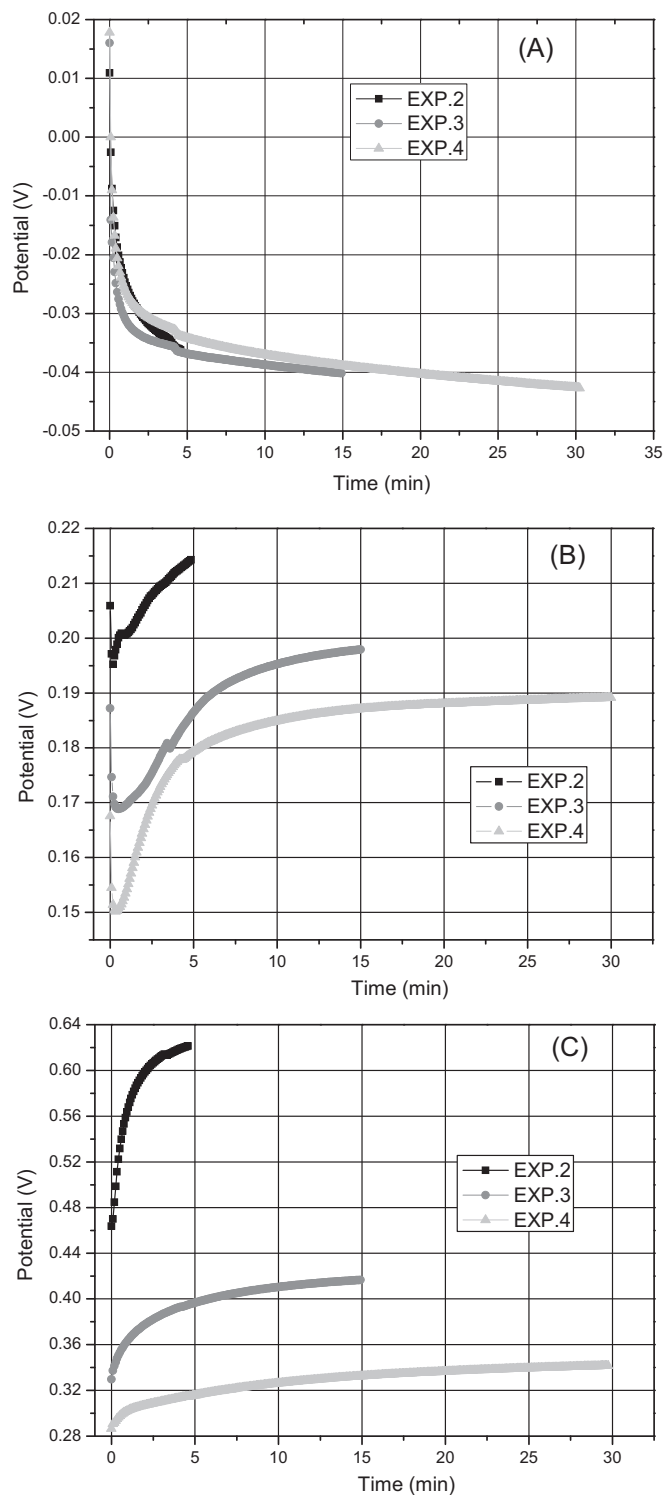

Fig. 9. Selected chronopotentiometric measurements of the relaxation processes within the soil compartment. The initial, middle and late stages of the experimental duration are represented by (A)–(C), respectively.

The re-equilibrium processes at the relaxation period represented by the chronopotentiometric analysis were given in Fig. 9 with (A) for the initial stage, (B) for the middle stage, and (C) for the late stage. At the initial stage (Fig. 9A), it can be seen that the similar relaxation trend was obtained in different pulse experiments. The EXP. 4 showed the best condition approaching the equilibrium followed by the EXP. 3, and the EXP. 2 was far from equilibrium. For a system, the more equilibrium a process approaches the less energy

it will require from the environment to drive the process, according to the thermodynamics [27]. The re-equilibrium process was determined by (1) the discharging of soil double layers driving by the electrostatic force, which was indicated by the sharp decrease of the potential after switching off the current; and (2) the diffusion caused by the concentration gradient build up during the time with applied current, which was indicated by the slow decrease in Fig. 9A. At the middle stage (Fig. 9B); the increased potential after the initial drop in all pulse current experiments was probably due to the diffusion potential. There is no simplified equation to quantitatively express the diffusion potential in the soil–water system. However, the pH and ionic strength are considered as the most important factors influencing the diffusion potential by changing the ionic mobility and the activity coefficient [28]. The H^+ ions produced by water dissociation near the anion exchange membrane and transported towards the cathode causes acidification resulting in dissolution process within the soil, which can give rise to huge difference in pH and ionic strength in the soil compartment, thus the diffusion potential increases. The different potential value in EXP. 2–4 was correlated to the voltage drop just before switching off the current (Fig. 7B). At the late stage (Fig. 9C); the discharging processes disappeared in all experiments which were possibly masked by the high diffusion potential. The potential range in this stage could be an indicator for the deviation of the system from equilibrium state after the remediation process. From Fig. 9C, it can be seen that the experiment with 5 min off time had the highest deviation from the equilibrium state while the experiment with 30 min off time was lowest. The experiment with 15 min was the medium. Therefore, it can be concluded that the suitable relaxation time for the present experimental soil was between 15 and 30 min from the viewpoint of both energy consumption and remediation time.

Finally, the voltage in the (C) part (Fig. 7C) has a highly similar pattern and value compared to the voltage applied to the working electrodes (Fig. 6) in all experiments. This means the highest voltage drop occurred in the part across the cation exchange membrane, and that this part was the mainly contributor of energy consumption. However, the voltage drop in this area was highly connected to the mass transport of ions in the soil pore fluid and the transport of ions within the membrane. The reason for an increasing voltage drop within the membrane is mainly membrane fouling, but the fouling phenomenon has not been observed in EDR soil cells. The transference number of the membranes and permselectivity did not change after being used in electrodialytic soil remediation experiments [29]. Therefore, the concentration polarization at the soil pore fluid and membrane interface is considered main responsible to the high voltage drop. The mass transport step in the interfacial region could be expressed by the well-known Nernst–Planck–Poisson equation, but due to the high ionic mobility it is shorten to electromigration [30]:

$$j = \left(\sum z_i F C_i u_i \right) \frac{dV}{dx} \tag{3}$$

where j is the current density, z_i is the valence of the ionic species, F is the Faraday constant, C_i is the concentration of ions, u_i is the mobility, and dV/dx is the electric field strength. It can be seen from Fig. 7C that the voltage in this part in the pulse current experiments was lower than that in the constant current experiments. This indicated that the energy saving effect caused by pulse current in the whole EDR system was expressed by the energy saving in (C) part. The reason was probably the diffusion of ions at the relaxation periods in the pulse current experiments, which diminished the concentration polarization and increased the conductivity in the vicinity of the cation exchange membrane. The term in the brackets in Eq. (3) is the expression of conductivity, which is determined by the concentration with other variables constant since the same

soil samples were used in all experiments. It can be seen from Eq. (3) that higher concentration leads to a lower electric force to drive the identical current density. The concentration could be qualitatively demonstrated by the conductivity in slice 4 of the soil compartment (Fig. 8), in which the highest value was obtained in the experiment with 30 min off followed by the order of relaxation time. When the cation exchange membrane was substituted by filter paper (EXP. 5), the energy consumption could be very low, but this impeded the removal of heavy metals significantly.

4. Conclusions

(1) Pulse current decreased the energy consumption with different extent depending on the pulse frequency. Among the pulse frequencies, lowest energy consumption (115 Wh) occurred in the experiment with 30 min relaxation time after every 60 min working time, followed by 15 min relaxation (210 Wh) and 5 min relaxation (293 Wh). Similar trend was also observed at the energy consumption per removed Cu and Cd.

(2) At different parts of EDR cells, it was found that the voltage drop of the area across cation exchange membrane was the major contributor of energy consumption, and the pulse current could decrease the voltage drop of this part effectively by re-distribution of ions.

(3) Substitution of the cation exchange membrane with filter paper induced a dramatic decrease of energy consumption (74 Wh), but this change hindered the acidification process and thus removal of heavy metals significantly.

(4) The removal efficiency of Cd (1.6–16%) was higher than that of Cu (0.1–1.2%). For Cu, there was no significant improvement caused by pulse current (EXP. 2–4) compared with constant current (EXP. 1), but the removal efficiency of Cd in EXP. 2–4 was higher than that in EXP. 1. The highest removal efficiency of Cd occurred in the experiment with lowest frequency (EXP. 4), and decreased with the increase of the frequency.

(5) The suitable relaxation time for the present experimental soil investigated on the basis of restoration of equilibrium was between 15 and 30 min from the viewpoint of both energy consumption and remediation time.

Acknowledgment

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Appendix IV

Electrodialytic soil remediation enhanced by low frequency pulse current –

Overall chronopotentiometric measurement

(Published in Chemosphere)

Technical Note

Electrodialytic soil remediation enhanced by low frequency pulse current – Overall chronopotentiometric measurement

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HIGHLIGHTS

- ► The pulse current could decrease the energy input during the EDR process.
- ► The detailed mechanism was given by chronopotentiometric study.
- ► The distribution of the energy consumption in EDR cells was demonstrated.
- ► The rate controlling step of EDR process was determined.
- ► Polarization of the membranes and clay particles were characterized.

GRAPHICAL ABSTRACT
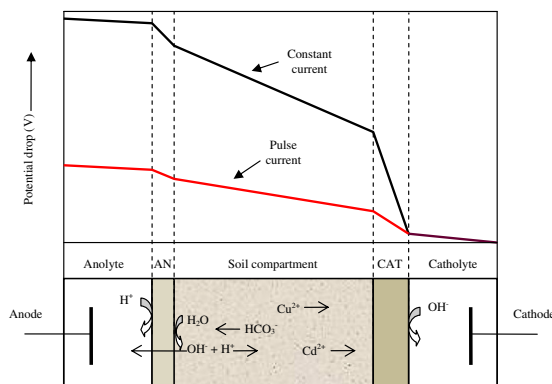
ABSTRACT

The effect of low frequency pulse current on decreasing the polarization and energy consumption during the process of electrodialytic soil remediation was investigated in the present work. The results indicated that the transportation of cations through the cation exchange membrane was the rate controlling step both in constant and pulse current experiments, thus responsible for the major energy consumption. After 180 h, a decrease in both the initial ohmic resistance in each pulse cycle and the resistance caused by concentration polarization of the anion exchange membrane were seen in the pulse current experiment compared to the constant current experiment. At the cation exchange membrane, only the resistance caused by concentration polarization decreased. In the soil compartment, an average of +60 mV overpotential caused by the polarization of the electric double layer of the clay particles was obtained from the Nernstian behavior simulation of the relaxation process, which was significantly lower than the ohmic voltage drop induced by pore fluid resistance. Therefore, the ohmic polarization was the major contributor to the energy consumption in the soil compartment and diminished by pulse current.

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1. Introduction

The energy consumption of the electrochemically based remediation techniques is an important factor influencing costs and thus the applicability (Acar and Alshawabkeh, 1996; Reddy and Saichek, 2004; Kornilovich et al., 2005; Zhou et al., 2006; Ryu et al., 2010). Polarization, as an inevitable process, is a key issue as it is responsible for extra and nonproductive energy consumption. In the electrodialytic soil remediation (EDR) system, it mainly includes the polarization of electrodes, membranes and clay particles in the soil.

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The electrode polarization could be controlled by electrochemical polarization and/or concentration polarization, depending on the different rates of the electrode reactions and mass transport processes (Bard and Faulkner, 2001). However, in EDR the electrodes are placed in compartments separated from the soil by ion exchange membranes and electrolytes are circulated in the electrode compartments (Ottosen et al., 1997), which reduce the electrode polarization. Concentration polarization occurs in all membrane separation processes owing to differences in the transport numbers of ions in the solution and in the ion exchange membrane (Strathmann, 2010). Passing an electric current through an ion exchange membrane, the ionic concentration on the desalting surface of the membrane is decreased due to concentration polarization, and reduced to zero at the limiting current density. In this circumstance, there are no more ionic species available to carry the current and the voltage drop across the boundary layer increases drastically resulting in a higher energy consumption and generation of water dissociation. In the water saturated soil system, the most active part interacting with the external electric field is the clay particles (Sposito, 1989). The induced polarization is related to the electrodialytic effects on the electrical double layer of the clay particles due to the inherent negatively charged surface and non-conductive bulk (i.e. the solid part of the clay). During application of a direct current to the saturated soil system, excess charge will be accumulated on one side of the clay particles and depleted on the other, giving rise to a concentration polarization (Nischang et al., 2007; Mischuk, 2010). Due to the incompatibility between the conductivity of the clay particles with low surface conductivity and the surrounding electrolyte solution (i.e. pore fluid) with high ionic conductivity, induced space charge will probably occur with a potential difference across the interface layer, similar to the charging of the ionic double layer at the electrode–electrolyte solution interface (Bard and Faulkner, 2001; Pamukcu et al., 2004). Considering the connection between clay particles and pore fluid as in series, the total voltage drop between two monitoring electrodes across the soil compartment in the EDR system under an external applied electric field can be expressed as:

$$V_t = (V_{eq} + V_R) + \eta \qquad (1)$$

ccording to the expression of the voltage drop in the electrolysis between anode and cathode (Bard and Faulkner, 2001; Pamukcu, 2009), where V_{eq} is the voltage drop under equilibrium state, V_R the ohmic voltage drop induced by the pore fluid, and η is the overpotential.

Pulse current as an approach to decrease the energy input in an electrodialytic desalination process, was investigated by Mischuk et al. (2001). The basic principle they applied was to keep the characteristic time of a pulse (at the interval magnitude of s) shorter than the time required for building up a concentration polarization layer near the membrane (transition time) in order to avoid water dissociation and nonproductive energy loss even at a current density above the limiting value (i.e. overlimiting current density). However, in EDR, the water dissociation at the anion exchange membrane at the overlimiting current density is of great importance and must necessarily be exceeded, since the resulting acidic front developing in the soil is a key factor for mobilization of the heavy metals. Therefore, the present work is focused on use of low frequency pulsed current (at the interval magnitude of h) to decrease the energy input compared to constant current during EDR. The detailed mechanism was given by chronopotentiometric analysis. Chronopotentiometry is an electrochemical characterization method measuring the electric potential response of a system to an imposed current. Usually, it is used to measure the polarization kinetics of an irreversible electrode process (Pletcher et al., 2006). The method allows a direct access to the voltage contribu-

tions in the different stages of the EDR process, because the dynamic voltage response over time can be analyzed.

2. Materials and methods

2.1. Soil sample

The experimental soil was contaminated by copper and cadmium, sampled from a pile of excavated soil. The soil was air-dried at room temperature, and gently crushed by hand in a mortar and passed through a 2 mm mesh sieve before the experiments.

Some chemical and mineralogical properties of the soil are presented in Table 1. Soil pH and conductivity were measured using a Radiometer pH electrode and conductivity electrode, respectively. The content of organic matter was found as a loss of ignition after 1 h at 550 °C. The carbonate content was determined volumetrically by the Scheibler-method when reacting 3 g of soil with 20 mL of 10% HCl. Grain size distribution was determined by wet-sieving approximately 100 g natural wet soil with 0.002 M $Na_4P_2O_7$ and the mineral composition of the bulk soil as well as the clay fraction was revealed by the XRD-analysis (Jensen et al., 2006).

2.2. Preparation of experimental setup

A schematic diagram of the experimental setup is shown in Fig. 1. The electrodialytic cell was made from polymethyl methacrylate. The cell had an internal diameter of 8 cm. The length of each cell compartment was 5 cm. The ion exchange membranes were from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum coated electrodes from Permascand were used as working electrode in compartments I and III. Between the two working electrodes, four monitoring electrodes (platinum coated electrodes) were used to monitor the voltage drop of three different parts of the cell, see Fig. 1. The soil (370 g) with adjusted water content of 23% was packed in compartment II. After assembly, the entire setup was placed on a slowly agitating table for 1 h to ensure a good distribution of soil particles.

2.3. Procedure

One constant current experiment and one pulse current experiment were made. In each of the electrode compartments 500 mL 0.01 M $NaNO_3$ adjusted to pH 2 with HNO_3 as electrolyte was circulated by pumps. After 24 h, 40 mA corresponding to a current density of 0.8 mA cm^{-2} was applied in both experiments by a power supply (Agilent E3612A). The voltage drop between anode and monitoring electrodes inserted in the different parts of the EDR cells as a function of time was automatically recorded by datalogger (Agilent 34970A) with a rate of once per 5 s. In the pulse current experiment, the pulse current was accomplished by a power supply timer instrument (Joel TE102), and the program

Table 1
Chemical and mineralogical properties of the soil sample.

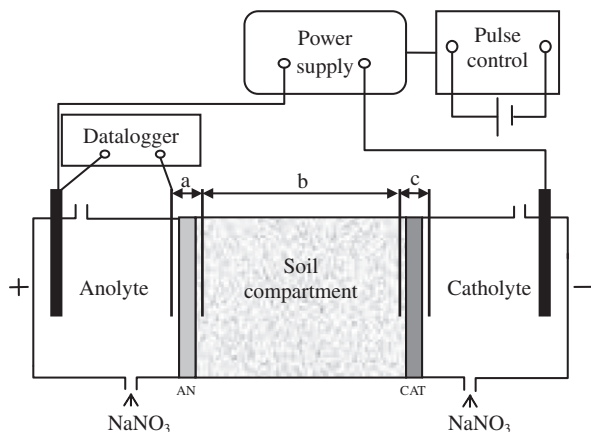|	
pH	7.6
Conductivity	2.1 mS cm^{-1}
Carbonate content	7.1%
Organic matter	6.5%
Grain size distribution	
Sand	24%
Silt	61%
Clay	15%
Clay mineral composition	Kaolinite, Illite and Smectite

Fig. 1. Schematic diagram of the laboratory cell for electrodialytic soil remediation (AN = anion exchange membrane, CAT = cation exchange membrane. Letter "a" indicates the part across the anion exchange membrane measured between monitoring electrodes in the anolyte and in the soil, "b" the part in soil compartment between, and "c" the part across cation exchange membrane between soil and in the catholyte).

Fig. 2. Distribution of voltage drop across the EDR cells, with (a) for constant current experiment and (b) for pulse current experiment.

was 60 min "on" and 30 min "off". The total duration for the constant current experiment was 120 h; while for the pulse current experiment it was 180 h. Although the total duration was different, the total working time was the same when the "off" time was taken into account in the pulse current experiment. Thus, the total charge passed through the cell in the two experiments was identical. Due to the electrode processes, pH-changes occurred in the electrolytes and the pH was manually kept between 1 and 2 by addition of HNO_3 and NaOH. The permselectivity of anion exchange membrane will decrease significantly if the pH in anolyte drops to below 1 and the precipitation when the pH in catholyte rises to above 2 will lead an extra voltage drop across the cation exchange membrane (Jensen et al., 2007). Therefore, the control of pH in both anolyte and catholyte was to eliminate the interference caused by the damage of the membranes.

