Removing heavy metals and organic contaminants from solids using an Upward Electrokinetic Soil Remedial (UESR) technology

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**Removing Heavy Metals and Organic Contaminants
From Soils Using An Upward Electrokinetic
Soil Remedial (UESR) Technology**

Huang Xiangjun

School of Civil & Environmental Engineering

**A Thesis Presented to the Nanyang Technological University
in fulfilment of the Requirements for the Degree
of Master of Engineering**

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TABLE OF CONTENTS

Table of Contents

ACKNOWLEDGEMENT.....i

TABLE OF CONTENTS.....ii

ABSTRACT.....vi

LIST OF FIGURES.....viii

LIST OF TABLES.....x

LIST OF SYMBOLS.....xi

CHAPTER 1 INTRODUCTION.....1

1.1 BACKGROUND.....1

 1.1.1 *Heavy Metals in Soils*1

 1.1.2 *Remediation Technologies for Metal-contaminated Soils*2

 1.1.3 *Dielectrophoresis in Soils*.....3

 1.1.4 *Heavy Metals Coexist with Organic Contaminations*.....3

 1.1.5 *The Need for this Study*.....4

1.2 OBJECTIVES OF THIS STUDY5

1.3 ORGANIZATION OF THIS REPORT.....5

CHAPTER 2 LITERATURE REVIEW.....7

2.1 CLAY MINERALS PROPERTIES7

 2.1.1 *Kaolinite Minerals*8

 2.1.2 *Surface Charges of Clay Particles*.....9

2.2 DIFFUSED DOUBLE LAYER IN CLAY.....9

 2.2.1 *The Origin of Diffused Double Layer*.....9

 2.2.2 *Theories of Double Layer*10

 2.2.2.1 Poisson-Boltzmann Equation.....10

 2.2.2.2 Gouy-Chapman Theory11

2.3 ELECTROKINETIC PHENOMENON.....11

 2.3.1 *Electrophoresis*12

 2.3.2 *Electromigration*.....12

 2.3.3 *Electroosmosis*13

2.4 ELECTRIC FIELDS IN SOILS.....16

TABLE OF CONTENTS

2.4.1	<i>Electric Fields of Point Charges</i>	16
2.4.2	<i>Electric Potential in Electric Fields</i>	17
2.4.3	<i>Capacitors and Dielectrics</i>	17
2.4.4	<i>Soil Dielectric Constant</i>	18
2.4.5	<i>Effects of Dielectrophoresis</i>	19
2.4.5.1	<i>Dielectrophoretic Force on Ideal Dielectrics</i>	19
2.4.5.2	<i>The Bunching Effects and Pear-Chain Formation</i>	20
2.4.5.3	<i>Dielectrophoresis in Weakly Conducting Materials</i>	20
2.4.5.4	<i>Dielectrophoresis as a Dewatering Technology</i>	21
2.4.6	<i>Electric Fields of Different Electrodes Configurations</i>	21
2.5	ELECTROKINETIC SOIL REMEDIATION PROCESSES	24
2.5.1	<i>Physicochemical Processes in Soils</i>	24
2.5.1.1	<i>Electrolysis Reactions</i>	24
2.5.1.2	<i>Adsorption and Desorption</i>	24
2.5.1.3	<i>Precipitation/Dissolution</i>	25
2.5.1.4	<i>Oxidation/Reduction</i>	25
2.5.2	<i>Heavy Metal Speciation and Migration</i>	26
2.5.3	<i>Organic Contaminants in Soil</i>	27
2.6	BACKGROUND OF ELECTROKINETICS REMEDIATION	28
2.6.1	<i>Field Scale Studies</i>	28
2.6.2	<i>Laboratory Scale Studies</i>	29
	CHAPTER 3 MATERIALS AND METHODOLOGY	38
3.1	INTRODUCTION	38
3.2	THE PROPOSED ELECTROKINETIC SYSTEM: UESR	38
3.2.1	<i>Electric Fields in UESR</i>	38
3.2.2	<i>Progressive Migration of Contaminants</i>	39
3.2.3	<i>Organic Contaminants Removal Using UESR</i>	39
3.2.4	<i>Effect of Gas Generation</i>	40
3.2.5	<i>Factors Affecting the Performance of UESR</i>	40
3.3	REACTOR SETUP	41
3.3.1	<i>Electrokinetic Cell</i>	41
3.3.2	<i>Electrodes and DC Power Supply</i>	42

TABLE OF CONTENTS

3.3.3	<i>Experimental Program and Parameters</i>	43
3.4	SOIL CHARACTERIZATION.....	45
3.5	CONTAMINATED KAOLIN PREPARATION.....	45
3.5.1	<i>Spiking of Kaolins with Heavy Metals</i>	45
3.5.2	<i>Spiking of Kaolins with Organic Compounds</i>	46
3.6	EXPERIMENTAL PROCEDURES.....	46
3.6.1	<i>Reactor Packing and Monitoring</i>	46
3.6.2	<i>Sampling Procedures</i>	47
3.7	ANALYTICAL METHODS.....	48
3.7.1	<i>Measuring pH</i>	48
3.7.2	<i>Measuring Moisture Content</i>	48
3.7.3	<i>Measuring Zeta Potential</i>	48
3.7.4	<i>Measuring Particle Size</i>	48
3.7.5	<i>Measuring Conductivity</i>	49
3.7.6	<i>Measuring Heavy Metal Concentrations</i>	49
3.7.7	<i>Measuring Xylene and Phenanthrene Concentrations</i>	50
	CHAPTER 4 RESULTS AND DISCUSSION	51
4.1	SOIL CHARACTERIZATION.....	51
4.1.1	<i>Kaolin Particle Size</i>	51
4.1.2	<i>Kaolin Zeta Potential</i>	51
4.2	CONCENTRATION OF SPIKED CONTAMINANTS	52
4.3	ACCUMULATION OF METALS ON CATHODE AND CRACKS DEVELOPMENT ...	54
4.3.1	<i>Accumulation of Metals on Cathode</i>	54
4.3.2	<i>Development of Cracks in the Soil</i>	54
4.4	SOIL WATER CONTENT AFTER UESR TREATMENT.....	55
4.5	SOIL PH AFTER UESR TREATMENT	57
4.6	HEAVY METAL REMOVAL AFTER UESR TREATMENT	59
4.6.1	<i>Effect of Reactor Size</i>	59
4.6.2	<i>Effect of Cathode Chamber Influent</i>	61
4.6.3	<i>Effect of Treatment Duration</i>	62
4.6.4	<i>Mobility of Heavy Metals</i>	64
4.6.5	<i>Effect of Soil Types on Heavy Metal Removal</i>	65