3. Results and discussion

3.1. Distribution of voltage drop

The current density was identical in the two experiments and the voltage variation is thus an indicator of the energy consumption. The distribution of the voltage drop is shown in Fig. 2, (a) for the constant current experiment and (b) for the pulse current experiment. The voltage drop is shown after different durations for a direct comparison of the voltage drop after the same working time between the constant current and the pulse current experiments. It can be seen from Fig. 2a that the total voltage drop increased over time in the constant current experiment from initial 10.5 V to 66.5 V at the end of the experiment. The increase was fastest in beginning of the experiment. The voltage drop was at its lowest in the anolyte and the catholyte compartment during the whole experiment. This was due to the circulation systems and that pH was controlled around 2 during the experiment. The voltage drop in part c was significantly higher than a and b after 12 h working time and increasing, which can be seen from the slopes of section c, therefore, the part c was the most energy consuming part. In other words, when constant voltage was applied, the step transporting cations through the cation exchange membrane was the rate controlling step, by which the kinetics of the whole EDR process was determined. The voltage drop of parts a and b increased in the beginning, and reached a constant value
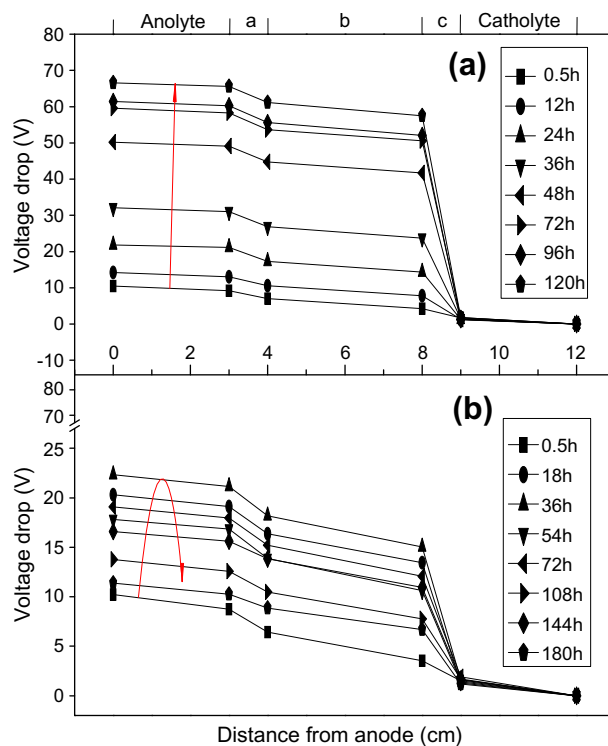
hereafter, which could be seen from the slopes. Compared to the constant current experiment, the total voltage drop in the pulse current experiment (Fig. 2b) was much lower and the voltage drop was not continuously increasing, but decreasing after about 36 h. The voltage range was from 10.23 V to 22.33 V and at the end 11.37 V. This demonstrated the positive effect of the pulse current on energy saving aspect of the EDR cells. The highest voltage drop also occurred in part c in pulse current experiment. The voltage drop of the electrolytes was constant in the entire duration and significantly lower than other parts, which indicated the low extent of electrode polarization as expected.

3.2. Overall chronopotentiometric analysis of pulse current experiment

The chronopotentiogram of the membranes is shown in Fig. 3. It can be seen from the working time (section above the straight lines on the x-axis) that the voltage drop increased first and obtained the maximum value after a period, then decreased for both of the membranes. Fig. 4 is the chronopotentiometric curve for the first cycle (the square boxes in Fig. 3). In Fig. 4a, the curve consists of seven parts. At time 0–10 min (Section 1) no current was applied and the voltage difference was due to the different composition and concentration between the electrolyte in the anode compartment and soil pore fluid, i.e. the membrane potential. After 10 min, a fixed current density was applied causing an instantaneous increase in voltage (Section 2) due to the initial ohmic resistance of the system composed of solution and membrane between the monitoring electrodes. Section 3 commenced a slow increase in voltage drop in time due to the depletion of the electrolyte concentration in the pore fluid near the anion exchange membrane governed mainly by electromigration. At a certain time this was followed by a strong voltage increase (Section 4). The point at which this increase occurs is the transition time (τ) which can be determined as the intersection of the tangents to Sections 3 and
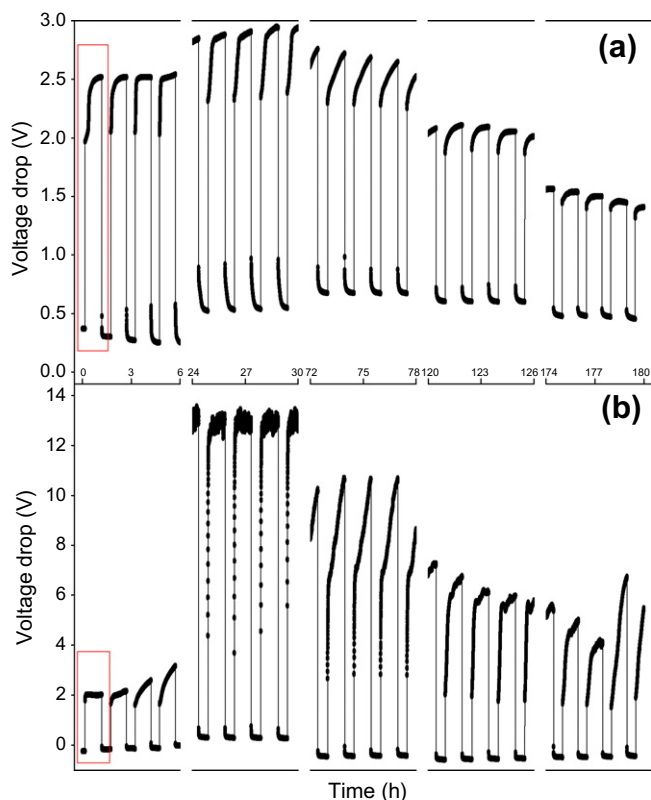
Fig. 3. Selected chronopotentiogram of membranes with (a) for anion exchange membrane and (b) for cation exchange membrane.
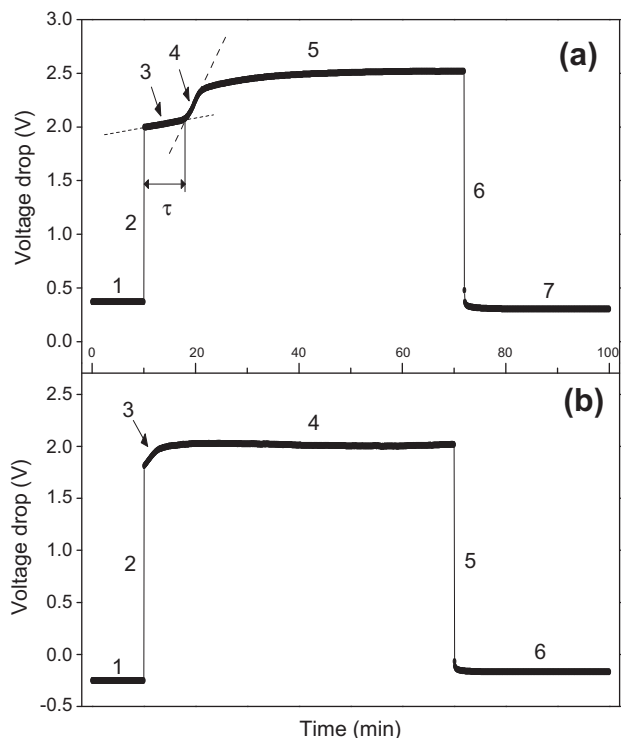

Fig. 4. Chronopotentiogram of the first cycle of membranes which was denoted in Fig. 3 by square box, with (a) for anion exchange membrane and (b) for cation exchange membrane. The numbers in the graph refer to the different stages explained in the text.

4 of the curve (Pismenskaia et al., 2004). The transition time is the time for the concentration at the membrane surface decreases to zero. The transition time as a function of applied current density is derived from Fick's second law and given by:

$$\tau = \frac{\pi D}{4}\left(\frac{C_i^0 z_i F}{T_i - t_i}\right)^2 \frac{1}{i^2} \qquad (2)$$

where D is the diffusion coefficient of the electrolyte in the pore fluid of soil, C_i^0 and z_i are the concentration in the bulk and the charge of the counter-ion, respectively, T_i and t_i are the transport numbers of the counter-ion in the membrane and pore fluid, respectively, i the current density and F is the Faraday constant. Eq. (2) is equivalent to the Sand equation frequently used in studies of electrode systems (Bard and Faulkner, 2001). The occurrence of transition time indicated that the overlimiting current density has been applied to the anion exchange membrane as well as the water dissociation could be expected (Krol et al., 1999). This transition state was not seen for the cation exchange membrane (Fig. 4b), which means that current density applied was sublimiting. The measured soil pH after experiment was 3.4–6.6 from the anion exchange membrane side to cation exchange membrane side, indicating that water dissociated at anion exchange membrane but not at cation exchange membrane, which is the requirement during EDR. The limiting current density of anion exchange membrane is lower than that of cation exchange membrane because there are fewer anions than cations in the electric double layer of the soil. Further, next to the anion exchange membrane is the negatively charged soil surface which forms a bipolar interface depleting ions rapidly. Finally, the system reached a steady state (Section 5) where the voltage drop levels off. The voltage difference of Section 6 is equal to the ohmic voltage drop over the polarized membrane system at the moment of the current switching off. The last Section (7) describes the relaxation of the system determined by a diffusion process and the relaxation time is correlated to the reciprocal of the diffusion coefficient (Tanaka, 2007).

A further analysis of the details of the pulses (Fig. 3a) showed that the transition time decreased sharply and disappeared after a few cycles. This is probably owing to the decrease in the transport number of negative ions. When the overlimiting current density was applied over the anion exchange membrane, the H+ ions from the water dissociation contributed in carrying current. As the mobility of H+ ions is significantly higher than other ions, the transport of the negative ions decreased and gave rise to a short transition time (Eq. (2)). With an increased number of H+ ions produced, the transition time disappeared. An increased voltage drop during the working time of each cycle is seen from Fig. 3a (equivalent to Section 4 in Fig. 4a). It was led by the ohmic resistance increase in the diffusion layer because of the applied overlimiting current density. For the cation exchange membrane which was below the limiting current density (Fig. 3b), the increased resistance was probably due to the re-precipitation of the mobilized ions in the higher pH region. Overall, it could be seen from Fig. 3 that the pulse current decreased the energy consumption across the anion exchange membrane by means of decreasing both the initial ohmic voltage drop and the resistance within the diffusion layer at the working time. However, the initial ohmic voltage drop did not change much at the cation exchange membrane. The energy was mainly consumed by concentration polarization of the membrane and the pulse current induced resistance decreasing in the diffusion layer of the membrane was the main reason responsible to energy saving.

The chronopotentiogram across the soil compartment is shown in Fig. 5. Before switching on the current, the voltage difference was −0.12 V, and most probably due to the heterogeneity of the soil sample. After switching on the current, a large ohmic resis-
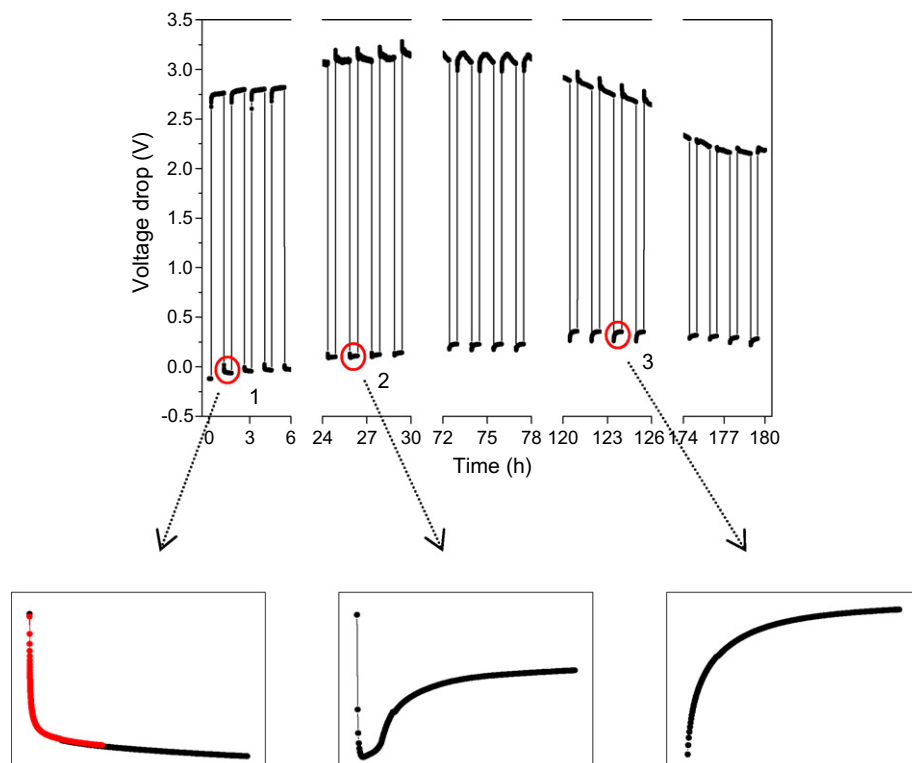
Fig. 5. Selected chronopotentiogram across the soil compartment. The circles in the graph refer to the different stages explained in the text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tance induced voltage drop appeared, which could be seen from the straight lines at the first cycle. Taking this voltage drop into the differential form of the ohmic's law given by:

$$i = \sigma_s E \tag{3}$$

where i is the current density, σ_s the conductivity of the soil–water system and E is the electric strength, one can obtain σ_s = 1.45 mS cm^{-1}. Attention must be paid here since the linear electric field over the soil has been assumed in the calculation, but probably it is not. However, this deviation will not hinder the utilization of Eq. (3) to estimate the average conductivity variation as a function of time across the soil compartment. After the initial ohmic voltage drop, a slight and slow voltage increase over time showed, which indicates the polarization of the clay particles. As it was mentioned in Eq. (1), the voltage drop of the soil compartment consists of the ohmic voltage drop in the pore fluid and the voltage drop across the clay electric double layer. However, the ohmic resistance in the pore fluid is not constant. The predominated impact factor is the dissolution and precipitation equilibriums (Wada and Umegaki, 2001). When the pH is low near the anion exchange membrane, the equilibriums shift to the dissolution side and decrease the local resistance; on the contrary, the equilibriums shift to the precipitation side in the high pH region near the cation exchange membrane and increase the local resistance. Therefore, the shift of the equilibriums within the soil influenced the change in ohmic voltage drop. Correspondingly, the polarization arising from the clay-pore fluid system could be divided into the ohmic polarization followed the terminology in electrochemistry and the polarization of the electric double layer of the clay particles. At the very beginning, the produced H$^+$ ion by water dissociation and its dissolution is small compared with the conductivity of the pore fluid, thus it is reasonable to consider the slow voltage increase in first cycle as the polarization of the electric double layer of the clay particles.

Electrochemically, the overpotential of an electrode is the deviation of the electrode potential when electron is passing through

from its equilibrium potential (Bard and Faulkner, 2001). However, the clay particles are not electrodes and it is not possible to change their surface potential and measure the overpotential of a single clay particle by passing electrons. In the present work, the difference in voltage drop between current and the voltage drop of equilibrium with no current is utilized to express the overpotential of the entire soil compartment instead of a single clay particle (Eq. (1)). Circles 1, 2 and 3 in Fig. 5 are the periods without current representing the initial, middle and late stage of the remediation process, respectively. It can be seen from circle 1 that after switching off the current, the potential decreased sharply and reached the equilibrium state. The potential drop in this figure was more precise for estimating the polarization of the electric double layer of the clay particles, since the ohmic resistance disappeared right after switching off the current. However, due to the limitation of scan rate (once per 5 s), the overpotential could not be read directly from the figure. Following, a simulation of the relaxation period was introduced.

To describe the relaxation process, a simulation of the diffusion profile was attempted. The diffusion equation (Fick's second law) was solved with boundary conditions at the clay surface and in the infinity from the surface:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \tag{4}$$

where D is the diffusion constant, C the concentration, t the time and x is the one-dimensional distance from the clay surface. The differential equation needs two boundary conditions, (1) far from the clay particles, the concentration is unchanged, and (2) in the vicinity, the concentration is controlled by the applied current density. The time boundary is zero, when the experiment starts. The simulation was performed using an implicit Crank–Nicholson scheme with a lambda about 1 (Britz, 2005). The potential as a function of time is calculated from the Nernst equation:

$$E = Const - \frac{RT}{nF} \ln \frac{C_1}{C_2} \tag{5}$$

where R is the gas constant, T the absolute temperature, F the Faraday constant, C_1 and C_2 are the concentrations at two measuring points – one is far away from the clay particle and the other is near the clay particles, respectively. Assuming that C_1 does not change, the relaxation could be simulated to follow the experimental results (the red line in circle 1). The Nernstian factor in the simulation was 60 mV, which is the overpotential caused by the polarization of the electric double layer of the clay particles. Compared to the voltage drop induced by the ohmic resistance, the overpotential was significantly lower, which means the ohmic voltage drop was the major contributor to the energy consumption in the soil compartment. The average conductivity calculated by Eq. (3) was 1.47, 1.32 and 2.13 mS cm^{-1} for initial, middle and late stage, respectively. After a minimum value of 60 h, the conductivity increased over time although fluctuating, this effectively decreased the initial ohmic voltage drop after each "switching on". A possible reason for this is that the rate of dissolution caused by H$^+$ ions is slow compared to the transport rate of ionic species when the current is "on". A relaxation period when the current is "off" then allows the system to precede the chemical mechanisms of dissolution and the species concentration in solution increases. Thus, it can be concluded that the pulse current demonstrated a decrease in the energy consumption across the soil compartment by means of re-organization of the ionic concentration distribution.

In Fig. 5 circle 2, the potential decreased first and then increased and after a period the potential only increased in time (circle 3). This increased potential drop in the absence of current is probably due to the diffusion potential. Since the composition and the distribution of the ionic concentration in pore fluid are complicated, there is no simplified equation to quantitatively express the diffusion potential in the soil–water system. However, the pH and ionic strength are considered as the most important factors influencing the diffusion potential by changing the ionic mobility and the activity coefficient (Yu and Ji, 1993). The H$^+$ ions produced from the water dissociation near the anion exchange membrane and transported towards the cathode causes acidification as well as dissolution process within the soil, which could give rise to a huge difference in pH and ionic strength between the anion exchange membrane region and the cation exchange membrane region, thus the diffusion potential increased.

Finally, the pulse current did not show enhancement of the heavy metal removal compared to constant current (data not shown).

4. Conclusions

Pulse current (in low frequency) could decrease the energy consumption of EDR. A decrease in both the initial ohmic resistance in each pulse cycle and the resistance caused by concentration polarization of the anion exchange membrane were seen in the pulse current experiment compared to the constant current experiment. At the cation exchange membrane, only the resistance caused by concentration polarization decreased. The transportation of cations through the cation exchange membrane was the rate controlling step both in constant and pulse current experiments, thus responsible for the major energy consumption. In the soil compartment, the ohmic polarization was determined as the major contributor to the energy consumption and diminished by pulse current.