TABLE OF CONTENTS

4.6.6	<i>Effect of Current Density and Voltage Gradient</i>	66
4.6.7	<i>Effect of Contaminant Composition</i>	68
4.6.8	<i>Distribution of Heavy Metals after UESR Treatment</i>	69
4.7	ORGANIC CONTAMINANTS REMOVAL AFTER UESR TREATMENT	72
4.7.1	<i>Effect of Reactor Size</i>	73
4.7.2	<i>Effect of Cathode Chamber Influent</i>	73
4.7.3	<i>Effect of Soil Type</i>	74
4.7.4	<i>Distribution of Organic Compounds after UESR Treatment</i>	75
4.8	CATHODE EFFLUENT IN UESR.....	76
4.8.1	<i>Effluent pH</i>	76
4.8.2	<i>Contaminants in Cathode Effluent</i>	77
4.9	SOIL RESISTANCE AND ENERGY CONSUMPTION	79
4.9.1	<i>Current and Voltage Variation during UESR Treatment</i>	79
4.9.2	<i>Energy Expenditure</i>	83
4.10	ELECTRIC FIELDS IN SOIL	84
4.11	EFFECT OF ELECTROOSMOSIS AND DIELECTROPHORESIS IN UESR.....	86
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS		90
5.1	CONCLUSIONS ON HEAVY METAL REMOVAL IN UESR	90
5.2	CONCLUSIONS ON ORGANIC CONTAMINANTS REMOVAL IN UESR.....	92
5.3	CONCLUSIONS ON ENERGY EXPENDITURE	93
5.4	RECOMMENDATION FOR FUTURE STUDY	94
REFERENCES		96
APPENDIX A KAOLIN PARTICLE SIZE DISTRIBUTION		103
APPENDIX B FINAL PH OF TREATED KAOLIN		104
APPENDIX C WATER CONTENTS OF KAOLIN		106
APPENDIX D TREATMENT CONDITIONS AND REMOVAL		108
APPENDIX E CATHODE EFFLUENT PH		109
APPENDIX F HEAVY METALS IN CATHODE EFFLUENT		112
APPENDIX G VOLTAGE AND CURRENT		114
APPENDIX H DISTRIBUTION OF HEAVY METALS		117
APPENDIX I DISTRIBUTION OF ORGANIC CONTAMINANTS		133

SUMMARY

Abstract

An innovative upward electrokinetic soil remedial (UESR) technology was proposed to simultaneously remove heavy metals and organic contaminants from contaminated soils. The proposed technology was demonstrated to be effective through a series of laboratory scale experiments on clayey soils. In the UESR systems, rod-shaped anode was inserted into the bottom of the soil and ring-shaped cathode was placed on the soil surface to establish the non-uniform vertical electric fields in the soil. Driven by the electric fields, the contaminants were transported to the surface of the tested soil and removed via cathode effluent.

As (III), Cr (III), Ni (II), Cu (II), Pb (II), Zn (II), and Cd (II) were selected as heavy metal contaminants. P-xylene (one of the BTEX compounds) and phenanthrene (one of the PAH compounds) were chosen as the target organic contaminants. Two types of kaolin clays were loaded either with heavy metals only or with a mixture of heavy metals and organic contaminants. The contaminated kaolin soils were packed into reactor cells of different sizes and treated under either constant current densities or constant voltage gradients for durations ranged from 4 to 30 days. The effects of specimen size, treatment duration, cathode chamber influent, current density, contaminants compositions, as well as soil type were investigated in 19 experiments.

As(III) and Cr(III) were found to be the least mobile metals while Ni(II) and Cd(II) were found to be the most mobile metals. In most cases, the mobility of heavy metals followed the order $\text{Ni(II)} > \text{Cd(II)} > \text{Zn(II)} = \text{Cu(II)} > \text{Pb(II)} > \text{As(III)} > \text{Cr(III)}$. The removal efficiencies of p-xylene in all experiments were higher than those of phenanthrene probably because p-xylene has much higher solubility than phenanthrene in water.

It was found that acid flushing of the cathode electrode had significant effect on the removal of contaminants and saving of energy consumption. The upward movement of soil pore water by electroosmosis seemed to be the main mechanism that transported the organic compounds. Nevertheless, it was evident that dielectrophoresis affected the migration of phenanthrene and pore water.

SUMMARY

The experimental results showed successful removal of heavy metals and organic contaminants simultaneously from kaolin clays. The UESR technology was proven to be viable and the idea of transporting contaminants upwards was therefore feasible. The removal efficiencies obtained were 43.1% for As, 49.7% for Cr, 68.3% for Ni, 71.5% for Cu, 59.3% for Zn, 52.5% for Pb, 67.2% for Cd, 92.8% for p-xylene, and 66.9% for phenanthrene in durations between 6 to 9 days. Higher removal efficiencies could be achieved when longer durations were used.

LIST OF FIGURES

List of Figures

Figure 2.1 Silica tetrahedron (a) and silica tetrahedra arranged in hexagonal network (b) (Grim 1962).....	8
Figure 2.2 Octahedral unit (a) and sheet of octahedral units (b) (Grim 1962)	8
Figure 2.3 Diffused double layer (Mitchell 1993).....	9
Figure 2.4 Electroosmotic flow in clay capillary.....	13
Figure 2.5 Soil capillary in Schmid's model (Mitchell 1993).....	16
Figure 2.6 Lines of forces from two positive charges (a) and a positive and negative charge (b)	16
Figure 2.7 Electric field in a parallel-plate capacitor.....	17
Figure 2.8 Electric fields with electrodes of different configuration (Segall and Bruell 1992)	22
Figure 2.9 Hydraulic fractures electrodes (a) and Electric field potential (b) (Murdoch and Chen 1997).....	23
Figure 3.1 Vertical electric fields by pairs of point charges at different spacing	38
Figure 3.2 Schematically UESR reactor setup.....	41
Figure 3.4 Sampling procedure of treated soil.....	47
Figure 4.1 Zeta potential of the kaolin soils	52
Figure 4.2 Water Content of samples with different diameter for 6 days under constant current (a) and for 18 days under constant voltage (b).....	56
Figure 4.3 Water content change in T8S1, T8S2, and T8S3	57
Figure 4.4 Soil pH after treatment	58
Figure 4.5 T8S1, T8S2, and T8S3 treated sample pH	59
Figure 4.6 Heavy metal removal for different cell diameter	60
Figure 4.7 Correlations between removal rate and cell diameter	61
Figure 4.8 Effect of treatment duration on metal removal for experiment conducted on constant current (a) and constant voltage (b).....	63
Figure 4.9 Correlations between removal rates and treatment durations.....	63
Figure 4.10 Removal efficiencies of Pb in test T8S1, T8S2, and T8S3	66
Figure 4.11 Correlation of heavy metal removal and current density	67
Figure 4.12 Change in pH of soil specimen after treatment	67