Acknowledgement

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Appendix V

Reduction of Hexavalent Chromium in Contaminated Clay by Direct Current

Transported Ferrous Iron: Kinetics, Energy Consumption, and Application of

Pulse Current

(Submitted)

Reduction of Hexavalent Chromium in Contaminated Clay by Direct Current Transported Ferrous Iron: Kinetics, Energy Consumption, and Application of Pulse Current

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Abstract

Direct current enhanced reduction of Cr(VI) at clay medium is a technique based on inputting extra energy into the clay to drive the favorable redox reaction. Despite the importance of the redox reaction, no mechanistic or kinetic information are available, which are needed to determine the rate of Cr(VI) reduction and to assess the corresponding energy consumption. In this study, Fe(II), as reducing reagent was electrokinetically transported into Cr(VI) spiked kaolinite clay to investigate the dependency of reaction rate on energy consumption. Results showed that the reduction rate of Cr(VI) was significantly increased by application of current with the pseudo-first-order rate constant k_{pse} from 0.002 min^{-1} at current density of 0 mA/cm^2 to 0.016 min^{-1} at current density of 0.6 mA/cm^2. But the increasing rate decreased at higher current range (0.3-0.6 mA/cm^2) compared to lower current range (0-0.3 mA/cm^2), probably due to the competitive transport of H$^+$ ions produced by electrolysis reaction. Mass transport process of Fe(II) in clay pore fluid was the rate controlling step and responsible for the major of energy consumption, which was confirmed from both aspects of kinetics and energy conversion. Application of pulse current could decrease the non-productive energy consumption which is due to the resistance increase in pore fluid caused by formation of precipitates (Cr,Fe)(OH)$_3$ by decreasing the initial Ohmic drop of each cycle. This

effect was more significant in lower pulse frequency due to the better restoration of equilibrium state of clay medium during relaxation period. Therefore, a re-equilibrium mechanism at relaxation period was proposed to determine the optimal pulse frequency for its application in field remediation.

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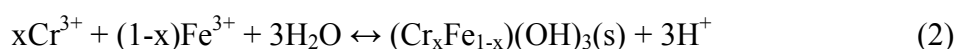
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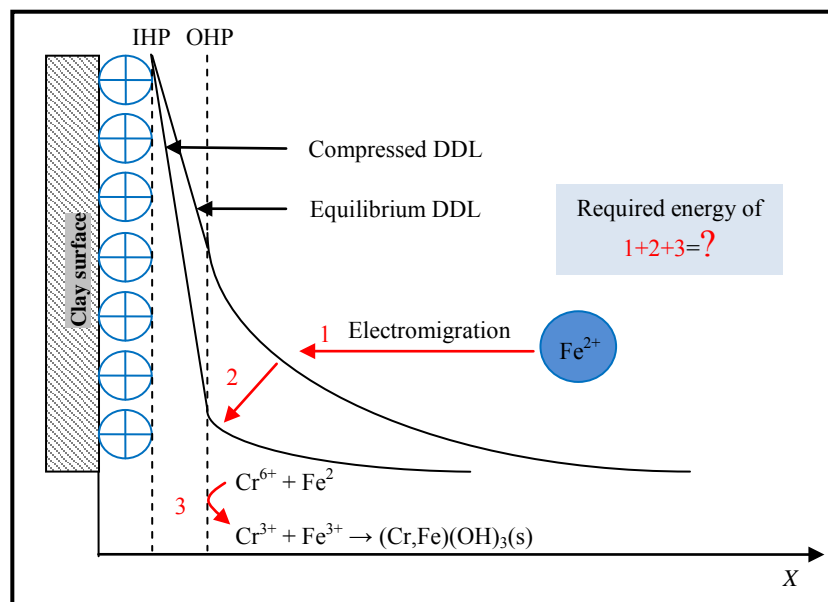
1. Introduction

The Cr(VI) caused soil contamination attracts great concern due to its high toxicity and the broad range of industrial processes which are sources of contamination [1-4]. A widely accepted method to reduce the impact of chromium in the environment is to convert Cr(VI) to the less toxic and less mobile Cr(III) [5-8]. The successful removal of Cr(VI) depends on the formation and stability of Cr(III) precipitates. Ferrous iron, Fe(II), is a very strong reducing agent, which will be used to reduce Cr(VI) over a wide range of pH[9-12]; hence injection of excess Fe(II) to a Cr(VI) contaminated soil can enhance the desired process. However, achieving uniform distribution of a reagent by injection in tight clay soils is often difficult owing to the low hydraulic permeability of these soils.

Electrokinetically caused migration of ions in soils is a proven method of transport in tight clay soils [13,14]. The ionic migration is most efficient when the clay is water saturated, but it also takes place in less than fully saturated states of the clay as long as there is continuity of the water phase through the pore structure. More importantly, when electrical energy is supplied to saturated clay, as in an electrolytic cell, it is possible to bring about non-spontaneous oxidation-reduction reactions that could further enhance the desired results, i.e. to cause the reaction to move forward by rendering more products than what the Nernst equation predicts. The laboratory evidence of enhanced Cr(VI) reduction to Cr(III) by electrokinetics was given in [15-18]. During the reduction of Cr(VI) at clay surface, the energy consumption is highly related to its kinetics like other heterogeneous chemical reactions. Similar to an electrode surface exchange, the reduction process at the clay surface could be divided into three steps [19] as depicted in supporting information (SI) Figure S1a, (1) mass transport of Fe(II) from the pore fluid to clay surface, (2) the electron transfer and (3) the formation of new products. The transport of Fe(II) produces a high ionic concentration in the pore fluid, thus the Cr(VI) within the electric double layer diffuse and accumulate toward the

clay surface. As the electrokinetic potential shifts to lower negative values, the potential difference between the inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP) increases until the electron transfers from Fe(II) to Cr(VI). In this case, the clay essentially acts as a barrier with the diffused double layer (DDL). The reaction between Fe(II) and Cr(VI) under anoxic conditions and acidic environments is as follows:

$$Cr_2O_7^{2-}+14H^++6Fe^{2+} \leftrightarrow 2Cr^{3+}+6Fe^{3+}+7H_2O \tag{1}$$
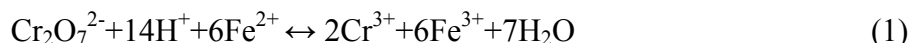
The formation of new product after reaction is known as:

$$xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \leftrightarrow (Cr_xFe_{1-x})(OH)_3(s) + 3H^+ \tag{2}$$

where x varies from 0 to 1. For example, it was reported x=0.75 when Cr(VI) was reduced at FeS surface [20], whereas x=0.25 when Cr(VI) was reduced by aqueous Fe(II) [21,22]. The formation of this new solid phase is desirable for remediation since it had rapid precipitation and dissolution kinetics and yielded lower solubility than that of Cr(OH)$_3$. Among these three steps, the step with the lowest rate becomes the rate controlling step, in other words, the most energy will be consumed at the controlling step if a constant current is applied to the system. The first objective of the present work has been to investigate the kinetics of the reduction process at clay surface and determine the energy consumption in each step.

The pulse mode of current has been widely used in analytical electrochemistry and conventional electrolysis, e.g. pulse voltammetry and electrodeposition [19,23,24], to examine the kinetics of processes on electrode surfaces. The concept of using a pulse current is that after switching on the current, it causes a depletion layer to be formed in the immediate vicinity of the electrode. After switching off the current (completion of pulse) the concentration of ionic species will be replenished by convective diffusion to avoid the nonproductive energy consumption caused by Ohmic resistance and polarization. Similar application was reported in soil electro-remediation [25-28], where it was found that the pulse current could increase the ionic conductivity in soil pore fluid

and decrease the energy consumption for transport. The energy consumption of electrochemically based remediation techniques is an important factor influencing costs and thus the applicability, for an application of these techniques beyond bench and pilot scale setups, this aspect is very important [29,30]. Therefore, the second objective of this study is to investigate the effect of pulse current on energy consumption during the Cr(VI) reduction process and discuss its mechanism from the viewpoints of interaction between transport and surface reaction and re-equilibrium process at relaxation period.

Materials and Methods

Preparation of clay samples. High-purity (china grade, Ward's Earth Science) kaolinite clay with nominal particle size of 2 μm was used as the test clay medium in all experiments. Kaolinite was selected due to its low swelling property and low impurity content to minimize possible influence of background iron and other ions on double-layer interactions. The spiked clay samples were prepared by adding 20 mL freshly mixed potassium dichromate (1200 mg/L $K_2Cr_2O_7$) stock solution to 10 g dry kaolinite clay. The mixture was allowed to equilibrate under agitation for 24 h. Afterwards the mixture was dried at 30 ºC avoiding the loss of lattice water in kaolinite and damaging its structure. The dry clay sample was saturated by distilled water before experiment. The consistency of the resulting moist clay was a soft, smooth paste, allowing for full liquid saturation and uniform distribution of chromium. The measured initial concentration of Cr(VI) after spike was 800 mg/kg dry clay. The initial pH of the mixture was 4.9.

Experimental setup. A schematic diagram of the experimental setup is shown in SI Figure S1b. The setup was modified from a commercially available electrophoresis (EP) cell supplied by C.B.S Scientific (San Diego, CA). The cell is a rectangular transparent box with a sample tray. The standard EP cell was equipped with internal working electrodes. The modified EP cell allowed

direct measurement of the redox potential in the clay by use of 0.25 mm diameter platinum wire electrodes embedded in the base plate of the sample tray. Three wires were stretched transversely along the length of the base plate. These electrodes were labeled as E1-E3 starting from the anode end, as shown in Fig. 1. The conductive glue was used to hold these platinum wires without contact to the insulated base plate. All platinum wires were purchased from Alfa Aesar (Ward Hill, MA). There are two liquid chambers on each side of the sample tray and a lid which covers the whole apparatus. The liquid chambers were used to hold the stock solutions of $FeSO_4$ (90 mg/L) as anolyte and Na_2SO_4 (0.01M) as catholyte in all experiments. The pH of Na_2SO_4 solution was kept at 3 by addition of HCl to prevent the extra precipitation of iron or chromium caused by OH^- ions produced from the electrolysis reaction. The $FeSO_4$ solution was deoxygenated with 99.999% ultra purified grade nitrogen gas (N_2) for a minimum of 1 h prior to testing. All stock solutions were made from ACS reagent grade materials.

A thin (5 mm) uniform clay paste containing the reacting agent, Cr(VI), was placed in the middle of the tray separated from the liquid by filter paper. The thickness of the clay paste was kept small to achieve as uniform distribution of charges and current on the clay cross section as possible. An Ag-AgCl reference electrode (electrode potential = +0.200 V vs. SHE, Fisher Scientific) was located in the anode chamber, close to the working electrode. The redox potentials were measured at platinum wire electrode E2 with reference to the Ag-AgCl electrode when the current was switched off. The levels of the liquids in the anode and cathode chambers were kept slightly below that of the clay in the sample tray to avoid flooding of the clay cell with excess liquid. Setting the liquid levels as such required an approximate volume of 66.5 mL of electrolyte in each chamber.

Procedures and analysis. A series of constant current levels were applied across the working electrodes for 1 h duration each time in all tests. The applied current densities which were calculated for the orthogonal cross-sectional area of clay were from 0.1 to 0.6 mA/cm^2. This range

of current density was selected to remain within the linear range of the power supply used and also prevent excessive gas generation by electrode reactions. The potential drop between platinum wire electrodes E1 through E3 was automatically recorded by a data logger (Agilent 34970A) using a scan rate of 1 s^{-1}. In the pulse current experiments, the pulse current was accomplished by a power supply timer switch device. The pulse program followed the sequence of 10 s, 1 min, and 5 min "off" sessions of current with 5 min "on" sessions in between every "off" session. So the frequency of pulse was approximately 12, 10, and 6 cycles per hour, respectively. At the end of each test, the clay and electrolyte samples were analyzed for total chromium, hexavalent chromium, total and ferrous iron concentrations, and pH. The trivalent chromium and ferric iron concentration were calculated by subtracting the hexavalent chromium and ferrous iron from their total concentration. All clay and liquid samples were collected, preserved, extracted, and diluted in accordance with the approved, standardized U.S. EPA guidelines (Method 3050B and 3060A). The iron and chromium analysis was conducted using a Perkin-Elmer AAnalyst 100 flame atomic absorption spectroscopy (AA) and a Hach DR/4000U spectrophotometer (UV).

Results and Discussion

  Post-test Distribution of Chromium and Iron. The normalized concentration of chromium and iron after treatment as a function of applied current density was shown in Figure 1. The experiment without current (0 mA/cm^2) is a control test conducted to assess the spontaneous reduction of chromium in the absence of an applied electric field. It can be seen that the reduction of Cr(VI) was significantly improved by current since in clay the residual concentration of Cr(VI) decreased with the increase of applied current density. Similar trend was found for Fe(II) in anolyte indicating that the improvement of Cr(VI) reduction was caused by the enhanced transport of Fe(II) from anolyte to clay. The transport of Fe(II) was governed by electromigration and diffusion. However, the

electric mobility of Fe(II) (470×10^{-6} cm^2 V^{-1} s^{-1}) is much higher than its diffusion coefficient (7.2×10^{-6} cm^2 s^{-1}), therefore, electromigration becomes the major contributor to the total flux. Moreover, only slight amount of Fe(II) were found in clay which accounted for less than 1.6% of total mass, and there was no Fe(II) detected in catholyte. This suggested that the reaction rate between Fe(II) and Cr(VI) at clay surface was faster than the transport rate of Fe(II) in clay pore fluid, thus the transport of Fe(II) was the rate controlling step in reaction kinetics. The Cr(III) and Fe(III) in clay were mainly found in precipitates $(Cr,Fe)(OH)_3$. Formation of the precipitates $(Cr,Fe)(OH)_3$ was seen in all experiments and evident by its brownish color. Dissolving the precipitates by acid revealed the increased concentration of Cr(III) and Fe(III) with the increased current density.

The electromigration and diffusion of $Cr_2O_7^{2-}$ were observed in anolyte and catholyte, respectively. The chromium was found as Cr(III) in anolyte due to the reduction by Fe(II), while in catholyte as Cr(VI). In anolyte, the concentration of Cr(III) increased with the applied current, whereas the reverse trend was demonstrated in catholyte since the diffusion of $Cr_2O_7^{2-}$ to catholyte was diminished by electromigration which has an opposite direction to diffusion when applying the current. But due to the adsorption of chromium on clay, both transport processes were retarded. As it is shown that the highest concentration percentage of chromium obtained in anolyte and catholyte were 3.5 and 1.8%, respectively. The pH profile after treatment was shown in SI Figure S2. Since the pH in catholyte was kept constant at 3, the pH in clay was expected to be mainly determined by anode reaction. In anolyte, the pH decreased with the increase of current density, which followed the prediction from anode reaction. But in clay, the pH was lower than that in anolyte indicating other mechanism rather than anode reaction determined the pH variation. The hydrolysis reaction (eq 2) was probably the explanation to this phenomenon. Nevertheless, the decreased pH in the present work implied an increased adsorption capacity of Cr(VI) on clay according to previous

study that the adsorption of Cr(VI) on kaolinite increased with the decrease of pH [31]. The Fe(III) found in anolyte (less than 5.3%) was due to the oxidation of Fe(II) by $Cr_2O_7^{2-}$ migrated from clay and oxygen produced from the anode reaction, despite the nitrogen gas purging conducted.

Kinetics as a Function of Applied Current Density. It is well-known that reduction of Cr(VI) by Fe(II) involves three one-electron-transfer steps (i.e. Cr(VI)→Cr(V)→Cr(IV)→Cr(III)), so it is not possible to simply give the rate law and reaction order of eq 1 by its stoichiometric number [32]. It is seen that the rate of the reaction can depend on three different species: $Cr_2O_7^{2-}$, Fe^{2+} and H^+. Accordingly, the rate law for the reduction reaction may be expressed by eq 3, where k is the rate constant and the exponents (m, n, and p) are the reaction orders with respect to each reactant:

$$R = k[Cr_2O_7^{2-}]^m[Fe^{2+}]^n[H^+]^p \tag{3}$$

However, it has been shown that the concentration of Fe(II) was low in clay and its transport was the rate controlling step, indicating Fe(II) was the rate limiting reactant. Therefore, the rate law of overall reaction (eq 1) could be approximately reduced to eq 4 by monitoring the concentration loss of Fe(II) in anolyte:

$$-\frac{3d[Cr(VI)]_{clay}}{dt} = -\frac{d[Fe(II)]_{anolyte}}{dt} = k_{pse}[Fe(II)]_{anolyte} \tag{4}$$

where k_{pse} represents a pseudo-first-order rate constant. Similar method on rate law approximation was reported in [32] where the Cr(VI) was reduced at polyaniline film surface.

Representative kinetic plots under different current densities were shown in Figure 2 to fit the first order reaction kinetics. The goodness of fit ($R^2 > 0.99$) indicated that the pseudo first order reaction was suitable to simulate the reduction kinetics for the duration of 60 min measurement period. The k_{pse} in the experiment without current (i.e. spontaneous reaction) was 0.002 min^{-1}, which is lower than previous reported rate constant of first order behavior, for example the Cr(VI) was reduced at a polypyrrole-coated carbon substrate [33,34], reduced by hydrogen peroxide [35], reduced by iron [36], and reduced by hydrogen sulfide [37]. With the increase of applied current

density, the rate constant increased and the highest value (0.016 min^{-1}) was obtained in experiment with current density of 0.6 mA/cm^2. However, a two-stage increase of k_{pse} as a function of applied current density is shown in the inset diagram that the increasing rate was lower in higher current range (0.3-0.6 mA/cm^2) than that in lower current range (0-0.3 mA/cm^2). This might be due to the excess produce of H$^+$ ions (with high electric mobility, 3240·10^{-6} cm^2 V^{-1} s^{-1}) at higher current density, which led to a lower ionic transport number of Fe(II) compared to lower current density and diminished the transport of Fe(II).

Energy Consumption of Cr(VI) Reduction. The potential drop measured across the clay by E1 and E3 was shown in Figure 3a. Generally, the potential drop increased with the applied current density. The potential drop curve could be divided into three stages—initial Ohmic drop, polarization potential drop and stationary state. The initial Ohmic drop (the instantaneous increase in potential drop) was determined by applied current density since the initial ionic condition was uniform, therefore increased with the increase of applied current density. The initial resistance calculated based on Ohm's law with measured initial Ohmic drop and applied current was 2.1±0.1 kΩ (the deviation was based on experiments with current), which confirmed the uniform initial ionic condition before applying current. The polarization process (the slow increase in potential drop after initial Ohmic drop) included concentration polarization which was correlated to the concentration loss (compared to initial value) of ionic species caused by reduction of Cr(VI), and Ohmic polarization due to the retarded transport of Fe(II) in pore fluid by formation of precipitates (Cr,Fe)(OH)$_3$. The total polarization extent was possible to be used as a prediction of Cr(VI) reduction since it was the inducement of polarization. Therefore, corresponding to the rate constant of Cr(VI) reduction, the polarization potential drop increased with the applied current density. When the transport rate of Fe(II) in pore fluid equals to the reaction rate at clay surface, the system reached stationary state (indicated by the stable potential drop in time after polarization). The

decrease in the potential drop at around 35 min for the highest current density of 0.6 mA/cm^2 applied was probably due the dissolution of the precipitates caused by the excess H$^+$ ions produced at anode reaction.