LIST OF FIGURES

Figure 4.13 Distribution of heavy metals as ratio of final content over initial
content in inner and outer zone of treated kaolin in test T1D1 (a) and T8V1 (b)
.....71

Figure 4.14 pH profile of T7M3 and T7M4 after UESR treatment.....74

Figure 4.15 Change of cathode effluent pH with treatment time77

Figure 4.16 Heavy metals in effluent for test T8V378

Figure 4.17 Concentration of p-xylene in effluent for T7M3 and T7M479

Figure 4.18 Change of reactor voltage for experiments conducted with constant
current 15 mA and used (a) distilled water and (b) 10⁻² N HNO₃80

Figure 4.19 Change of reactor current for experiments conducted with (a) constant
voltage of 3.5 V and diameter 100 mm, and (b) constant voltage 20 V and
diameter 140 mm82

Figure 4.20 Electric fields for T8V3 (constant voltage 3.5 V), T8S1(constant
voltage 20 V) and T8S1 (constant voltage 20 V)85

Figure 4.21 Pb concentration in kaolin after UESR treatment in T8S1, T8S2, and
T8S387

Figure 4.22 Phenanthrene concentration in kaolin after UESR treatment in T8S1,
T8S2, and T8S387

Figure 4.23 Moisture content of kaolin after UESR treatment in T7M3 and T7M4
.....88

Figure 4.24 Moisture content of kaolin after UESR treatment in T8S1, T8S2, and
T8S388

LIST OF TABLES

List of Tables

Table 2.1 Coefficient of electro-osmotic permeability of various soils (Mitchell 1993)14

Table 2.2 Field scale studies conducted using electrokinetics.....29

Table 2.3 Past studies related to this research37

Table 3.1 Parameters of tests performed44

Table 3.2 Chemical properties of kaolin 145

Table 4.1 Properties of kaolin I and kaolin II51

Table 4.2 Concentration of contaminants before treatment (mg/kg).....53

Table 4.3 Moisture contents and pH of soil before treatment53

Table 4.4 Cracks development in soils55

Table 4.5 Metal removal for tests using different cathode chamber influent (%)...61

Table 4.6 Removal efficiencies of different types of metals (%)64

Table 4.7 Effect of different contaminants compositions.....68

Table 4.8 Distribution of heavy metals after UESR treatment70

Table 4.9 Organic contaminants removal after UESR treatment73

Table 4.10 P-xylene and phenanthrene concentration after treatment (mg/kg).....76

Table 4.11 Energy consumption and cost.....83

LIST OF SYMBOLS

List of Symbols

A	Total cross sectional area
A_o	Concentration of surface charge
C	Capacity of capacitor
D	Dielectric Constant
F	Faraday's constant
Q	Total flow (m^3/s)
T	Temperature
V_i	Velocity of species i
e	Unit electronic charge
u_i	Ionic mobility of ion i
a	Polarizability
k_h	Hydraulic conductivity
k_e	Electro-osmotic permeability
k	Boltzmann constant
i_e	Electric potential gradient
n_i	Concentration of ions i in a force field
n	Porosity
q	Flow rate
ρ	Charge density
η	Viscosity
ψ	Electric potential
Φ_E	Electric field flux
σ	Surface charge density
v_i	Ionic valence
∇	Del vector
ϵ_o	Permittivity of space
ϵ_i	Absolute permittivity of medium i
ξ	Zeta potential

Chapter 1

Introduction

1.1 Background

1.1.1 Heavy Metals in Soils

Metals including lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), nickel (Ni), copper (Cu) and mercury (Hg) are considered as heavy metals or trace metals. This group of metals, when existing at certain concentrations, may cause serious environmental problems and impose a threat to animals and humans. It can happen through direct contact or through ingestion. Most heavy metals are hazardous and some are deadly poisonous. Cadmium is known to cause kidney damage, anemia and painful bone disorder, and many other diseases are known to be induced by heavy metals accumulated in human body (LaGrega et al. 1994).

A major source of heavy metals is believed to be land disposal of municipal/industrial refuse and of sludge (Yaron et al. 1996). Elevated concentrations of heavy metals are found in many contaminated sites worldwide due to extensive industrial development and urbanization over the past years. In the United States alone, 756 sites (or 63% of the total) on the National Priority List (NPL) were reported to have toxic heavy metals (Hazardous Waste Consultant 1996).

Heavy metals can exist in airborne particles, in water as soluble compounds, and in solid carriers such as in biomasses, rocks and soils. Their toxicity depends on the mobility, accessibility and bioavailability. As a metal accumulates in soils, it transforms into many forms along with the surrounding ionic species, minerals, compounds, complexes, and/or particles. Generally, the mobile forms are those easily soluble in groundwater such that they are free to be transported to rivers or lakes. Heavy metals involved in other forms are relatively immobile as they are strongly sorbed onto solid particles. The fate and transport of a metal in soils is a complicated physiochemical and hydraulic phenomena. It is affected by the type

and valence of the metal, the chemical compositions of the soil and groundwater, etc. Any alteration of these conditions might cause a change in mobility of the metal. For instance, a small drop in pH value of groundwater might cause immobile metal contaminants in the soil to be mobile and increase their toxicity.

1.1.2 Remediation Technologies for Metal-contaminated Soils

Many technologies, in-situ or ex-situ, were developed to treat heavy metal contaminated soils. Mechanical separation is an ex-situ process that separates soil particles according to their sizes. The smaller and more polluted particles are removed from the larger and cleaner particles. Chemical treatments aim to reduce the toxicity of a contaminant by oxidative or reductive mechanism, and very often precipitation of the metals. Soil washing/soil flushing is a process where extracting solutions or chelating agents are passed through or mixed with the contaminated soil. Phytoremediation uses metal up-taking plants to accumulate metals from soils that support the plant growth. These technologies are often limited by the permeability of the soil, the cost of energy and involved chemicals, and the depth of soil contamination.

Electrokinetics is an emerging technology that treats a contaminated soil with a low level DC current. Electric fields are created between the anode electrode(s) and cathode electrode(s) inserted in the soil. Ions, charged particles and pore water are transported across the soil by the electric fields through one or more of the four mechanisms namely, electromigration, electro-osmosis, electrophoresis, and diffusion (Acar and Alshawabkeh 1993). Electrokinetics can be used in (in-situ or ex-situ) contaminated soils with very low permeability where other technologies do not yield favorable results. This technology has been developed over the past decade to treat different soils and was reported to be capable of treating both inorganic and organic contaminants (Hamed et al. 1991; Acar et al. 1992; Segall and Bruell 1992; Shapiro and Probststein 1993; Hicks and Tondorf; 1994; Chung and Kang 1999; Mulligan et al., 2001; and Virkutyte et al., 2002).

1.1.3 Dielectrophoresis in Soils

Dielectrophoresis has been observed since 600 B.C. when people found rubbed amber could attract small bits of fluff and other matter. But it was only since the last century that the forces exerted upon neutral matter by nonuniform electric fields were intensively studied. The unique ability to exert forces to neutral matter through electric field and to separate matters by their dielectric constants has made dielectrophoresis a useful technology in electronics, biology, nanoelectromechanics, etc. The application of dielectrophoresis in geotechnical areas as a dewatering technology has also made progresses in the past few decades (Inculet and Lo 1988, Lo and Shang 1994). However, the use of dielectrophoresis as a soil remedial technology has not been attempted.

1.1.4 Heavy Metals Coexist with Organic Contaminations

Contaminated sites usually contain both inorganic contaminants, such as heavy metals, and organic contaminants, such as BTEX (Benzene, Toluene, Ethyl Benzene, and Xylene) and PAHs (Polycyclic Aromatic Hydrocarbons). A landfill leachate, for instance, may have high concentration of heavy metals as well as various organic compounds which may consist of organic solvents, organic acids, petroleum hydrocarbons, pesticides, and halogenated hydrocarbons. This is especially true for the case when industrial wastes are included in the landfill. For oil spills or underground storage tank leakages, the contamination of groundwater and soil by both BTEX and Pb may cause damage.

The physicochemical and biological processes governing the speciation, migration, and degradation of a mixture of heavy metals and organic contaminants are not well understood. Organic contaminants could attach to soil particles due to sorption, dissolve into pore water, occur as non-aqueous liquid phase, or involve as vapor phase. Little knowledge is currently obtained about the influences they have on each other's absorption and speciation behaviors when both are present in soils. Electrokinetic remediation is probably the only viable in-situ technology that can treat clayey soils contaminated with both heavy metal and organic contaminants.

The features of this technology that make it potentially more applicable than others include:

- It can be applied in-situ,
- It can treat low permeable soils, such as clay,
- It consume relatively low energy,
- It can be used in combination with other remedial technologies such as bioremediation,
- It can control the direction and rate of contaminant transportation, and
- It can remove both inorganic and organic contaminants.

1.1.5 The Need for this Study

Electrokinetically removing heavy metals from soils has been proven effective in many studies. Other studies have shown promising results for flushing organic compounds out of soils, and for injecting nutrients and TEA (terminal electron acceptor) into contaminated soils to enhance biodegradation (Thevanayagan and Rishindran 1998). Moreover, a few investigations have demonstrated the possibility of transporting bacteria in soils and stimulating bacterial activities using electric fields. Its capability of transporting heavy metals, purging soluble organic compounds, and enhancing biodegradation of organic contaminants seems to provide an optimal solution for many soil contamination problems.

Nevertheless, the use of this technology to simultaneously remove heavy metals and organic contaminants remained relatively untouched. The effects on neutral substances by dielectrophoresis as a result of overall or local electric field inhomogeneity while applying electrokinetics were not considered in the past studies. There is a lack of studies on the transportation of contaminants in a non-uniform electric field. In addition, previous studies have been all focused on using horizontal electric fields in soils. The idea of vertically transporting contaminants and pore water has received little attention despite the fact that a vertical configuration could integrate most advantages of electrokinetics and offer better field applicability. The potential benefits of a vertical configuration are listed as follows:

- To minimize the physical disturbance of soils since only anode electrodes are inserted into soils via electrode wells,
- To enable progressive removal of contaminants,
- To have contaminants accumulated on the soil surface for easier handling and removal,
- To reduce the installation, operation and maintenance costs for field applications, and
- To use the oxygen generated to enhance biodegradation.

1.2 Objectives of this Study

The main objective was to study the feasibilities of removing heavy metals vertically from clayey soils using the proposed upward electrokinetic soil remedial (UESR) technology, in comparison with the horizontally applied electrokinetic studies. This study also attempted to examine the effectiveness of simultaneous removing heavy metals and organic contaminants from artificially spiked soils. The scope included:

- To develop a vertical electrokinetic soil remedial system,
- To investigate simultaneous removal of heavy metals and organic contaminants, as well as the impact of their removal by one to the other,
- To determine the effects caused by operational parameters including treatment duration, current density, voltage gradient, and sample size,
- To study the effectiveness of neutralizing the cathode electrolyte with weak acid as an enhancement technique, and
- To examine the effects of soil type on the treatment efficiency.

1.3 Organization of this Report

This report contains 5 chapters that cover the work conducted. Chapter 1 introduces the soil contamination problem and electrokinetic soil remediation technology. Chapter 1 also states the significance and objectives of this study. Chapter 2 first

describes the theories and principles of electrokinetic soils remediation and then presents the past studies conducted in this area. The mechanisms involved in electrokinetic treatment are illustrated. Chapter 3 presents the design of the proposed upward electrokinetic soil remedial (UESR) reactor, the laboratory bench-scale experiments, testing materials and experiment methodologies used in this study. It covers the procedures for preparing and running the experiments as well as the analytical methods used. Chapter 4 presents the experimental results obtained and the discussions of these results. Chapter 5 summarizes the findings and conclusions of this study. Recommendations on further studies are also included. This report includes an appendix section which presents the detailed experiment data and results.

Chapter 2

Literature Review

Soils contain materials of very diverse composition and behavior. They are porous and heterogeneous media consist of aggregates and particles of different sizes, ranging from less than 1 μm to a few meters in equivalent diameter. The physical and chemical properties of a soil are largely governed by the small particles in the soil since they possess greater surface areas. Clays, having very small grain sizes (less than 2 μm) and exhibiting many interesting behaviors, are extensively studied in soil mechanics and geo-environment engineering.