Corresponding to the three stages of potential drop, the respective energy consumption at different current densities is shown in Figure 3b. The total energy consumption (W_T) was calculated based on the total potential values given in Figure 3a. The formula for the calculation is $W_T = \int VIdt$, where the W is energy consumption (mWh), V is the potential difference (V), I is the current (mA), and t is the duration (h). The energy consumption of initial resistance (W_R) was calculated by $W_R = I^2Rt$ with R=2.1 kΩ as discussed earlier. The increased current density on one hand transported more Fe(II) into the clay raising the reactant concentration and on the other hand overcame the activation energy (i.e. maintaining the compressed DDL) of the reduction of Cr(VI) and increased the reaction rate. Therefore, W_T is the sum of that due to the mass transport of Fe(II) in clay pore fluid (W_t) and that due to the reduction of Cr(VI) at clay surface (W_r). In ideally non-polarized process, $W_T = W_R = W_t + W_r$ represents the productive energy consumption. It can be seen that with the increased reduction of Cr(VI), more productive energy was consumed as expected. However, in this study the existence of polarization process required additional energy input (W_P) to sustain the reduction process. As discussed, the W_P was due to the resistance rise caused by concentration loss of ionic species and formation of precipitates in clay pore, therefore represented non-productive energy consumption. The increased W_P in current indicated that more non-productive energy was also consumed with the increased reduction of Cr(VI) and accounted up to 40% of total energy consumption (see inset diagram).

ORP Measurement. The oxidation-reduction potential (ORP) variation in clay measured by E2 and reference electrode was shown in Figure 4a. It can be seen that the ORP decreased in time and the decrease extent increased with the applied current density. If setting the ORP value in the

experiment without current as reference, then the overpotential η could be obtained and equals to the ORP difference between experiment with current and without current after 60 min experimental time. Numerically, the ORP differences are negative, but the absolute values of the difference are plotted in Figure 4b for convenience of comparison. For example, the measured ORP at the end of the experiment with the current of 0.6 mA/cm^2 was 642 mV, so the ORP difference between this experiment and experiment without current (ORP=713 mV) was -71 mV, and the absolute value was 71 mV. The overpotential here was used to estimate the electric energy (W_r) on accelerating conversion of the system's chemical energy (i.e. the decrease of Fe(II) and Cr(VI) concentration), and written in thermodynamic form as below:

$$|\Delta(\Delta_r G_m)| = nF|\Delta E| = W_r \tag{5}$$

where $\Delta_r G_m$ is the free (or chemical) energy of molar reaction (J/mol), $\Delta E = \eta$ (V), and n is the electron transfer number of molar reaction according to eq. 1, in this case n=6. Detailed explanations of eq 5 is given in SI Figure S3. Therefore it has the same physical meaning as that in electrode process [19], also represents the extra energy applied to accelerate a redox reaction. The eq 5 is not strictly applicable in thermodynamics because the system was not at equilibrium state when measuring the ORP, but due to the slow rate of spontaneous reduction of Cr(VI) with respect to the measuring time it is practically applicable [19]. The ORP variation in clay was determined by the reduction rate of Cr(VI) since a similar two-stage increase of overpotential in applied current density was observed in Figure 4b. Moreover, it can be seen from the inset diagram that the W_r was much lower than W_R (less than 1.6% of W_R) and decreased with the increase of current density, which indicated that the transport of Fe(II) in pore fluid was the major contributor to energy consumption, corresponding to the kinetic data (Figure 1).

Effect of Pulse Current. The pulse program followed the sequence of 10 s, 1 min, and 5 min "OFF" sessions of current with 5 min "ON" sessions in between every "OFF" session. So the

frequency of pulse was approximately 12, 10, and 6 cycles per hour, respectively. Although the pulse program was different in each experiment, the total working time was kept identical to ensure the same charge transfer in the pulse and constant current experiments. Therefore, the direct comparison of the energy consumption and removal efficiency could be made.

After the experiments, pulse current did not show enhancing effect on the reduction of Cr(VI) as there was no significant difference in residual concentration of Cr(VI) among experiments with pulse current (see Figure 5a). The aim of applying a pulse current is to precede more chemical reactions at clay surface than transport in pore fluid at the relaxation period when the current is switched off. A simulation of the relationship between the residual concentration of Fe(II) in clay and the reaction rate constant at clay surface shown in Figure 6 was used for qualitatively analysis of the pulse mechanism. The accumulation rate of Fe(II) in clay was simulated by one-dimensional mass transport-reaction equation [38] as:

$$\frac{\partial C_c}{\partial t} = \frac{it}{zF} + D(\frac{\partial C_a}{\partial x})_t - k_{pse} C_c \tag{6}$$

where i is the current density, t and z is the transport number and charge of Fe(II), respectively. D_{Fe} is diffusion coefficient, C_a and C_c is the concentration of Fe(II) in anolyte and clay, respectively. The calculation of diffusion flux was simplified by three initial and boundary conditions: t=0, C_a= C_0, t>0, in anolyte, C_a= C_0, and t>0, in clay, C_c=0. C_0 is the initial added concentration of Fe(II). It can be seen that if the transport rate is faster than the reaction rate under certain applied current density, there will be accumulation of Fe(II) in clay pore fluid. For example, with applied current density of 0.6 mA/cm^2, if the rate constant is lower than around 0.0043 min^{-1}, the concentration of Fe(II) increases. In this case, the reaction will probably be improved by the application of pulse current due to the additional proceeding of chemical mechanism at the relaxation period. Otherwise, no improvement will be given by pulse current. As it has been shown in Figure 1 that the reaction

between Fe(II) and Cr(VI) was faster than the transport of Fe(II) in all current level, therefore there was no effect induced by pulse current in this study.

In aspect of energy consumption, the positive effect of pulse current was shown in Figure 5a. The total energy consumption was lower in pulse current experiments than that with constant current and it decreased with the frequency. The lowest energy consumption (16.8 mWh) was obtained in the experiment with the frequency of 6 cycles per hour. The lower energy consumption in pulse current experiments is probably due to the compensation of ionic species by convective diffusion and self-scattering of $(Cr,Fe)(OH)_3$ which released more pore space for current transport at relaxation period. As it is shown in Figure 5b that the pulse current effectively decreased the initial Ohmic drop of each cycle. The entire potential drop curve across the clay in pulse current experiments are given in SI Figure S4. The select of relaxation time is important since it determines both of the efficiency of pulse current on energy consumption and the duration of treatment. It should be on one hand long enough to complete a relaxation and on the other hand short enough to save the treatment time. The maximum time for relaxation is the restoration of equilibrium state. The ORP measurement as a function of time could be used to estimate the re-equilibrium processes in the present system since the platinum wire E2 was inserted into clay and variation was determined by ionic conditions. The re-equilibrium processes in clay at the relaxation period of initial, middle and late stage estimated by ORP variation were given in Figure 5c. It can be seen that the experiment with pulse frequency of 6 cycles per hour showed the best condition approaching the equilibrium followed by 10 cycles per hour, and the experiment with 12 cycles per hour was far from equilibrium, which was in the same order as their demonstrated energy saving effect.

Implications for Field Remediation. This study evaluated the effect of direct current on enhancement of chromium reduction in contaminated clay from the aspects of kinetics and energy consumption. The application of current simultaneously improved the transport of Fe(II) in clay

pore fluid and the reduction of Cr(VI) at clay surface. Therefore, the reduction rate significantly increased with the increase of applied current density. Correspondingly, the increased reduction rate required more energy input to drive the reduction process. However, it was found that not only the productive energy consumption increased in current, but the non-productive energy consumption which is due to the resistance increase in pore fluid caused by formation of precipitates $(Cr,Fe)(OH)_3$ also increased in current and accounted for up to 40% of total energy consumption. Application of pulse current could decrease the non-productive energy consumption by decreasing the initial Ohmic drop of each cycle. This effect was more significant in lower pulse frequency due to the better restoration of equilibrium during relaxation period. Therefore in practical application, the determination of optimal pulse frequency could be done by identifying the proper current "OFF" time for re-equilibrium of a system with respect to different applied current "ON" time which determines the deviation of a system from equilibrium.

There was no enhancing effect observed on reduction of Cr(VI) in pulse current experiments compared to constant current experiment which was probably due to the faster reaction rate between Fe(II) and Cr(VI) than the transport of Fe(II). But faster transport of Fe(II) than surface reaction is expected in real contaminated soil where both pore size and conductivity in pore fluid are higher than that in kaolinite clay used in this study. In this case, the reduction will probably be improved by the application of pulse current due to the additional proceeding of chemical mechanism at the relaxation period. The passivation effect of $(Cr,Fe)(OH)_3$ has been widely reported [22,39]. By covering the surface reaction site of either aqueous Fe(II) or solid iron, further reduction of Cr(VI) is stopped after a certain time. Similar effect was expected but not seen in this study probably due to the short experimental time, therefore long-term interaction between transport and surface reactions as well as the effect of competitive electron acceptors existed in contaminated soil (manganese

oxide and sulfur oxides, etc) on surface reactions still need to be evaluated in future research to optimize the balance between remediation efficiency and energy consumption.

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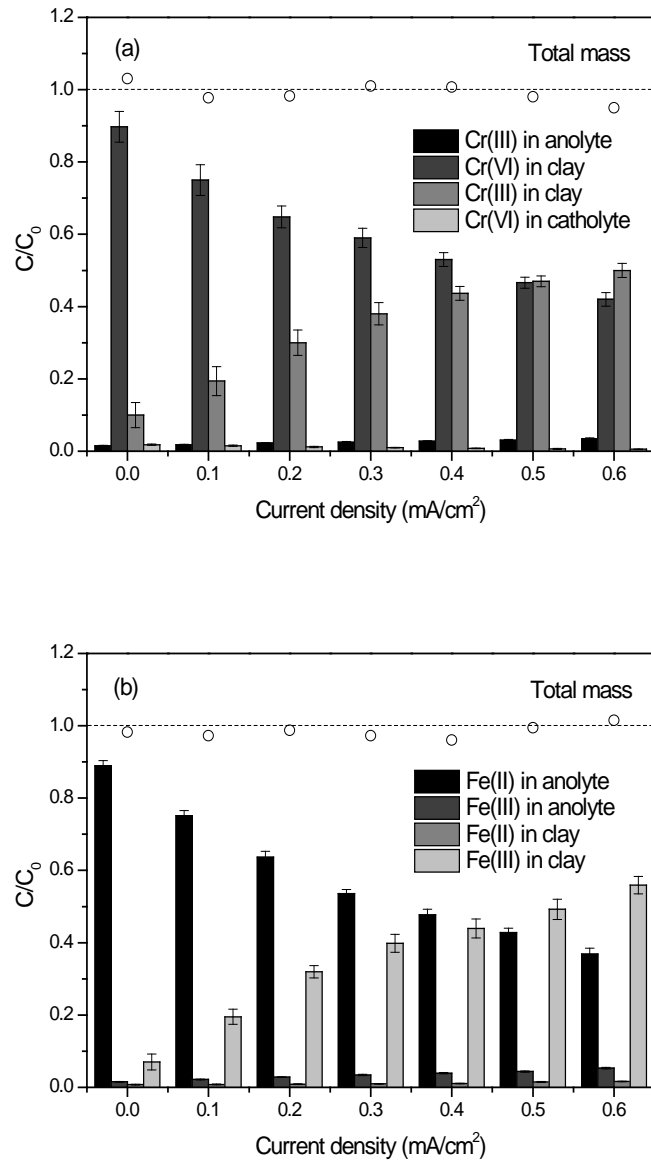
Figure 1. Normalized concentration of Cr(VI), Cr(III) (a) and Fe(II), Fe(III) (b) in each part of electrophoresis cell after experiment. The total mass indicates the mass balance after experiment to initial added concentration of Cr and Fe. Error bars represent the standard deviation of duplicate measurements.
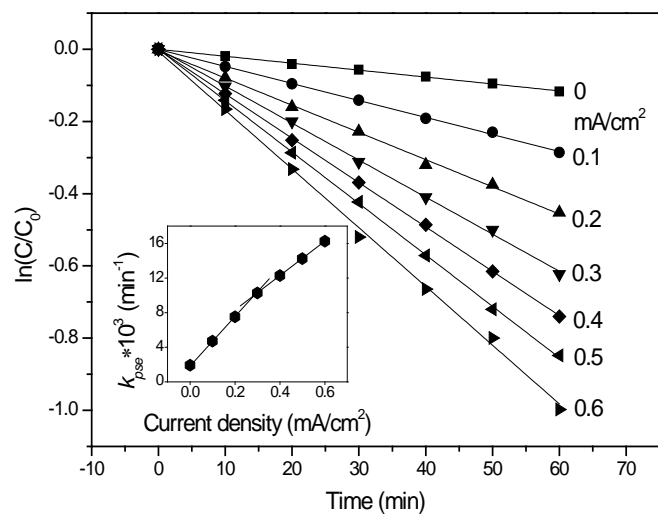
Figure 2. Pseudo-first-order kinetics plot as a function of time for Cr(VI) reduction at applied current density from 0 to 0.6 mA/cm². Symbols are observed concentration data and lines represent the first order model fit. Inset: The variation of rate constant as a function of applied current density.
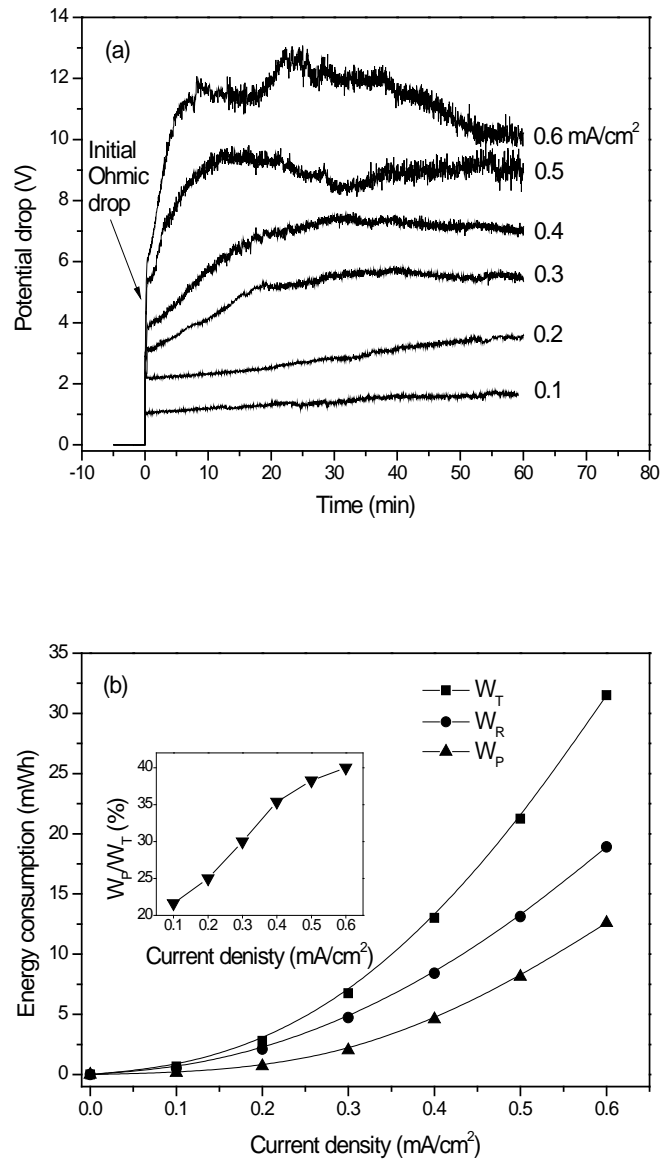
Figure 3. (a) Potential drop measured between platinum wire E1 and E3 at applied current density from 0.1 to 0.6 mA/cm^2. (b) Energy consumption at different applied current density. W_T is the total energy consumption. W_R is the energy consumption of initial resistance. W_P is the energy consumption of polarization process and equals to $W_T - W_R$. Inset: Percentage ratio of W_P to W_T at different current density.
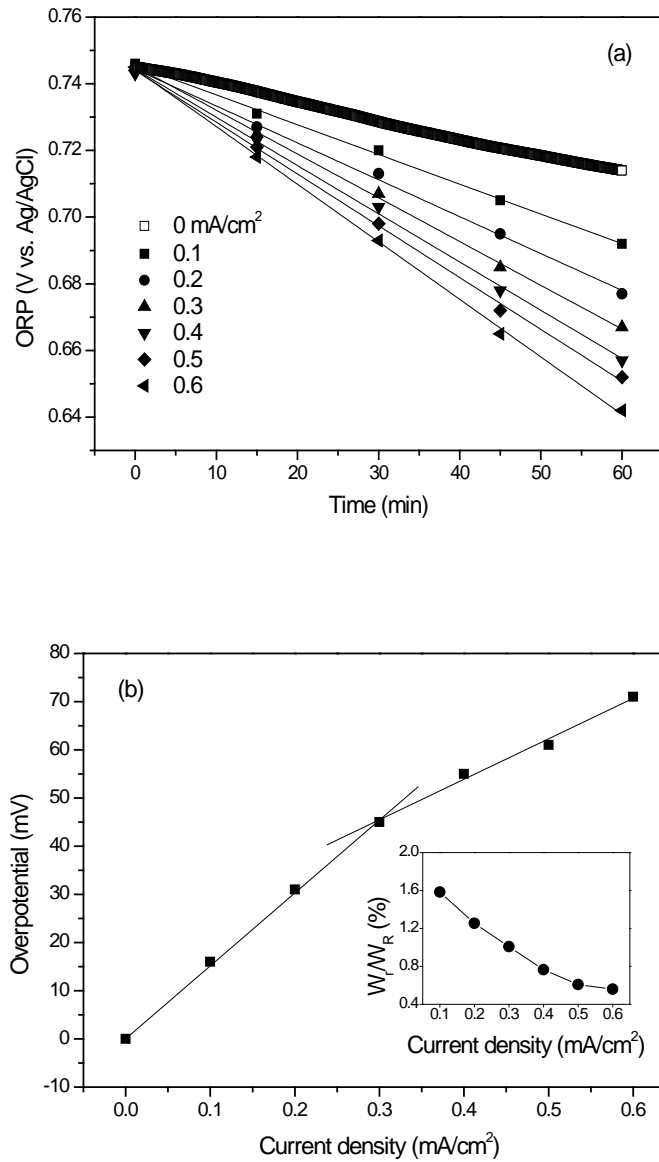
Figure 4. (a) ORP decay measured between the reference electrode and platinum wire E2 inserted into clay. The ORP in experiment without current (0 mA/cm^2) was automatically recorded by a data logger using a scan rate of 5 s^{-1}. In other experiments, the ORP was measured manually at every 15 min. (b) Two-stage increase of overpotential η as a function of current density. The overpotential is the absolute value of the ORP difference between experiment with current and without current after 60 min. Inset: Percentage ratio of W_r to W_R, in which $W_r = 6F\eta$ and W_R is from Figure 3b. Solid lines are linear fit.
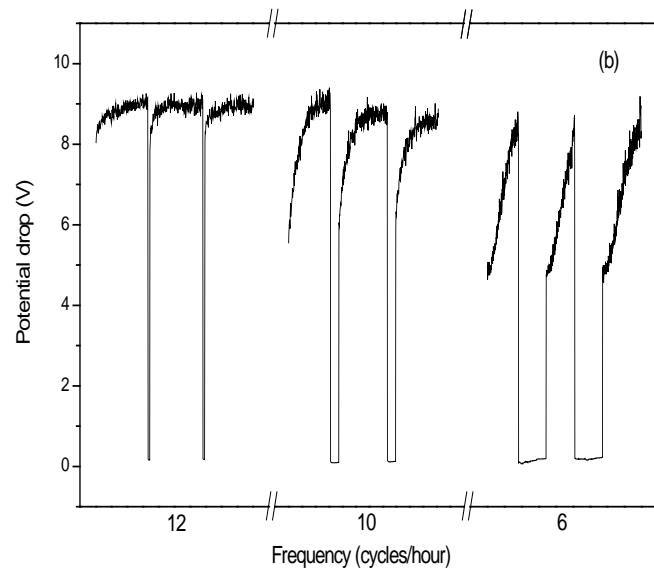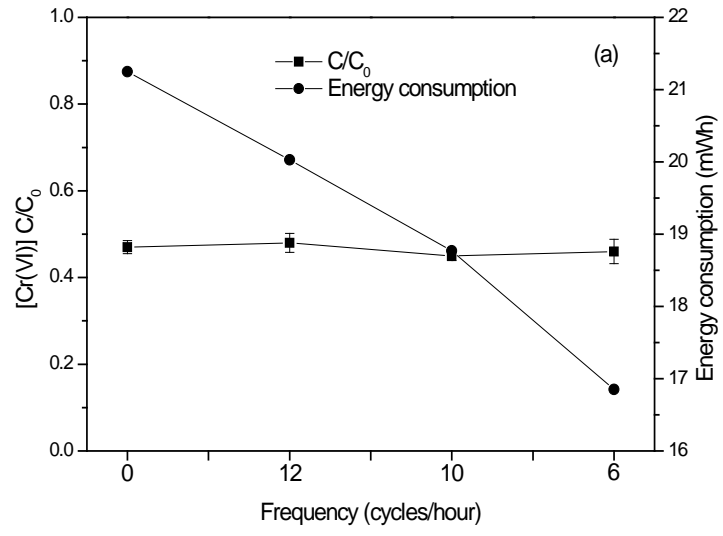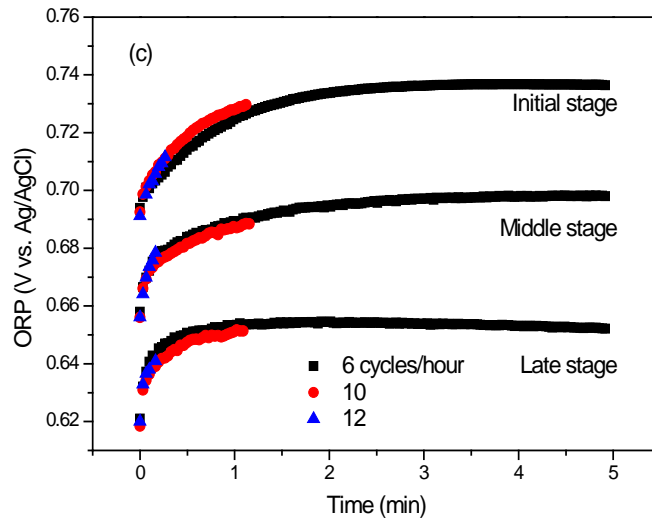
Figure 5. (a) Normalized concentration of Cr(VI) in clay and total energy consumption after experiment at different frequencies of pulse current. The applied current density is 0.5 mA/cm^2 for all experiments with pulse current. Error bars represent the standard deviation of duplicate measurements. (b) Selected potential drop measured between platinum wire E1 and E3 at pulse current experiments. The potential drop of 0 cycle/hour is given in Figure 3a. (c) The re-equilibrium processes in clay at the relaxation period of initial, middle and late experimental stages estimated by ORP variation.
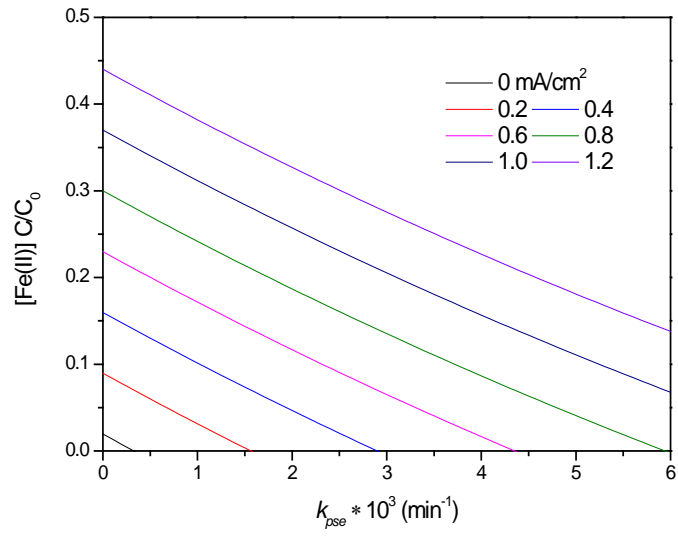
Figure 6. Effect of reaction rate between Cr(VI) and Fe(II) at clay surface on accumulation of Fe(II) in clay pore fluid.
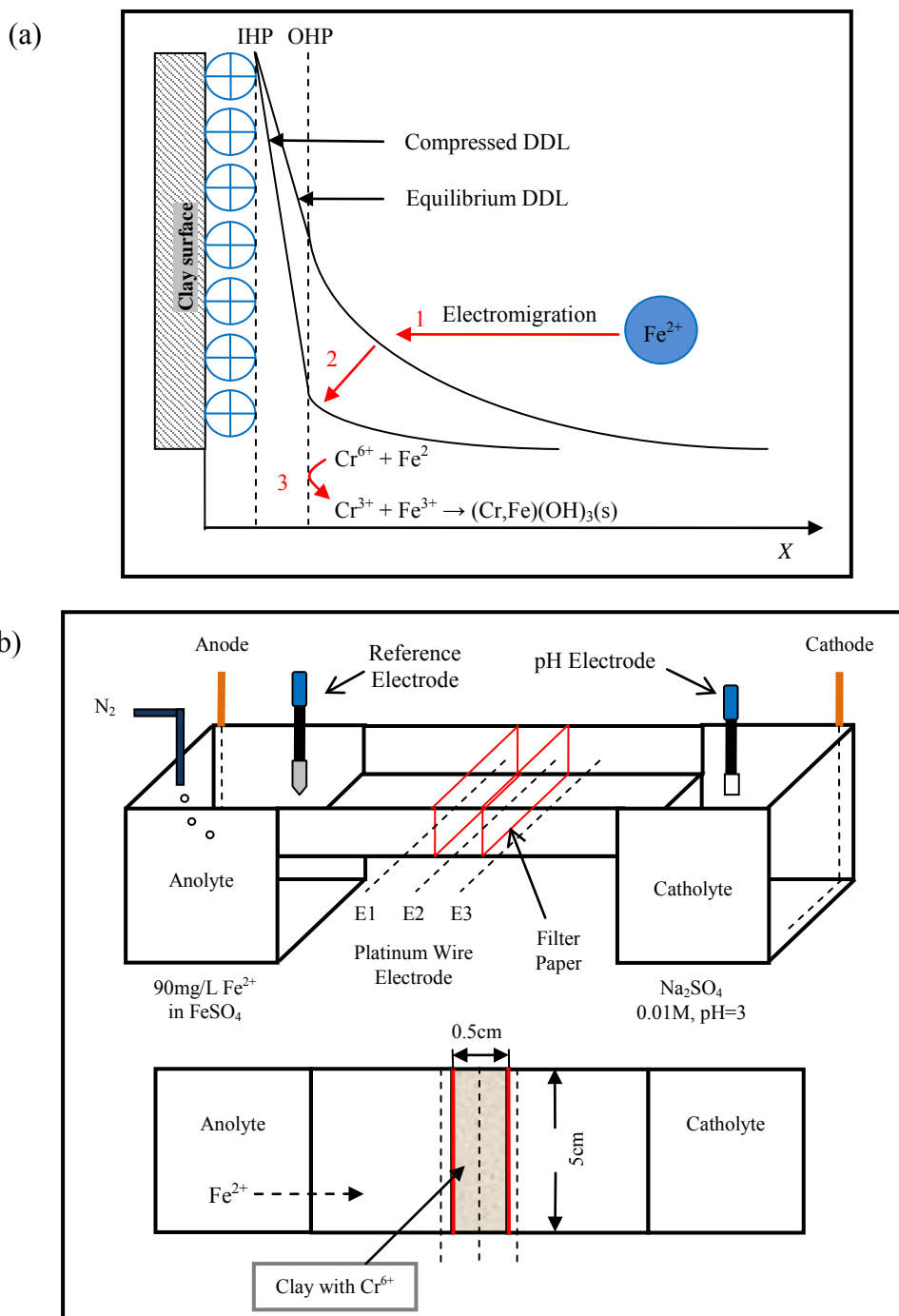
Supporting Information