2.1 Clay Minerals Properties

Clay minerals are a small group of minerals derived from weathering of the primary rock minerals. Clay materials consist of essentially the extremely small crystalline particles of one or more members of the clay minerals. Detailed study of clay mineralogy and engineering properties of clays as well as clayey soils can be found in the literature (Grim 1962; Mitchell 1993).

There are two basic crystal structure units in clay minerals: the tetrahedral sheet of silicon and oxygen, and the octahedral gibbsite sheet of aluminum and hydroxyl (Figures 2.1 and 2.2). The first structure unit (the silica sheet) is formed by repeating the hexagonal network formed by tetrahedral groups in lateral directions. In such a unit, the tips of all the tetrahedrons are pointing in the same direction and the bases of all tetrahedrons are in the same plane. The second structure unit is formed by two sheets of compactly packed oxygen atoms and hydroxyls in which embed aluminum atoms appear in octahedral coordination. All clay minerals are formed by stacking the basic structure units one on top of the other in different patterns. Different types of bonding between the sheets and different metallic atoms in the crystal lattice give rise to different clay minerals.

2.1.1 Kaolinite Minerals

The kaolinite mineral structure consists of a single tetrahedral sheet and a single octahedral sheet combined in a unit such that the tips of the silica tetrahedrons and one layer of the octahedral sheet form a common layer. Such units continuous in lateral directions and stack one above the other to form the minerals of kaolinite.

The kaolinite minerals have theoretical composition, expressed in oxides, of SiO_2 46.54%, Al_2O_3 39.5%, and H_2O 13.96% (Grim 1962). The cleavage planes are usually the plane between the unit layers. Due to the fairly tight hydrogen bonds between the unit layers, the cleavage is not so pronounced.

Figure 2.1 Silica tetrahedron (a) and silica tetrahedra arranged in hexagonal network (b) (Grim 1962)

Figure 2.2 Octahedral unit (a) and sheet of octahedral units (b) (Grim 1962)

2.1.2 Surface Charges of Clay Particles

Most clay particles develop charges on their surfaces due to lattice imperfections, isomorphous substitution and chemical reactions on particle surface. The net surface charge of clay particles is normally negative except at very low pH condition.

The isomorphous substitutions in clay minerals at crystallization stage give rise to permanent charges. A negative charged clay particle has large number of sites on its surface which retain cationic ions by electrostatic forces. The soil particles can also develop variable charges through gain or loss of protons from the functional groups ($-OH$, $-COOH$, or $-NH$) on particle surface during their reaction with ions in soil solution. The amount of such charge is usually pH dependent.

2.2 Diffused Double Layer in Clay

2.2.1 The Origin of Diffused Double Layer

Soil clay particles develop charges on their surfaces, but the soil media are always electrically neutral. The negative charges are balanced by adsorbing the ions of the opposite charge (counter-ions) in soil solution. Because the adsorbed ions have tendency to diffuse away from the clay surface due to concentration gradient but are electro-statically attracted by the negative charges (Figure 2.3), these adsorbed ions form a diffused layer close to the clay surface.

Figure 2.3 Diffused double layer (Mitchell 1993)

At the same time, the co-ions (ions have same charge as the surface) are repelled by the charged surface therefore have lower concentration in the diffused layer. The negatively charged surface and the distributed ions in the interface between soil solids and soil solution are collectively termed diffused double layer (Mitchell 1993). The double layer developed by soil particles gives rise to many interesting phenomena, such as electro-osmosis, and enable clayey soils to display many unique geophysical properties.

2.2.2 Theories of Double Layer

Over the years, different double layer models were proposed and developed. They include Gouy-Chapman theory, Stern theory, and a triple layer model which was developed in the 1970s (Yates et al. 1974; Davis and Leckie 1978). The detailed discussions on the first two models were presented by Mitchell (1993) and Grim (1962).

2.2.2.1 Poisson-Boltzmann Equation

The Boltzmann equation relates concentration of ions to the potential in an electric field. The concentration of an ion in a force field at equilibrium is given by

$$n_i = n_{io} \exp\left(\frac{-v_i e \psi}{kT}\right) \quad (2.1)$$

where n_i is the concentration of ions i in a force field expressed in ions/cm³, k : Boltzmann constant, T is temperature, v_i is ionic valence, e is unit electronic charge, ψ is electric potential.

The Poisson equation, which relates potential, charge, and distance, is

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{D} \quad (2.2)$$

where x is the distance from the surface, ρ is the charge density, and D is the dielectric constant of the solution.

Combining of the Poisson equation with Boltzmann equation and assuming single cation and anion species of equal valence gives the Poisson-Boltzmann equation:

$$\frac{d^2\psi}{dx^2} = \frac{8\pi n_0 v \epsilon}{D} \sinh \frac{v \epsilon \psi_o}{kT} \quad (2.3)$$

where ψ_o is surface potential (mV).

Since the term $\frac{v \epsilon \psi_o}{kT} \ll 1$ in the case where the surface potential is small (less than 25 mV), the above equation may be approximated by

$$\frac{d^2\psi}{dx^2} = K^2 \psi \quad (2.4)$$

$$\text{where } K^2 = \frac{8\pi n_0 \epsilon^2 v^2}{DkT} \quad (\text{cm}^{-2})$$

The thickness of the double layer is given by

$$\frac{1}{K} = \left(\frac{DkT}{8\pi n_0 \epsilon^2 v^2} \right)^{1/2} \quad (2.5)$$

2.2.2.2 Gouy-Chapman Theory

Based on Gouy-Chapman theory, the surface charge density σ_o and double layer thickness t (cm) are given as

$$\sigma_o = \left(\frac{2nDkT}{\pi} \right)^{1/2} \sinh \frac{v \epsilon}{2kT} \psi_o, \text{ and} \quad (2.6)$$

$$t = \left(\frac{DkT}{8\pi n v^2 \epsilon^2} \right)^{1/2} \quad (2.7)$$

The equations indicate that the thickness is inversely related to the valence and the square root of the ion concentration and is proportionate to square root of dielectric constant and temperature.

2.3 Electrokinetic Phenomenon

Electrokinetic phenomenon includes a series of electro-chemical processes which take place in soil solution when a voltage gradient is established across the soil. As

a result of the presence of an electric field, the charged particles, ions, and pore waters migrate towards the electrodes. Three mechanisms, namely electrophoresis, electromigration and electro-osmosis, are generally believed to cause the migrations.

2.3.1 Electrophoresis

Many clay particles, such as those from montmorillonite clay, occur as extremely small units in water. These fine clay particles and other colloids carry charges and suspend in soil solutions. Under the driving forces from an electric field, these charged particles and colloids swim towards one direction or the other depends on the charges they carry.

2.3.2 Electromigration

Ions, both cations and anions, are subjected to electrostatic forces under an established electric field. The cations are driven towards the cathode while anions are driven towards the anode. The mechanism that migrates the ions in soil solutions by electric field is called electromigration (Hamed et al. 1991).

An ion of charge number v_i , and mobility u_i migrate at an average velocity V_i , in a field of strength $d\Phi_e/dx$, according to

$$V_i = -\frac{|v_i|}{v_i} u_i \frac{d\Phi_e}{dx} \quad (2.8)$$

where $u_i = \frac{|v_i|FD_i}{RT}$ according to Nernst-Einstien law, and D_i is the diffusion coefficient.

The movement of ions by electromigration is faster under larger voltage gradient, which means bigger field strength. The rates of ion movement are also affected by soil tortuosity, the transference number, and permeability of the soils (Acar and Alshawabkeh 1993).

2.3.3 Electroosmosis

As described in the previous sections, the concentration of count-ions (such as metal cations) is higher than the concentration of the co-ions (such as Cl^- and NO_3^-) in the diffused layer. As a result, the thin layer has net positive charges. When electric field drives the cations and ions in the soil solution by electrostatic forces, the water molecules are dragged by the migrating ions due to friction. Since there are more cations than anions in the thin layer, the pore water in the thin layer has an over movement towards the cathode (Figure 2.4).

Furthermore, in capillaries with diameter small enough, which is typical in clayey soils, the thin layer at the side of a capillary exert shear forces to the pore water in capillary and push it to flow in the same direction as the movement of pore water in the thin layer. Electroosmosis is the phenomenon where pore water in clayey soils is slowly dissipated under the influence of an electric field.

Figure 2.4 Electroosmotic flow in clay capillary

Electro-osmosis is a coupled flow and the flow rate is practically given by

$$q = vA = k_e i_e A \quad (2.9)$$

where q is the electro-osmosis flow rate, k_e is the coefficient of electro-osmotic permeability, i_e is the electric potential gradient, and A is the total cross sectional area norm to the direction of flow.

The coefficient of electro-osmotic permeability is analogous to the hydraulic conductivity. It is a soil property and represents the pore water flow velocity under a unit electric potential gradient. Typical values for soil with fresh water permeant are listed in the Table 2.1. The table suggests that the voltage gradient is more efficient in moving water through saturated clayey soils than a hydraulic gradient.

Table 2.1 Coefficient of electro-osmotic permeability of various soils (Mitchell 1993)

Material	Water content (%)	k_e in 10^{-6} (cm ² /sec-V)	Approximate k_h (cm/sec)
London clay	52.3	5.8	10^{-8}
Boston blue clay	50.8	5.1	10^{-8}
Kaolin	67.7	5.7	10^{-7}
Clayey silt	31.7	5.0	10^{-6}
Rock flour	27.2	4.5	10^{-7}
Mica power	49.7	6.9	10^{-5}
Fine sand	26.0	4.1	10^{-4}
Quartz power	23.5	4.3	10^{-4}

The rate of electro-osmosis flow depends on soil properties, especially the zeta potential, salinity and particle size, as well as the applied voltage gradient. Theories were developed to explain electro-osmosis and provide basis for quantitative prediction of the flow rates.

Helmholtz-Smoluchowski Theory

The theory was based on a model introduced by Helmholtz (1879) and later refined by Smoluchowski (1914). It is one of the earliest and still widely used theoretical descriptions of electro-osmosis phenomena. The charges and ions distribution in a liquid filled capillary is assumed to like in Figure 2.4. The balance of the electrical forces and the friction between the liquid and the wall governs the rate of flow. The velocity gradient between the wall and the center of the positive charges is $\frac{v}{\delta}$, and the drag force per unit area is

$$\eta \frac{dv}{dx} = \eta \frac{dv}{d\delta} = \sigma \frac{\Delta E}{\Delta L} \quad (2.10)$$

where v is the velocity at a distance δ to the wall surface, η is the viscosity, σ is the surface charge density, and $\frac{\Delta E}{\Delta L}$ is the electric potential gradient.

When zeta potential ξ is taken as $\frac{4\pi\sigma\delta}{D}$, the equation can be rewrite as

$$v = \left(\frac{\xi D}{4\pi\eta} \right) \frac{\Delta E}{\Delta L} \quad (2.11)$$

Thus the electro-osmosis flow rate for a total cross sectional area A with porosity n is:

$$q = \left(\frac{\xi D}{4\pi\eta} \right) n \frac{\Delta E}{\Delta L} A \quad (2.12)$$

By analogy with the previous equation for electro-osmosis flow rate and $i_e = \frac{\Delta E}{\Delta L}$,

$$k_e = \frac{\xi D}{4\pi\eta} n \quad (2.13)$$

Unlike the hydraulic conductivity k_h , which is dependent on the pore size, the coefficient of electro-osmotic permeability is independent of pore size. It is related to the porosity, zeta potential, and dielectric constant of the solution.

Schmid Model

Unlike the Helmholtz-Smoluchowski theory, the Schmid model was developed for small pore size (less than 1000Å). It also accounts for the ions in the solution in excess of those needed to balance the surface charges, and assumes a uniform distribution of counter-ions as shown in Figure 2.5. The resulting equation for the flow is

$$Q = \frac{A_o F r^2 n}{8\eta} \left(- \frac{\Delta E}{\Delta L} \right) A \quad (2.14)$$

where Q is total flow (m^3/s); A_o is the concentration of surface charge; r is the radius of capillary; and F is the Faraday's constant (C/equivalent).