Figure S1. (a) Hypothesized electron transfer steps from electromigrated Fe(II) to Cr(VI) at clay surface. (b) Schematic diagram of the experimental setup. The length and width of the used electrophoresis cell is 18 and 5 cm, respectively. The clay sample in the middle of the cell is 0.5 cm thick.
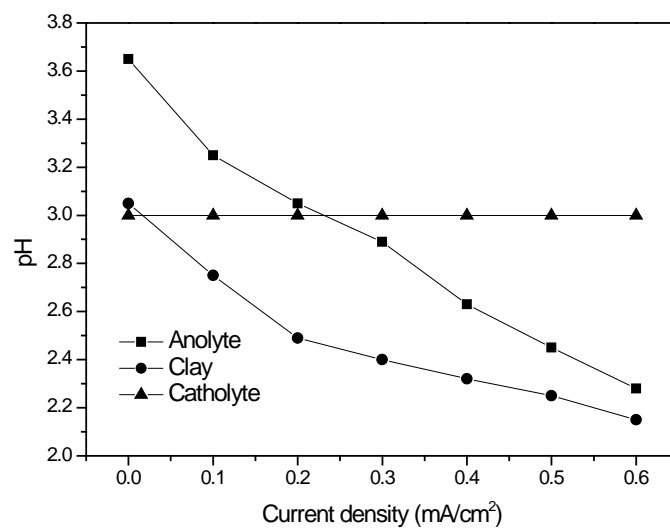
Figure S2. Final pH profile in each part of the electrophoresis cell at different applied current density. The pH in catholyte was kept at 3 by adding HCl.
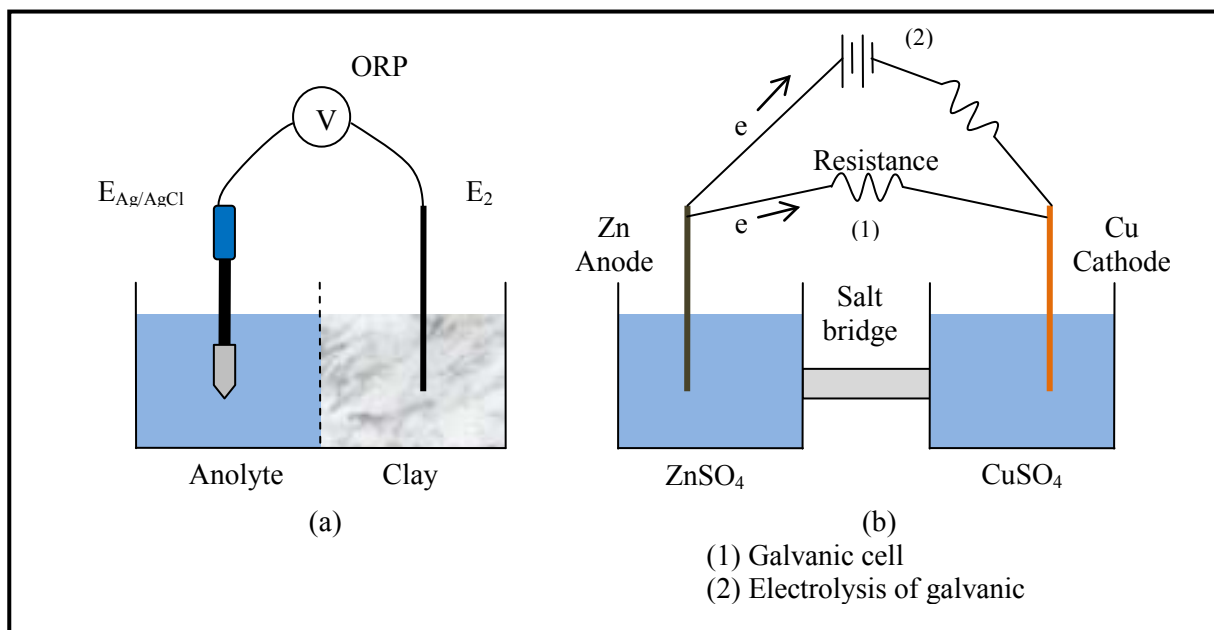
Figure S3. (a) Description of ORP measurement in this study. (b) Schematic diagram of electrolysis of galvanic cell.

The measured ORP (when switching off the current) in this study is the potential difference between the platinum wire (E_2) and reference electrode ($E_{Ag/AgCl}$) as shown in Figure S3a:

$$ORP = E_2 - E_{Ag/AgCl} \tag{S1}$$

Since $E_{Ag/AgCl}$ is constant, so the ORP difference between experiments with current E_2' and without current E_2'' is caused by the potential change of E_2 and written in absolute value as:

$$|\Delta ORP| = |\Delta E_2| = |E_2' - E_2''| = |\eta| \tag{S2}$$

In reversible process, the maximum work a system could do equals to the loss of its free energy:

$$|\Delta_r G_m| = 6F|E_2| \tag{S3}$$

where $\Delta_r G_m = \Delta_r G_m^{\ominus} + RT \ln Q$ with $Q = \frac{[Cr^{3+}]^2[Fe^{3+}]^6}{[Cr_2O_7^{2-}][H^+]^{14}[Fe^{2+}]^6}$.

Although there is no work but heat produced by Fe(II) and Cr(VI) in the present system, eq S3 gives the maximum capability of a system (in this case, Fe(II)/Cr(VI) system) to do work. Rewriting eq S3 by substitution of eq S2 gives:

$$|\Delta(\Delta_r G_m)| = 6F|\Delta E_2| \tag{S4}$$

Eq S4 indicates the loss of the capability of doing work due to the increase of Q by passing the current which is equivalent to the electrolysis of a galvanic cell (Figure S3b) and the inputted energy equals to the loss and gives to:

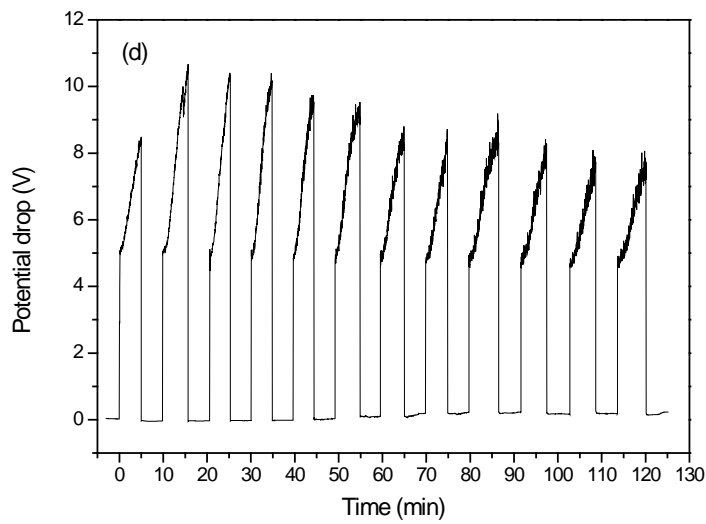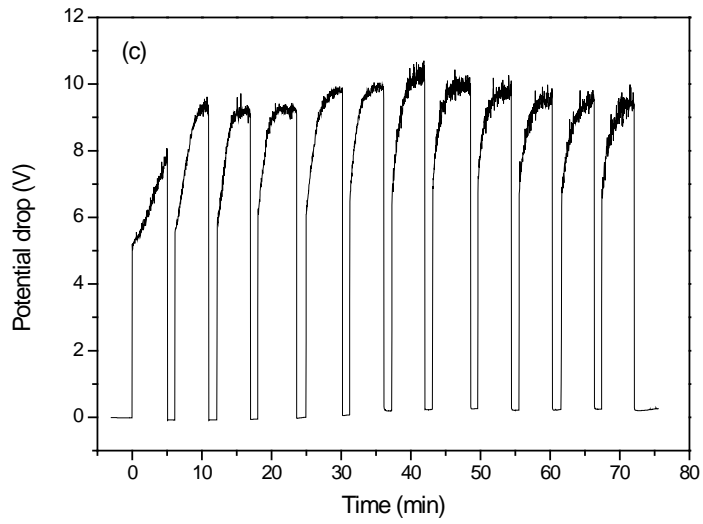$$|\Delta(\Delta_r G_m)| = 6F|\Delta E_2| = 6F|\eta| = W_r \tag{S5}$$
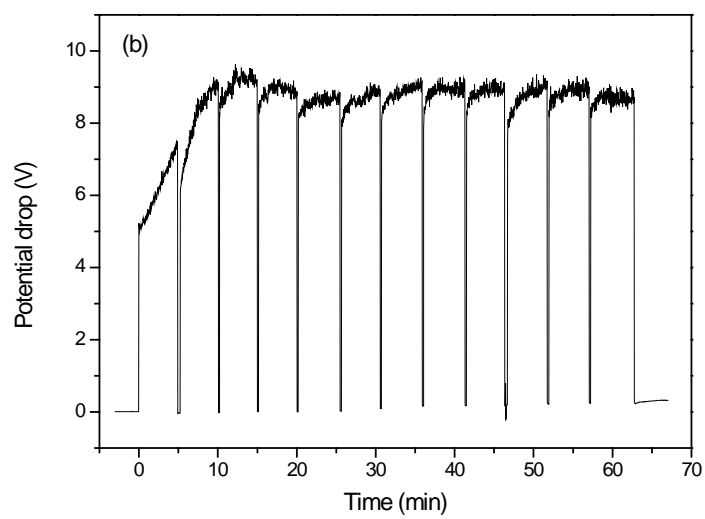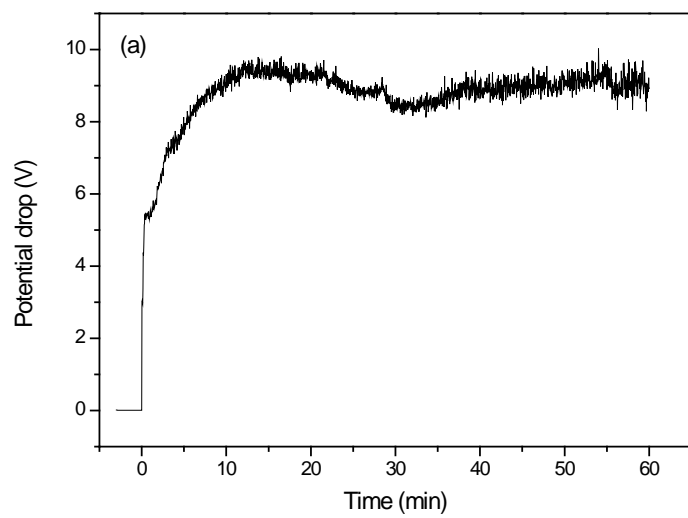
Figure S4. The potential drop measured between platinum wire E1 and E3 in experiments with different pulse frequency: (a) 0 cycles/hour, (b) 12 cycles/hour, (c) 10 cycles/hour, and (d) 6 cycles/hour. The applied current density was 0.5 mA/cm^2.