Figure 2.5 Soil capillary in Schmid's model (Mitchell 1993)

2.4 Electric Fields in Soils

2.4.1 Electric Fields of Point Charges

The magnitude of the electric field at a point generated by a charge q at distance r away can be calculated using Coulomb's law:

$$E = \frac{F}{q} = \frac{1}{4\pi\epsilon_o} \frac{q}{r^2} \tag{2.15}$$

Figure 2.6 Lines of forces from two positive charges (a) and a positive and negative charge (b)

And the combined electric field at certain point generated by multiple charges is just the vector sum or superposition of the fields generated at that point by individual charges. The direction of electric field at any point is given by the lines of forces (lines of electric field). Typical lines of forces originate from positive charges and terminate on negative charges. Figure 2.6 show the lines of forces of two charges at certain distance to each other.

2.4.2 Electric Potential in Electric Fields

The potential at any arbitrary point P can be calculated using

$$V_p = - \int_{\infty}^p E \cdot ds \quad (2.16)$$

To visualize the electric field, a family of surfaces can be drawn by connecting points having the same value of electric potential. These surfaces are called equipotential surfaces. The equipotential surfaces of a point charges are a series of concentric spheres while those of a uniform electric field are a family of parallel planes.

2.4.3 Capacitors and Dielectrics

A simple capacitor can be formed by placing two charged metal plates close to each other while both are isolated from their surroundings. A generalized capacitor can consist of two arbitrary shaped conductors. In a parallel-plate capacitor, the plates

Figure 2.7 Electric field in a parallel-plate capacitor

are assumed to be so large and are placed so close that the electric field E in between the plate can be assumed constant and uniform as shown in Figure 2.7.

The charge q and capacity for such a capacitor are given by

$$q = CV \quad (2.17)$$

$$C = D\epsilon_o \frac{A}{d} \quad (2.18)$$

where V is voltage drop across the capacitor, C is the capacity of the capacitor, A is the area of the plates, d is the separation of the plates, and D is the dielectric constant of the material present between the plates.

Dielectric constant is a fundamental property of a dielectric material and is independent of the size or shape. More polar materials have higher dielectric constant while a very low dielectric constant indicating a nonpolar material or a material that is very hard to be polarized. Dielectric constant of vacuum is defined to be unity. Air has dielectric constant close to 1, and for water is roughly 80. With the same voltage drop across a capacitor, stronger electric field will be generated if the space of the capacitor is filled with a medium of higher dielectric constant.

In electrokinetic soil remediation, a capacitor is formed when two conductive plates, such as graphite plates, are at a distance from each other and separately connected to the anode and cathode of a DC power source. With soil filling the space between the plates, the capacity of this capacitor and the field strength in the soil are related to the voltage drop across the capacitor, the area of the plates, and the dielectric constant of the soil. The electric field generated in the soil can be assumed uniform when the separating distance is relatively small and the plate has relatively large area.

2.4.4 Soil Dielectric Constant

Soils are mixtures of soil solids and soil liquid. The dielectric constants of soils are strongly related to their moisture content. The dry soil has the lowest dielectric constant (less than 4) and the value increases as moisture content increases. Besides

water content, temperature of the soil matrix can also affect dielectric constant, especially in the range of a few degrees near freezing point (Wang and Schmugge 1980; Dobson et al. 1985; Ulaby et al. 1986; Hallikainen et al. 1985).

For different type of soils of known constituent and moisture content, the dielectric constant can be estimated through empirical models and charts are available. Even if the electrodes in the soil are assumed as parallel-plates, the electric field distribution in the soil would not be uniform unless the dielectric constant of the soil is homogeneous.

2.4.5 Effects of Dielectrophoresis

Neutral matters (uncharged matters) can be made to move in an electric field by dielectrophoretic forces where the field intensity is nonuniform, such as the field shown in Figure 2.6. Dielectrophoresis is the translational movement of neutral objects caused by polarization effects in a nonuniform electric field. A comprehensive work on dielectrophoresis was provided by Pohl (1978).

As a result of polarization, positive charges are induced on the side of the particle where electric field potential is lower (or near the cathode) while negative charges are induced on the opposite side (or near to the anode). For a neutral particle, the induced positive charges and negative charges are equal. The applied electric field then exerts forces to these charges and a net force is resulted as the field is nonuniform across the two ends of the particle. When the particle has higher dielectric constant than the surrounding medium, it moves toward the region where electric field is stronger. This phenomenon is called *paraelectric* effect or “Positive Dielectrophoresis”. The exceptions to the usual *paraelectric* field where particles are repelled from the region of stronger field are called *apoelectric* effects or “Negative Dielectrophoresis”.

2.4.5.1 Dielectrophoretic Force on Ideal Dielectrics

The net electric force F by a static electric field E on an isotropically, linearly and homogeneously polarizable neutral body can be shown to be

$$F = \alpha \nabla (E \cdot \nabla) E = \frac{1}{2} \alpha \nabla |E|^2 \quad (2.19)$$

where ∇ is the del vector, α is the polarizability or dipole moment per unit volume in unit field, and v is the volume of the body.

For a small spherical particle of relative dielectric constant K_2 in an ideal fluid of relative dielectric constant K_1 in which an electric field E is present, the force is given by

$$F = \frac{3}{2} (\text{volume}) \epsilon_1 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} \right) \nabla |E|^2 \quad (2.20)$$

where ϵ_1 and ϵ_2 are absolute permittivity of the medium and particle, respectively.

2.4.5.2 The Bunching Effects and Pear-Chain Formation

With an external electric field, particles of high dielectric constant suspended in a medium that has lower dielectric constant undergo dielectrophoresis. The suspended particles often observed to clump or bunch together, as a result of mutual *dielectrophoresis*, even the external field is uniform. The initially uniform field in the medium is distorted due to the presence of these polarizable particles. Each particle then experiences a nonuniform field near the other and is attracted to the region of higher field intensity close to each other. The resulted clumped particles further enhance the field nonuniformity and eventually form ‘pearl chains’ or other clusters the medium. It is often found that the association of suspended particles by the bunching effect enhances the separation of the particles and the medium. Dielectrophoresis in many cases is actually more effective than predicted by simple theoretical calculations.

2.4.5.3 Dielectrophoresis in Weakly Conducting Materials

Since all materials conduct current to some extent, the actual response observed for particles can be different from what is predicted for ideal insulating dielectrics especially when the high voltage or high frequency is used. With free ions in pore water, the soil water can conduct current and the dielectrophoretic behavior of these particles can be difficult to predict.