Appendix VI

Electrodialytic remediation of suspended soil – Comparison of two different soil fractions

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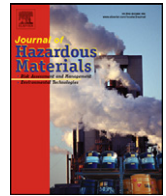
Electrodialytic remediation of suspended soil – Comparison of two different soil fractions

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ABSTRACT

Electrodialytic remediation (EDR) can be used for removal of heavy metals from suspended soil, which allows for the soil remediation to be a continuous process. The present paper focused on the processing parameters for remediation of a soil polluted with Cu and As from wood preservation. Six electrodialytic treatments lasting from 5 to 22 days with different liquid to solid ratio (L/S) and current intensity were conducted. Among treatments, the highest removal was obtained from the soil fines with 5 mA current at L/S 3.5 after 22 days where 96% of Cu and 64% of As were removed. Comparing the removal from the original soil and the soil fines in experiments with identical charge transportation, higher removal efficiency was observed from the soil fines. Constant current with 5 mA could be maintained at L/S 3.5 for the soil fines while not for the original soil. Doubling current to 10 mA could not be maintained for the soil fines either, and doubling L/S to 7 at 5 mA entailed a very fast acidification which impeded the removal. The results showed that a very delicate balancing of current density and L/S must be maintained to obtain the most efficient removal.

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1. Introduction

Electrodialytic soil remediation (EDR) is one of a group of electrochemically based soil remediation methods whose purpose is to remove heavy metals from polluted soil. EDR was originally applied to soil that was moist and consolidated in attempts at in situ treatment [1]. A faster and continuous process was then developed, which can be used ex situ [2–4]: the soil is suspended in a solution (most often water) during such treatment. The overall idea is to combine the method with soil washing and develop a continuous process for heavy metal removal from the fine fraction. Larger debris or soil particles are separated out by the washing procedure, leaving only a highly contaminated sludge for EDR. The soil portion containing sand needs only initial rinsing treatment because contaminants do not strongly adhere to the sand particles. While for the fine fractions like silt and clay, need more extensive remedial treatment because contaminants are easily adsorbed by this fine-grained fraction [5]. The adsorption is either specific or non-specific, or both of them, which depends on the clay mineralogy and the composition of soil organic matter.

In a reported study, remediation of soil fines (<63 μm) in suspension in distilled water was shown to be efficient for the removal of Pb, and a maximum of 96% of Pb was removed [2]. The method was also used for the remediation of soil polluted by the wood preservation industry, but the pollutants in this soil were not concentrated in the fine fraction as had been expected. As the pollutants were also found in the larger soil particles, soil washing as pretreatment was not possible [6]. In this case the major soil body (<4 mm) was treated in suspension using EDR.

In the present paper, electrodialytic remediation of the original soil (<2 mm) is compared to the remediation of the soil fines (<63 μm). No such comparison appears to have been made. The hypothesis is that remediation of suspended soil fines is more efficient than remediation of suspended original soil, not only because a large fraction of the material is left for simpler and cheaper soil washing, or because the material is kept suspended, thereby reducing the concentration polarisation and resistance [7], but also due to the higher conductivity of the soil fines, which is expected to allow a higher current density and thus faster remediation. Further, as the influence of L/S and current are considered to be important basic parameters, this work focuses on elucidating their role in the remediation process.

2. Materials and methods

2.1. Experimental soil

The soil was sampled from the top layer on an industrial site in Denmark, which had been highly polluted by a wood preservation plant. This investigation only considered Cu and As since

the Cr is well below the limiting value. The soil was air dried and sieved, and only the particles with size <2 mm were used. The term "original soil" was used for <2 mm soil particles. The "soil fines" were obtained by wet-sieving the original soil with distilled water through a 0.063 mm sieve. Concentrated dry soil fines were obtained by evaporating water on a heating plate under non-boiling condition.

2.2. Analysis of soil characteristics

The original soil and the soil fines were analysed for the following parameters. The concentrations of Cu and As were determined after pretreatment of the soil according to Danish Standard 259, where 1.0 g of dry soil and 20.0 mL (1:1) HNO_3 were heated at 200 kPa (120 °C) for 30 min. The liquid was separated from the solid particles by vacuum through a 0.45 mm filter and diluted to 100 mL. The concentrations of Cu and As were measured with AAS and ICP, respectively. Soil pH was measured in two ways: by suspending 10.0 g dry soil in either 25 mL 1.0 M KCl or 25 mL distilled water. After 1 h of agitation, pH was measured using a Radiometer pH electrode. The content of organic matter was found as a loss of ignition after 1 h at 550 °C. Carbonate content was determined volumetrically by the Scheibler method, which reacted 3 g of soil with 20 mL of 10% HCl. The amount was calculated and assumed that all carbonate was present as calcium carbonate. SEM-EDX analysis was performed on the original soil and the soil fines. The accelerating voltage of the SEM was 15 kV with a large field detector (and X-ray cone). Different areas of the sample were investigated by SEM and the element distribution was examined by element mapping using EDX.

2.3. Desorption of heavy metals as a function of pH

To examine the pH dependent desorption of Cu and As from the original soil and the soil fines, the following procedure was used: 5.0 g dry soil (dried at 105 °C for 24 h) and 25 mL HNO_3 in various concentrations (from 0.01 M to 0.9 M) were suspended for 48 h. The suspensions were filtered (0.45 mm) and the Cu and As concentrations were measured in the liquid phase with AAS and ICP respectively. Extractions in distilled water were made as a reference.

2.4. Sequential extraction of heavy metals

Sequential extraction was performed according to the method described in the Standards, Measurements and Testing Program of the European Union including (1) carbonate and exchangeable, (2) reducible, (3) oxidiseable, and (4) residual fractions, respectively, 0.5 g of dry and crushed soil was treated in four steps as follows: (1) extraction with 20.0 mL of 0.11 M acetic acid (pH 3) for 16 h, (2) extraction with 20.0 mL of 0.1 M $NH_2OH \cdot HCl$ (pH 2) for 16 h, (3) extraction with 5.0 mL of 8.8 M H_2O_2 for 1 h and heating to 85 °C for 1 h with a lid followed by evaporation of the liquid at 85 °C until it had been reduced to less than 1 mL by removal of the lid. The addition of 5.0 mL of 8.8 M H_2O_2 was repeated, followed by resumed heating to 85 °C for 1 h and removal of the lid for evaporation until almost dry. After cooling, 25.0 mL of 1 M NH_4OOCCH_3 (pH 2) was added, and extraction lasted for 16 h, and (4) digestion according to DS 259 with 20.0 mL (1:1) HNO_3 under the condition of 200 kPa and 120 °C was made for identification of the residual fraction. Between each step the sample was centrifuged at 3000 rpm for 15 min, and the supernatant was decanted and stored for AAS analysis. Before addition of each new reagent, the sample was washed for 15 min with 10.0 mL of distilled water and centrifuged at 3000 rpm for 15 min, and the supernatant was then decanted. All extractions
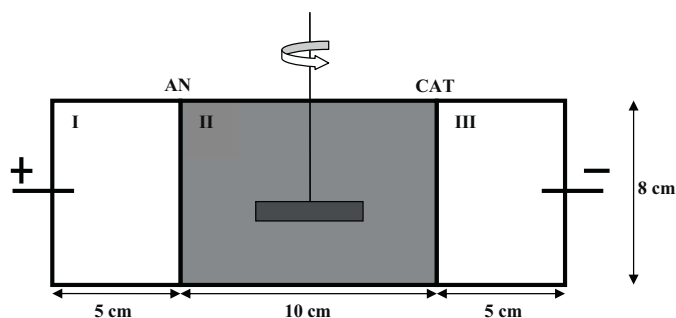

Fig. 1. Principle of electrodialytic remediation of suspended soil. (AN = anion exchange membrane, CAT = cation exchange membrane.)

were performed at room temperature, and samples in each step were taken in triplicate.

2.5. Experimental setup and experiments conducted

The electrodialytic experiments were conducted in cylindrical cells, as shown in Fig. 1. The cells were made from polymethyl methacrylate. Each cell had an internal diameter of 8 cm. The length of the central cell compartment was 10 cm and the length of the electrode compartments was 5 cm. The ion exchange membranes separating the central compartment from the electrode compartments were commercial membranes from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum coated electrodes from Permascand were used. A power supply (Agilent E3612A) was used to maintain a constant current. In each of the electrode compartments, 500 mL of 0.01 M $NaNO_3$ adjusted to pH 2 with HNO_3 was circulated. The soil was kept suspended in distilled water during the experiments by continuous stirring with a plastic-flap attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). The stirring was maintained identical conditions in all experiments.

Conductivity and pH in the soil suspension and the voltage between working electrodes were measured once every 24 h. Due to the electrode processes, pH changed in the electrolytes. The pH in the electrolytes was therefore manually maintained between 1 and 2 by addition of HNO_3 and NaOH. By the end of the electrodialytic experiments, the contents of Cu and As in the different parts of the cell (membranes, soil, solutions, and electrodes) were measured. The suspension from the central compartment was filtered. The sediment was dried and crushed lightly in a mortar by hand before the heavy metal concentrations and pH were measured. The contents of Cu and As in membranes and at the electrodes were measured after extraction in 1 M HNO_3 and 5 M HNO_3, respectively. The energy consumption after treatment can be calculated by equation $E = \int VIdt/W$, where E is the power consumption per gram soil (Wh/g); V, voltage between working electrodes (V); I, current (A); t, duration (h); W, the mass of soil (g).

To investigate the comparison between the original soil and the soil fines and the influence of current intensity and liquid to solid ratio (L/S) on the remediation efficacy of the soil fines, six electrodialytic remediation experiments were performed (Table 1). In Table 1, the L/S 3.5 corresponded to 100 g soil suspended in 350 mL distilled water and L/S 7.0 corresponded to 50 g soil suspended in 350 mL distilled water.

3. Results and discussion

3.1. Soil characteristics

The characteristics of the original soil and the soil fines are listed in Table 2 together with the Danish limiting values for Cu and As for
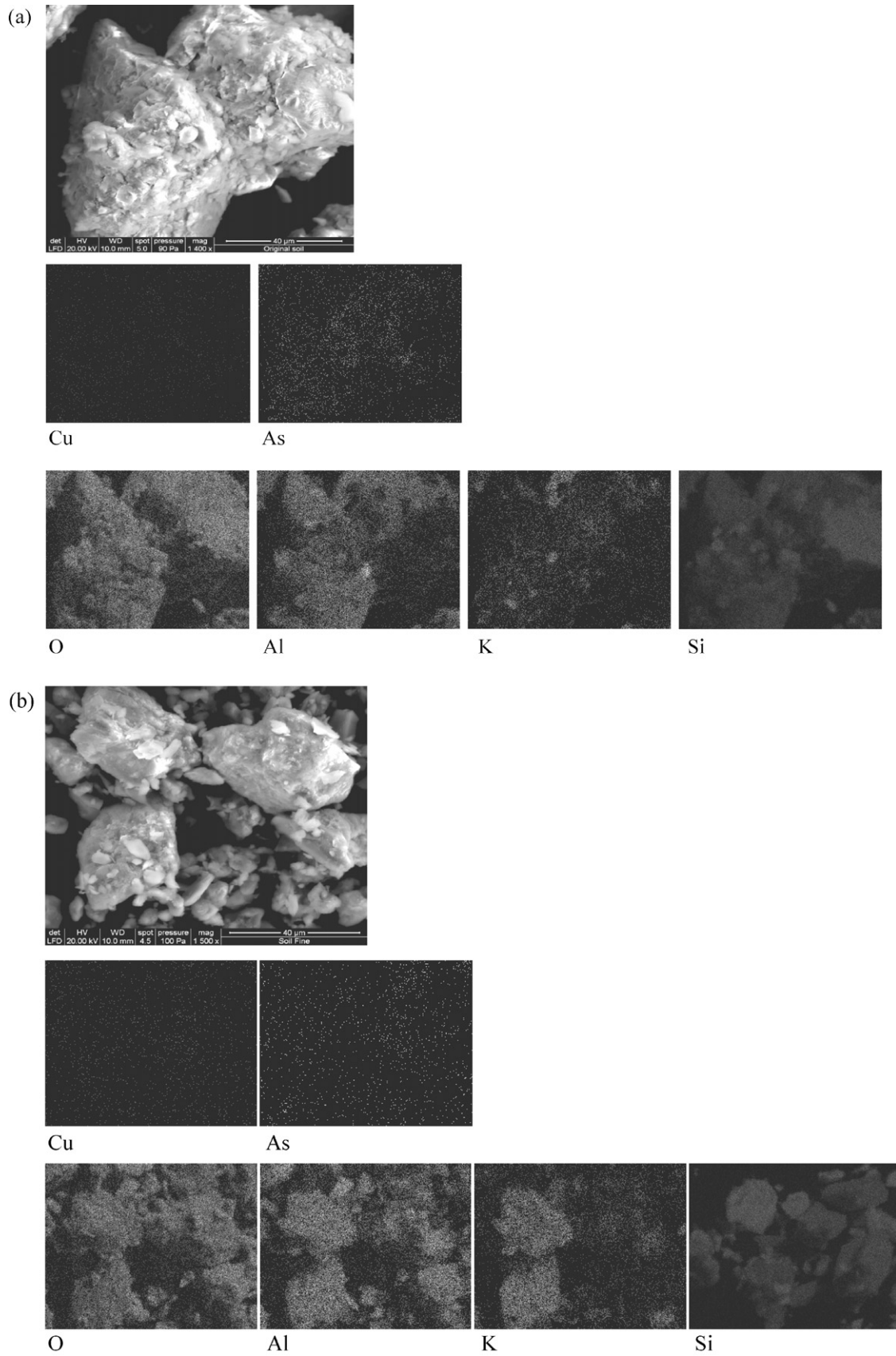
(a)

(b)

Fig. 2. SEM picture of original soil (a) and soil fines (b) and result from EDX mapping.

Table 1
Experimental design.

Treatments	Soil type	L/S	Current (mA)	Days
T1	Original soil	3.5	2.5	10
T2	Original soil	3.5	5	10
T3	Soil fines	3.5	5	5
T4	Soil fines	3.5	5	22
T5	Soil fines	3.5	10	10
T6	Soil fines	7.0	5	15

the most sensitive land use. The fine fraction accounted for about 35% of the soil per weight, and more than 90% Cu and 90% As were bound in this fraction, so the soil was suitable for a size fractionation prior to the electrodialytic treatment. Searching the soil samples by SEM-EDX investigation, there was no single particle with high concentrations observed, which might have led to the pollutants being concentrated in the sand fraction rather than in the fine fraction, as was found in [6]. It was found that Cu and As were distributed over the surfaces of the original soil and soil fines (Fig. 2). The low carbonate content in the original soil and the soil fines revealed a low buffering capacity. The pH measured when both the original soil and the soil fines were suspended in KCl was lower than the pH measured in distilled water (0.6–0.8 pH units). This showed that H^+ ions were present in the exchangeable sites at the surface of the original soil and soil fines, since more H^+ ions were released to the liquid in KCl (exchanged with K^+) than in distilled water.

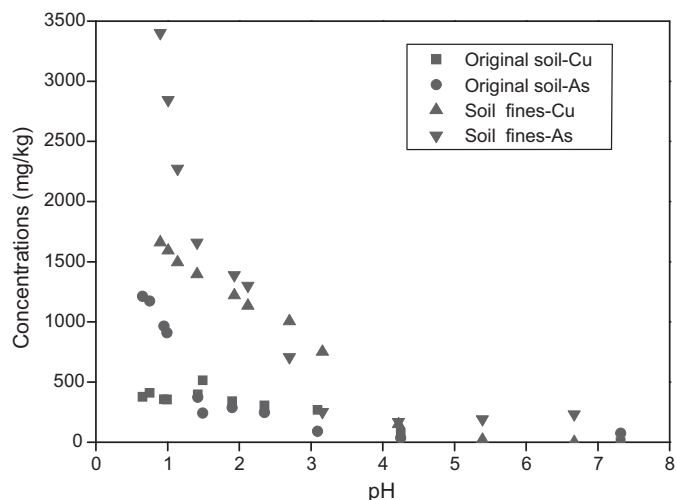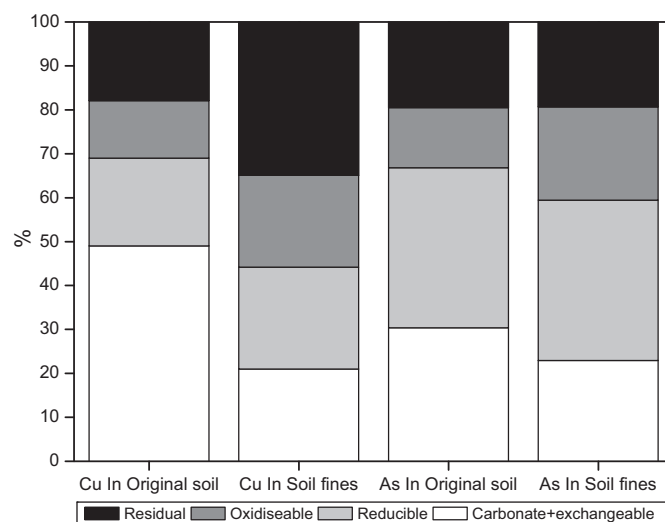### 3.2. Desorption of Cu and As as a function of pH

Fig. 3 shows the concentrations of Cu and As extracted from the original soil and soil fines at different pH values. It was found that the extractions of both Cu and As increased with the decrease in pH. In the original soil, Cu and As extractions started at pH values below about 4.5 and approached 90% and 103% respectively at approximately pH 1. The Cu and As extracted from the soil fines did not reach such high percentages, being 81% for Cu and 74% for As at the same pH level. At neutral pH of the suspension (in distilled water) no measurable amount of Cu was extracted from either the original soil or the soil fines, whereas about 100 mg/kg for the original soil and 200 mg/kg for the soil fines of As were extracted. This does not necessarily indicate that such concentration was present in the soil before the sampling. Mobile As would be expected to have been washed out to deeper soil layers in the 25 years (at least) since the spill occurred. Aeration of the soil sample during sampling and treatment is likely to have influenced the mobility of As.

3.3. Sequential extraction of Cu and As

Fig. 4 shows the result of the sequential extractions of Cu and As from the original soil and the soil fines. For both Cu and As, which showed a similar pattern, the carbonate and exchangeable fraction decreased from the original soil to the soil fines, while in contrast, the residual and oxidisable fractions increased. Cu was adsorbed less strongly in the original soil compared to the soil fines and As showed the same tendency even though not so clearly. The fine fraction was a part of the original soil and thus this result indicates that the small fraction of the two pollutants bound to the coarse fraction in the original soil was bound weakly to the soil particles in

Fig. 3. Desorption dependency on pH of Cu and As in original soil and soil fines.

Fig. 4. Sequential extraction of Cu and As in original soil and soil fines.

comparison to the adsorption in the soil fines. This was consistent with what would be expected when there were no insoluble or poorly soluble precipitates containing the pollutants in the soil (as seen in the SEM-EDX investigation).

3.4. Electrodialytic experiments. Overall results

An overview of the results obtained in the electrodialytic remediation experiments is given in Table 3. The mass balance of an element was defined as the relation between the sum of the mass found in the different parts of the cell at the end of the experiment and the initial mass, calculated on the basis of the measured mean initial concentration. The range of the mass balances was from 94% to 138%, which was an acceptable range for an inhomogeneous industrially polluted soil. The removal efficiency for each element was calculated as the mass of the actual heavy metal in the

Table 2
Characterisation of experimental soil and Danish limiting values for most sensitive land use.

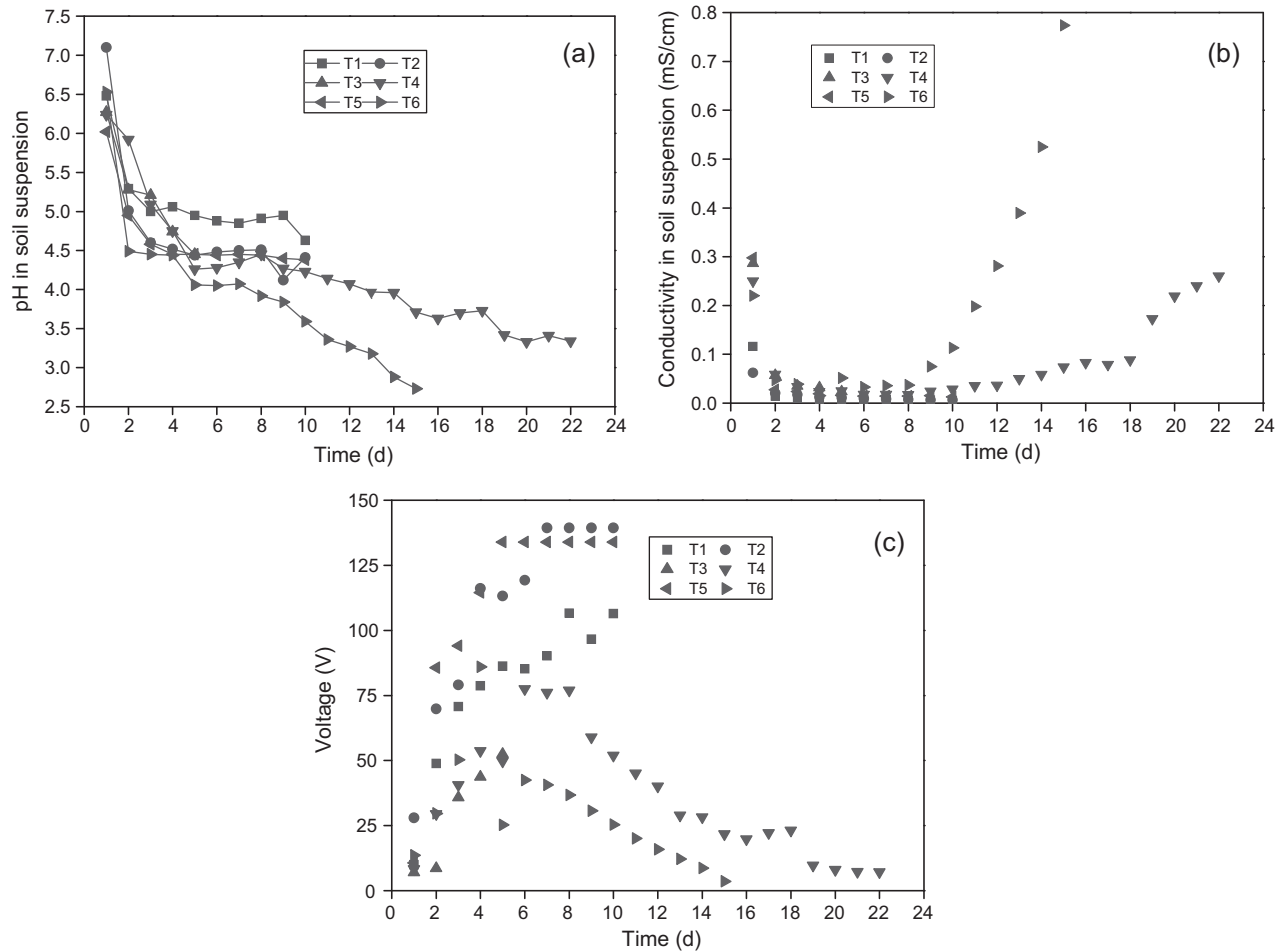|	Cu (mg/kg)	As (mg/kg)	Carbonate content (%)	Organic matter (%)	pH$_{H_2O}$	pH$_{KCl}$
Original soil	573 ± 33	1181 ± 29	0.6 ± 0.2	3.7 ± 1.0	7.4	6.6
Soil fines	2054 ± 62	4598 ± 167	0.2 ± 0.2	3.2 ± 0.8	6.4	5.5
Limiting values	500	20				

Fig. 5. (a) pH and (b) conductivity in the soil suspension and (c) voltage over the cells during the electrodialytic treatment.

electrode components (membranes, solutions in electrode compartments and on electrodes) divided by the total mass found in all parts of the cell at the end of the experiment. Among the treatments, the highest removal percentage was observed in experiment T4 for both Cu (96%) and As (64%). The lowest efficiency for both pollutants was obtained in experiment T6: 13% for Cu and 0.7% for As. The pH measured in KCl was 0.8 to 1.1 pH units lower than the pH measured in distilled water and this was in general a slightly larger difference than was found initially. The difference showed that H^+ ions were present in the exchangeable sites to a higher extent than before eletrodialytic treatment, due to acidification during the treatment. All exchangeable sites were thus not occupied by H^+ ions at the time of sampling.

The pH and conductivity of the soil suspension and the voltage across the cell during the experiments are shown in Fig. 5(a)–(c), respectively. The pH in suspension of all treatments decreased over time (Fig. 5(a)). During the first two days, a considerable drop in the pH of the suspension in the central compartment was seen,

followed by a moderate decrease. In other soils a "lag-period" had been observed before pH decreased in the soil suspension [2]. During the lag-period the H^+ ions overcame the buffering capacity of soil. In the soil of this investigation, the carbonate content was low (both in the original soil and the soil fines) (Table 2), indicating that the soil had a low buffering capacity. The fact that there was a fast drop in the pH of the suspension and that the lag-phase was missing in the present experiments indicates that the lag-phase is dependent on the buffering capacity of the soil. At the end of the experiments, the pH in the soil suspension varied significantly between the different treatments. The rapid acidification of the soil suspension could be due to the water splitting caused by the anion exchange membrane [8,9] and the exchange between H^+ ions from the acidic catholyte and other ions in the suspension over the cation exchange membrane. The pH in the catholyte was maintained between 1 and 2, so this exchange was likely to have a major influence. Moreover there was only 50 g of soil fines in experiment T6, which most probably means the buffering capacity in this soil

Table 3
Overall results of electrodialytic soil remediation.

Treatments	Cu (mg/kg)	As (mg/kg)	pH H$_2$O/KCl	Mass balance (%) Cu/As	Removal efficiency (%) Cu/As	Energy consumption (Wh/g soil)
T1	279 ± 12	600 ± 14	4.6/3.8	112/109	59/56	0.4
T2	367 ± 23	979 ± 30	4.6/3.7	94/138	36/44	1.2
T3	1426 ± 29	3036 ± 42	4.5/3.7	98/97	32/35	0.1
T4	107 ± 6	1715 ± 22	3.3/2.4	118/98	96/64	1.0
T5	1309 ± 35	2534 ± 37	4.5/3.7	105/98	43/47	2.5
T6	2078 ± 92	5529 ± 188	2.7/1.6	113/120	13/0.7	1.0

suspension was even lower than in experiment T4, which had 100 g of soil fines, so that fewer ions were available to exchange with H⁺ ions from the catholyte (Table 1).

At the beginning, the conductivity of the soil suspension decreased in all treatments. This could be ascribed to the depletion of free ions in the soil by the applied current (Fig. 5(b)). During the 5–10 day experimental periods, the pH in these treatments did not decrease to below 4.5 (Fig. 5(a)), which suggested that Cu and As had not been desorbed and thus mobilised for electromigration in accordance to the desorption pattern in Fig. 3. In general, the desorption and dissolution processes were expected to be limited at pH 4.5 compared to lower pH values, so the higher pH value in the suspension was one major reason for the lower conductivity, due to a smaller H⁺ ion concentration. Further, this might also be the reason for the limited acidification, because a limited amount of cations were available for exchange with H⁺ ions from the catholyte. However, in experiments T4 and T6, enough free ions were present in the suspension to overcome this limitation, so the pH decreased to levels where desorption started and was followed by an increase in conductivity.

At the beginning of all the experiments the voltage increased (Fig. 5(c)). In experiments T1 and T3, the voltage increased and did not reach the maximum for the power supply (around 135 V) during the experiments. In experiments T2 and T5 the voltage increased to the maximum of the power supply value and the experiments were stopped on the tenth day. In experiments T4 and T6, the voltage dropped from a maximum on the sixth day and continued to decrease during the remaining time of the experiment. Since the overpotential at the electrodes was low, because the electrolyte was continuously stirred, the voltage increase corresponded to an increase in electrical resistance across the cell. The electrical resistance in the electrolyte compartments was low, due to high ionic strength, so the increased resistance must be across the middle compartment or across the membranes. Initially, when the soil was suspended in distilled water, dissolved ions were removed by the current, resulting in a decrease in electrical conductivity. However, as the acidification started and proceeded, more ions were released and the electrical resistance decreased. This could explain the increase in voltage and also the decrease in voltage in experiments T4 and T6, and the voltage pattern also followed the pH pattern in the soil suspension.

Fig. 6(a) and (b) shows the distribution of Cu and As in the cell at the end of the experiments. Overall the distribution pattern of the two elements differed significantly. In all treatments the major part of the Cu was found either at the cathode or in the soil, whereas for As the major part was distributed either in the anolyte or in the soil. These different patterns indicate the different chemical behaviour of the two elements.

3.5. Comparison of remediation efficacy between original soil and soil fines

The results of experiments T2 and T4, which were performed with the original soil and the soil fines, respectively, with the same L/S and current but different duration, demonstrated a significant difference in remediation efficiency between them. The removal efficiency of Cu and As was 36% and 44% in the original soil against 96% and 64% in the soil fines. In fact, in the experiment with the original soil (T1) it was not possible to maintain the current at 5 mA for more than 10 days, as the resistivity increased until the maximum voltage of the power supply was reached, at which point this experiment was terminated. This means that 5 mA current was too high for this original soil at the actual L/S. However, large amounts of Cu and As were still removed under these conditions. This was possibly due to the large amount of exchangeable species of Cu and As (Fig. 4), which were directly mobile by electromigration [10]. A
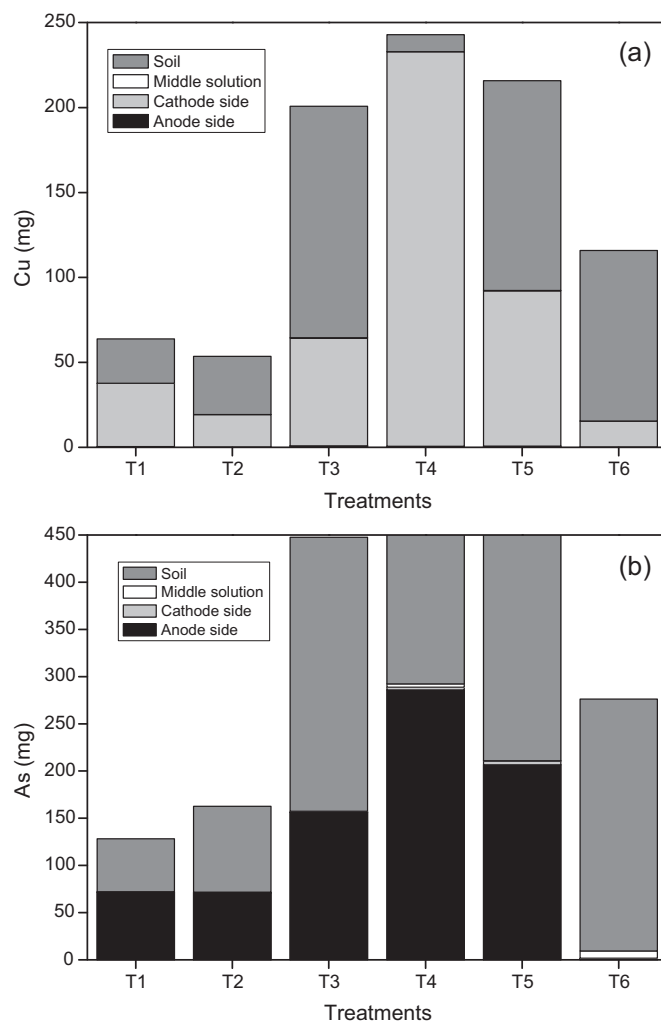

Fig. 6. Distribution of (a) Cu and (b) As in the different parts of the electrodialytic cell at the end of the experiments.

similar experiment performed by Ottosen et al. [6] indicated that constant current could be obtained at the current intensity 2.5 mA in the original soil, although the removal of Cu and As was less than that from the soil fines with 5 mA.

Experiments T1 and T3 were direct comparisons between original soil and soil fines where they had the same mass of charge migration and L/S. In experiment T1 2.5 mA was applied to the original soil to avoid charge overload. In this comparison, the removal efficiency in experiment T1 was much higher than in experiment T3, but the mass of Cu and As removed was reversed: 38 mg Cu and 72 mg As were removed from the original soil and 64 mg Cu and 157 mg As were removed from the soil fines. Moreover, from the viewpoint of energy intensity, the treatment with the soil fines commenced lower energy consumption than the original soil, which was 0.1 Wh/g and 0.4 Wh/g soil, respectively (Table 3).

3.6. Comparison of different conditions for electrodialytic remediation of soil fines

Based on experiences from the work of Jensen et al. [2], two ratios of liquid to solid (3.5 and 7.0), and two values of current intensity (5 and 10 mA, the corresponding current densities were approximately 0.1 and 0.2 mA/cm²) were investigated. The best conditions in the present investigation were experiment T4 where the L/S ratio was 3.5 and the current intensity was 5 mA. In

experiment T4, an interesting finding was that almost all the Cu and most of the As had been removed from the soil fines even though the pH did not decrease to below 1. In fact, the lowest pH value reached in the soil fines in experiment T4 was 3.5 (Fig. 5(a)). The pH is very important for the desorption and dissolution of heavy metals from soil, because H$^+$ can destroy the binding forces, induce the change of redox conditions between heavy metals and soil particles and release the heavy metals to solution. These reactions are equilibrium reactions, and they will move to the desorption side with the addition of more H$^+$ ions. On the other hand, if the products are consumed continuously by other materials or factors (i.e. current), the reactions will also move to the desorption side with the same H$^+$ concentrations. The constant current enabled continuous desorption due to continuous removal compared to the case where the acidification was performed in a single step (as in the pH desorption experiment). In experiment T4, 96% removal efficiency indicates that the majority of the different adsorbed Cu phases could be removed by the electrodialytic process, including the residual phase, which was expected to be the strongest bound and thus the most difficult to remove (Table 3). This could be mainly attributed to the transformation of heavy metals from the higher fractions of sequential extraction to the first fraction, caused by the combination of acidification and the applied electric field [11]. Not all of the heavy metals in the residual part are bound to the mineral lattice structure, because some of them exist in the form of precipitation and complex compounds, and fortunately they can easily be removed from soil. In general arsenic may be present as As (III) or As (V) in soil as well as in the solution. Which form prevails is dependent on the pH and the redox potential. It may be seen in Fig. 6(b) that a large amount of As was removed towards the anode in this treatment, probably as H$_2$AsO$_4$$^-$. Unlike the stationary EKR/EDR, oxygen and carbon dioxide concentrations in suspended EDR can be assumed to be in equilibrium with the atmosphere, which allows for oxidation of As (III) to As (V) during remediation. Further, under the moderately acidic and oxidising conditions created during the process of experiment T4, H$_2$AsO$_4$$^-$ should be the prevailing species of arsenic, which would be transferred to the anode side [12].

In experiment T5, the current intensity was increased to 10 mA compared with the 5 mA in experiment T4. However, it was obvious that the free ions in the soil fines were not sufficient to maintain the 10 mA constant current, and induced a higher energy consumption (2.5 Wh/g soil) than T4 (1.0 Wh/g soil). This experiment was an example of the ultimate consequence of forcing too much current through the system: the lack of ions became pronounced (seen from the conductivity of the suspension Fig. 5(b)). As a result, the resistance increased dramatically, and constant current could not be maintained. At the initial stage of the electrodialytic treatment, the current was mainly carried by the soluble and mobile ions from the soil itself. If the conductivity was low but the current was high, the current could not be maintained until desorption and dissolution of ions caused by acidification had taken place, so the process stopped.

The L/S ratio was increased to 7.0 in experiment T6, compared to 3.5 in experiment T4. In experiment T6, the lowest removal efficiency both for Cu and As was observed, while the pH declined to the lowest value and the conductivity attained its highest value at the end of the experiment (Fig. 5(a) and (b)). For Cu, this could be attributed to an expected effect of acidification, which was competition between H$^+$ ions and Cu^{2+} ions for electromigration. The experiment with the longer acidification time (T4) therefore showed better remediation efficacy than that with very fast acidification (T6), and in the search for optimal remediation conditions, it indicates that the fastest rate of acidification was not optimal. By contrast, the removal efficacy of As was even worse than Cu, which was related to the chemical behaviour of As. This might be because uncharged As species were present and this could very likely be

H$_3$AsO$_4$ (which was prevailing at high oxidation states and pH values less than about 3 [12]). Another report found that As was only slightly mobile at low pH value, and as a result, it was difficult to remove except in the presence of an enhancement agent [13]. Also due to the fast acidification, the energy consumption in T6 was the same with T4 even under the condition of much less heavy metals removed since the mobility of H$^+$ ions is high.

4. Conclusions

This paper reports a comparison of Cu and As removal from an original industrially polluted soil and from soil fines from the same soil. The results show that the range of removal efficiency in the original soil and soil fines were from 13% to 96% Cu and 0.7% to 64% As, the highest percentage of removal being from the soil fines in both cases. Among treatments, the highest removal efficiency occurred in soil fines with 5 mA current and with an L/S ratio of 3.5 in a treatment lasting 22 days. In a direct comparison between the original soil and the soil fines with exactly the same charge transfer, 38 mg Cu and 72 mg As were removed from the original soil and 64 mg Cu and 157 mg As were removed from the soil fines. In the suspension of soil fines, a constant current of 10 mA could not be maintained and in the original soil even a current of 5 mA could not be maintained. In treatment with a high L/S of 7.0, acidification took place too rapidly and the pH was very low in the suspension during the whole process, which impeded the transport of Cu and As. The conclusion is that the remediation current and the L/S ratio must both be optimised, as these two parameters are highly dependent on each other.

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Appendix VII

The effect of pulse current on energy saving during electrochemical chloride extraction (ECE) in concrete

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The effect of pulse current on energy saving during electrochemical chloride extraction (ECE) in concrete

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ABSTRACT: Energy consumption is a factor influencing the cost of electrochemical chloride extraction (ECE) in concrete. The aims of this work were to investigate the possibility for energy saving when using a pulsed electric field during ECE and the effect of the pulsed current on removal of chloride. Four experiments with artificially polluted concrete under same charge transfer were conducted. Results showed that the energy consumption was decreased 15% by pulse current in experiments with 0.2 mA/cm^2 current density, which was higher than that of 0.1 mA/cm^2 experiments with a decrease of 9.6%. When comparing the voltage drop at different parts of the experimental cells, it was found that the voltage drop of the area across the concrete was the major contributor to energy consumption, and results indicated that the pulse current could decrease the voltage drop of this part by re-distribution of ions in pore fluid during the relaxation period. However, probably due to the observed re-adsorption of chloride by concrete in pulse current, there was no significant difference between constant and pulse current experiments in relation to removal of chloride. Use of an anion exchange membrane impeded the H$^+$ ions from the anodic reaction entering the concrete, and the pulse current also demonstrated a positive effect on the energy consumption across the membrane by diminishing the concentration polarization.

1 INTRODUCTION

The electrokinetic remediation technology has been wildly utilized on various porous materials. The possibility of removing chlorides from concrete by using an electric current has been shown in previous investigations (Polder 1996, Toumi et al. 2007, Sánchez & Alonso 2011). The principle of ECE is to pass a DC current through the concrete, using the reinforcement as cathode and as anode a net is placed temporary on the concrete surface. Chlorides, as negatively charged ions, will be transported toward the anode by electromigration; thereby chlorides can be removed from the concrete in a relatively short time.

As result of electrode reactions, the electrolyte close to the anode will turn acidic during the ECE treatment. The concrete is not an acid resistant material, and thereby, the exposed concrete surface will be etched and weakened during the ECE. This issue can be avoided by adding a buffer such as lithium borate or calcium hydroxide to the electrolyte, but at same time, this will reduce the efficiency of extraction due to distributing the charge over more ions than in case of using electrolyte (Siegwart et al. 2002). Ion exchange membrane, as an approach hindering selected ions passing, could be introduced to

the ECE process. Membrane enhanced electrokinetic remediation technique has been investigated with soil, fly ash, and harbor sediment (Ottosen et al. 2009, Kirkelund et al. 2009, Pedersen 2003). In previous works including both lab and pilot scale experiments, this technique has demonstrated positive effect on removal of contaminants from materials and inhibition of extra ions injection. Thus, one objective of the present paper focus on the effect of an anion exchange membrane on protecting the concrete from the acid.

Due to the introduction of external electric field, the energy consumption becomes a factor influencing the application of ECE. It has been reported that the application of pulsed electric field could improve the electrochemical remediation and decrease the energy input during the process. For example, Mishchuk et al. (2001) reported that the pulsed electric field could intensify the electrodialytic desalination through diminishing concentration polarization and increasing the working current or voltage value. Kornilovich et al. (2005) indicated that pulse voltage changes the distribution of contaminations in soil and allows decreasing power inputs during electrokinetic remediation. Elsener & Angst (2007) found that a pulsed current could improve the removal efficiency of chloride from concrete by releasing the

bonding chloride at current off period. But no clear investigation about the effect of pulsed electric field on the energy consumption has been given. Therefore, the other objective of this work is to investigate the possibility of a pulsed electric field for energy saving during ECE and the effect on the removal of chloride. The theoretical considerations in the use pulse current are: (i) diminishing the polarization process and (ii) restoring the equilibrium condition at the cement-electrolyte interfaces.

2 MATERIALS AND METHODS

2.1 *Concrete sample preparation*

The concrete cylinders used in this study were prepared with Rapid Cement from Aalborg Portland, which is a CEM I cement. Aggregates were from sea materials with deionized water. Water to cement ratio and aggregates to cement ratio of the concrete were 0.4 and 4.9, respectively. Specimens with deionized water were cast in cylindrical mould (diameter = 8 cm, length = 10 cm) and stored sealed horizontally at 20ºC for 24 hours at which time they were demoulded and placed in a curing bath for 7 days. Afterwards, the cylindrical surfaces were sealed and the samples were subsequently placed standing in a container with 3% NaCl solution for 6 months to allow one-dimensional ingress of chloride.

2.2 *Experimental setup and design*

A laboratory cell for ECE is seen in Figure 1. The cells were made from polymethyl methacrylate. Each cell had an internal diameter of 8 cm. The length of compartment I and III were 5 cm, and compartment II was 3 cm. The compartment I and II was separated by an anion exchange membrane (AR204 SZRA B02249C) from Ionics. The concrete sample was between compartment II and III. Platinum coated electrodes from Permascand were used as working electrodes. Between the two working electrodes, three monitoring electrodes (platinum coated electrodes) were used to monitor the voltage drop of different parts (recorded by a multimeter). Before switching on the current, in each of the electrode compartments 500 mL 0.01 M $NaNO_3$ as electrolyte was injected and circulated by pumps, while in compartment II tap water was circulated. After 24 hours, a constant current was applied for all experiments by a power supply (Agilent E3612A). The pulse current was accomplished by a power supply timer instrument (Joel TE102), and the program was 1 hour "on", 0.5 hour "off". The total duration for constant current experiment was 240 hours; while for pulse current experiment was 360 hours. Although the total duration was different, the total working time was the same when the "off" time was considered in the pulse current experiment. In this way, the quantity of total charge passing through the experiments was maintained identical. The pH variation in compartment II was measured using a Radiometer pH electrode every 24 hours. At the end of the experiments, the concrete samples were segmented to four slices by a water cooling saw, dried and crushed before the measurement of chloride concentrations. Four experiments were performed as listed in Table 1.
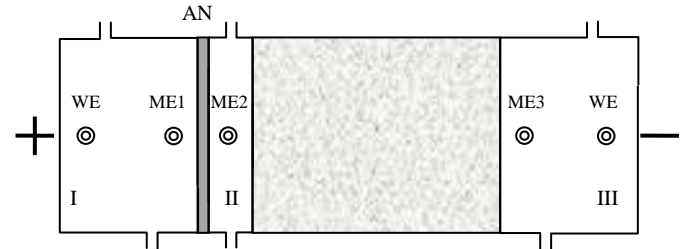

Figure 1. Schematic diagram of the laboratory cell for ECE. (AN = anion exchange membrane, WE= working electrode, ME = monitoring electrode).

Table 1. Experimental design.

Experiments	Current density (mA/cm^2)	Current type	Duration (h)
1C	0.1	Constant	240
1P	0.1	Pulse	360
2C	0.2	Constant	240
2P	0.2	Pulse	360

The energy consumption was calculated as:

$$E = \int VIdt \qquad (1)$$

where, E, is the energy consumption (Wh); V, voltage between working electrodes (V); I, current (A); t, duration (h).

3 RESULTS AND DISCUSSION

3.1 *Energy consumption*

In all experiments the current was constant when applied; therefore the variation in voltage is an indicator of the energy consumption. Figure 2 shows the variation of voltage (between working electrodes) as a function of experimental time. The pulse pattern was not shown in the figures because the data of voltage was recorded at the working (current on) time every 24 hours in both the constant and the pulse current experiments. In general it can be seen that the voltage increased with the increasing of current density since 1C, 1P and 2C, 2P were comparable. For each experiment, after a period of initial increasing, the voltage decreased with time. This is probably due to the transport of OH⁻ ions from the cathodic reaction into the concrete. OH⁻ ions have a much

higher mobility than other negative ions. A comparison of constant and pulse current experiments showed that the voltage of pulse current experiments were lower than that of constant current experiments although with different extents, which means that the pulse current showed positive effect for energy saving in these experiments. The decreasing extent between 2C and 2P was higher than that between 1C and 1P. This was probably because the free ions in the pore fluid of the concrete were almost sufficient for low current transport. For the higher current density experiments, the pulse current experiment had much lower voltage compared with the constant current experiment.
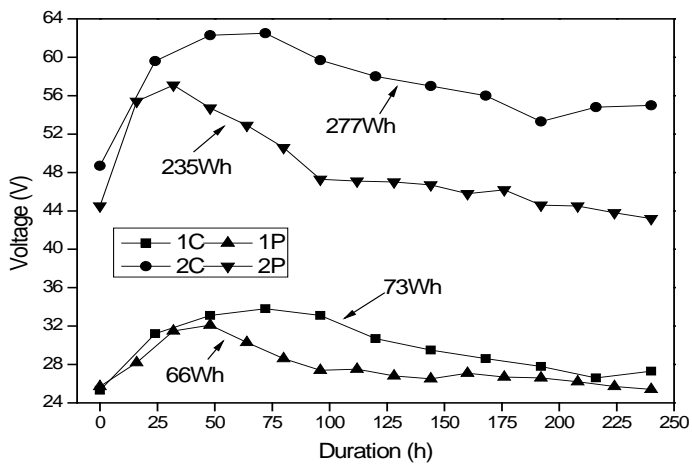

Figure 2. Voltage variation between working electrodes.

The voltage drop at different parts of the cell during experiments is shown in Figure 3 and 4. Figure 3 is the part across the anion exchange membrane measured between measuring electrodes ME1 and ME2, and Figure 4 is the part across the concrete measured between measuring electrodes ME2 and ME3. The voltage dropped in the electrolyte compartments was negligibly small compared to other parts, thus it is excluded in the following discussion.
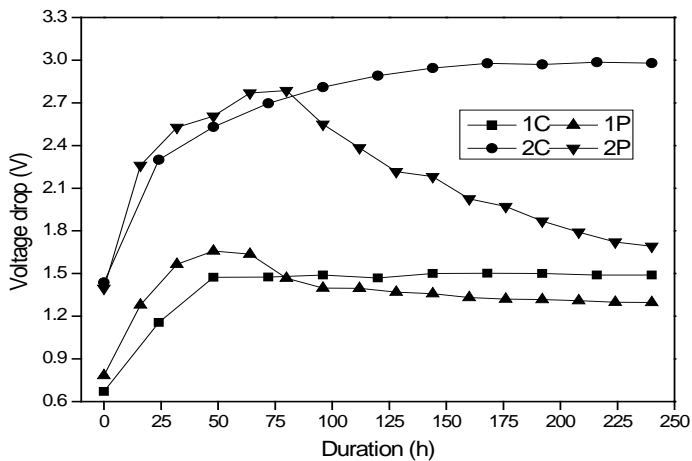

Figure 3. Voltage drop across the anion exchange membrane.

In Figure 3, it can be seen that the voltage increased at the initial stage in all experiment, which was probably caused by the depletion of ions at the surface of anion exchange membrane due to concentration polarization. The concentration polarization is correlated to the applied current density, thus the voltage drop of 2C and 2P was higher than that of 1C and 1P. Then after the initial increase, the voltage was relatively constant in the constant current experiment which means a stationary state reached. However, in the pulse current experiments the voltage decreased with time, which is probably due to the relaxation of the membrane surface diminishing the concentration gradient by diffusion. In this way, the pulse current effectively decreased the voltage drop and thus the energy consumption across the anion exchange membrane.

The voltage drop across the concrete (Fig. 4) had a similar pattern and value compared to the total voltage applied to the working electrodes (Fig. 2) in all experiments. This means the highest voltage drop was across the concrete, and that the concrete was the main contributor to the overall energy consumption. The voltage in this part in the pulse current experiments was lower than that in the constant current experiments. This showed that the energy saving effect caused by the pulse current in the whole system was due to the energy saving over the concrete. When a direct current is applied, excess charge will be accumulated at one end of the sample and depleted on the other due to the different conductivity between the pore wall surface and the pore solution. A non-equilibrium state and potential difference across the interface layer (i.e. diffused double layer, DDL) could arise. This is similar to the charging of the ionic double layer at the electrode-electrolyte solution interface (Bard & Faulkner 2001).
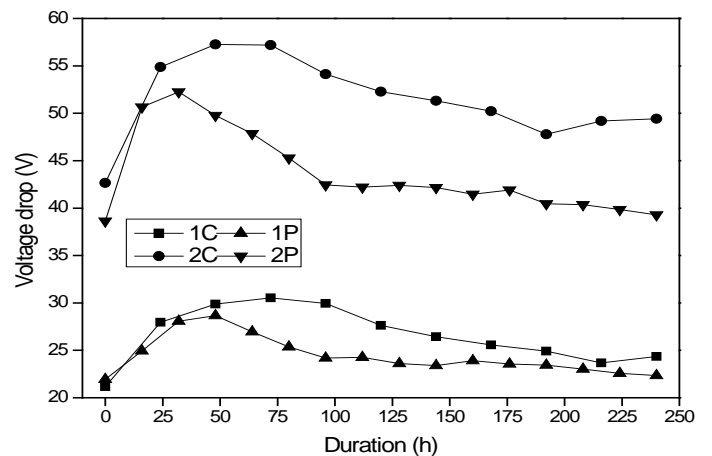

Figure 4. Voltage drop across the concrete.

Thus a resistance-capacitance model could be introduced to describe the voltage drop across the concrete,

$$V = IR_s + q^{DDL}/C_{DDL} \qquad (2)$$

where V is the voltage across the concrete, I is the current, R_s is the resistance, q^{DDL} is the surface charge density, and C_{DDL} is the capacitance of the double layer. The energy saving caused by charging and discharging of the double layer (the second term of right hand side of Equation 2) induced by pulse current is low, at the magnitude of mV, since the surface charge of the concrete is low compared to the electrode surface. Loche et al. (2005) has demonstrated by electrochemical impedance spectroscopy that during the migration of chloride ions, the capacitance of mortar paste remains roughly constant. Therefore, the pulse current enhanced energy saving effect within the concrete is mainly expected as decrease in pore fluid resistance. The reason for this is possibly that the rate of release of bound chloride is slow compared to the rate of chloride removal in the electric field and the process is inefficient as soon as the free chloride content in the pore solution is low. A relaxation period then allows the system to re-establish the equilibrium between bound and free chlorides. If then the current is switched on again, the treatment can proceed at a higher efficiency.

3.2 Removal of chloride

The pH variation in compartment II during the experiment is shown in Figure 5. In all experiments, a sharp increase of pH at initial stage was observed due to the electromigration of OH$^-$ ions from the concrete. Afterward a moderately stationary state was obtained, which means the migration rate of OH$^-$ ions equals to the consumption rate in the anode chamber.
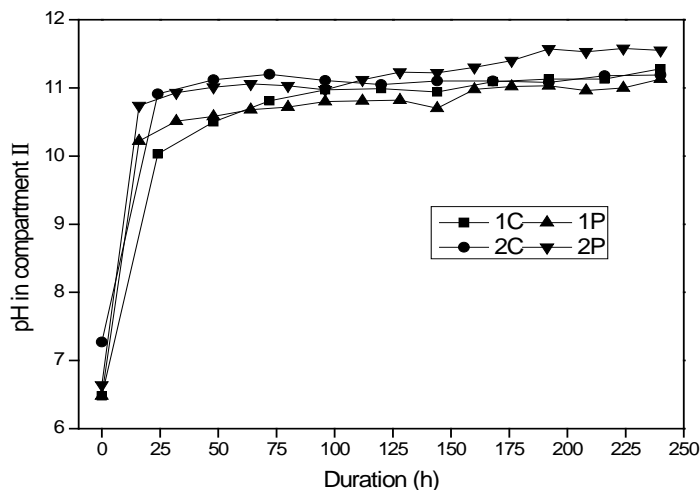

Figure 5. pH change in compartment II.

The high pH value indicated that the anion exchange membrane effectively prevented the H$^+$ ions from entering this compartment and most importantly the concrete. It is worth to note here water dissociation could happen at the membrane surface direct-

ing to the concrete if the applied current density reaches the limiting value of the anion exchange membrane. The limiting value is determined by the concentration of electrolyte reduce to zero; as a result, acidification appears. But in the present work, the decreasing of pH caused by acidification was not observed for any of the current densities applied; this was also supported by Figure 3. In Figure 3, the voltage drop of constant current experiments would be decreasing with time not constant if the water dissociation occurred.

The residual concentration of chloride in the concrete slices after treatment is shown in Figure 6. It can be seen that the chloride concentration in each slice was lower than initial value and the chloride was transported as negative ions, as it was the slices closest to cathode that was remediated first and the highest chloride concentrations were in slice 1.
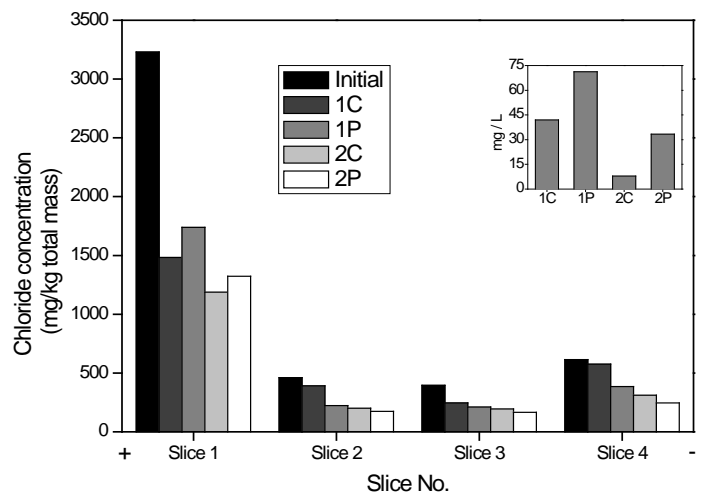

Figure 6. Chloride concentration of each slice in concrete after the treatments. The superimposed graph is the chloride concentration in compartment II of each experiment.

The removal of chloride from the concrete was highly related to the applied current density, the removal efficiency (defined as the decrease in chloride mass divided by the initial chloride mass) in 2C (59%) and 2P (59%) was higher than that in 1C (43%) and 1P (45%). However, there was no significant difference of chloride removal between constant and pulse current experiments for any of the current densities. The energy consumption was 1.7, 1.5 and 4.7, 4.0 Wh per percent removed chloride in 1C, 1P and 2C, 2P, respectively. In slice 2-4, the chloride concentration in the pulse current experiments were lower than that those of the constant current experiments, which supported the interpretation of the lower voltage drop of pulse current experiment across the concrete (Fig. 4). Re-equilibrium between bound and free chlorides gave rise to a high conductivity at the pore fluid during the relaxation period. However, in slice 1, a reverse phenomenon was observed in which the chloride concentration in

the pulse current experiments was higher. This could be explained by the transport by diffusion and re-adsorption of chloride from compartment II when the current was switched off. The superimposed figure in Figure 6 is the chloride concentration in compartment II, and it shows that the chloride concentration in the pulse current experiments was higher than that of constant current experiments. This is probably due to the interdiffusion between Cl^- ions from the anolyte and OH^- ions from compartment II, since the diffusion of Cl^- ions from the anolyte will be restricted by the diffusion potential.

4 CONCLUSIONS

The possibility for application of pulsed electric current for energy saving during electrochemical chloride extraction and the effect on removal of chloride were investigated. It was found that the voltage drop across the concrete was the major contributor of energy consumption and that the pulse current could decrease the voltage drop of this part effectively by re-distribution of ions in the pore fluid between bound and free form. The energy consumption was decreased by 15% by the pulse current in the experiments with 0.2 mA/cm^2 current density, which was higher than that of 0.1 mA/cm^2 experiments with a decrease of 9.6%. The removal efficiency increased with the applied current density, which were 59% and 59% in 2C and 2P, and 43% and 45% in 1C and 1P. Due to re-adsorption of chloride by the concrete in the pulse current experiments during the relaxation period, there was no significant difference between constant and pulse current experiments in relation to the overall removal of chloride. The use of an anion exchange membrane hindered the H^+ ions from the anodic reaction entering the concrete, and the pulse current also demonstrated a positive effect at decreasing energy consumption across the membrane by diminishing the concentration polarization.

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