Charges (both positive and negative) in a liquid medium are flowing when the liquid conducts current. The charges are free to hit and adhere to the particles that are neutral in the liquid medium. It is expected that equal amount of positive and negative charges will be deposited on the opposite faces of the particle. The deposited charges give rise to a current-induced dipole that is opposite to the originally field-induced. The induced charges on the particle will continue to attract nearby flowing ions that carry opposite charge until the accumulated charges on the particle neutralize the initially induced charges. Additional ions adhered on the surface give rise to a repelling force to the incoming ions. The polarization originally induced will eventually reverse and causing a reversed dielectrophoretic motion.

Furthermore, other abnormal effects were often reported when dealing with electrolyte media as well as colloidal suspension. It is believed that surface and/or interfacial (such as electric double layer) polarization might increase the effective dielectric constants of an aqueous suspension hundreds of times higher than the measured bulk dielectric constant (Pohl 1978).

2.4.5.4 Dielectrophoresis as a Dewatering Technology

In the 1980s, dielectrophoresis was applied in geotechnical engineering to consolidate clays (Inculet and Lo 1988). Clay pore water can be dissipated from clay in a nonuniform field because pore water and clay solids have different dielectric constants. Lo and Shang (1994) investigated the effects of intervening media on the strengthening of soft clay by dielectrophoresis. Shang and Lo (1997) studied the dewatering of phosphate clay by the combination of dielectrophoresis and electrokinetics. The theoretic aspects of dielectrophoresis in clay-water-electrolyte were developed by Lo et al. (1993).

2.4.6 Electric Fields of Different Electrodes Configurations

A uniform and constant electric field is very difficult to establish in media such as natural soils due to the heterogeneity of its composition and moisture content over the bulk of volume. However, approximately uniform electric fields are possible

when the electrodes have relatively large area and the space is filled with small volume of well prepared soil.

Most laboratory scale experiments carried out assumed condition of one dimensional constant electric field (Hamed et al. 1991; Acar et al. 1992; Segall and Bruell 1992; Acar and Alshawabkeh 1993; Shapiro and Probstein 1993; Chung and Kang 1999). The electrodes usually consist of plate shaped inert material (such as graphite and platinum coated steel) spaced over a relative small distance. The soil specimens were usually put in a cylindrical column with the electrodes at the ends. The voltage gradients were taken as the strength of the electric fields in the soil.

A few researchers have used larger specimen volume using rows of rode-shaped electrodes with rectangular container (Bruell and Segall 1992; Acar and Alshawabkeh 1996). Other investigators attempted small field tests using steel plates and wicks filled with activated carbon as electrodes spaced up to 3 meters apart (Ho et al. 1995, 1999a), relatively large distance of 6.3 meter was also investigated in a field test (Ho et al. 1999b). These studies reported reasonably uniform voltage distribution in the tested soil at early stage of the electrokinetic process, but the voltage drop near the cathode region built up after certain duration as the part of soil were slowly dried and consolidated, the raised temperature also gave rise to localized higher electric resistance. Despite the process-induced heterogeneity, overall one-dimensional electric fields were assumed.

A two-dimensional laboratory model was developed by Segall and Bruell (1992) using a 61 cm x 61 cm x 20 cm box of kaolin. Copper wires were inserted as electrodes in this experiment. The results were illustrated in the Figure 2.8 (the solid lines in the figure are equipotential lines).

Figure 2.8 Electric fields with electrodes of different configuration (Segall and Bruell 1992)

Segall and Bruell reported that the electric field varied significantly in different locations when there were only one or two pairs of point electrodes. As there were more and more pairs of electrodes and spacing between each pair getting closer, the electric fields were more and more uniform. The voltage contours in (d) of the Figure 2.11 suggests that a fairly uniform field distribution can be achieved with anode to cathode distance of $2a$ while pair to pair distance of not more than $0.75a$. This approximately uniform distribution is the result of the electric field generated by each pair superimposes on the neighboring pairs.

Ho et al. (1995, 1997) reported the use of layers of granular carbon as electrodes to produce horizontal or vertical one-dimensional electric fields. Murdoch and Chen (1997) studied the in-situ electroosmosis with horizontal graphite filled disk-shaped electrodes created by hydraulic fracturing (Figure 2.9). They reported that the gradient in the electric potential is roughly uniform between the fractures and decrease markedly beyond the radial extent (Figure 2.9).

Figure 2.9 Hydraulic fractures electrodes (a) and Electric field potential (b) (Murdoch and Chen 1997)

A study on the distribution of electric fields from different electrode lay out assumed that the electric fields in the soil do not penetrate insulating boundaries or the soil-air interface (Rasmussen and Budhu 1996). The electric fields were believed to be reflected back and superpose on the original field in the soil when encountering such a boundary.

2.5 Electrokinetic Soil Remediation Processes

2.5.1 Physicochemical Processes in Soils

Contaminants undergo many physicochemical processes in response to the changes in their surrounding conditions in soils. In electrokinetics soil remediation, the processes induced by applying an electric field to the soil are electrolysis, sorption/desorption, precipitation/dissolution, and oxidation/reduction.

2.5.1.1 Electrolysis Reactions

The applied direct current through the anode and cathode immersed in water causes the electrolysis of water in the immediate vicinity of the electrodes (Hamed et al 1991). Water is oxidized at anode to generate H^+ and oxygen gas (O_2) and is reduced at cathode producing OH^- and hydrogen gas (H_2) by the following reactions,

The rate of H^+ generation is governed by the current. The actual reactions occur at electrodes during electrokinetic process are more complicated and are depend on the material of the electrodes as well as the ions/compounds in soil solution.

The acid generated at the anode will advance through the soil towards the cathode due to different mechanisms including electromigration, electroosmosis, and chemical diffusion. The alkaline medium produced at the cathode will initially advance towards the anode due to electromigration and diffusion. As the advance of this front is retarded by the counter-flow due to electroosmosis and hydroxyl ions have a much smaller mobility than hydrogen ions, the chemistry across the soil is dominated by the acid front (Acar and Alshawabkeh 1993).

2.5.1.2 Adsorption and Desorption

The soil clay particles are generally negatively charged in natural condition. The cationic ions in the soil solution are attached to the clay surface through various physical/chemical processes which are collective called adsorption. The adsorbed

metal ions are fixed to a certain extent to the soil particles depending on the exact mechanism. These metal ions can form either inner-sphere surface complex or outer-sphere surface complex with particle surfaces, or held loosely in the diffusion swarm at the interface of soil solution and soil particle.

Metal ions forming outer-sphere complex or held in the diffuse layer are considered to be non-specifically adsorbed. This kind of adsorption is usually rapid and largely reversible as they are only retained by electrostatic forces. The metal ions under non-specific adsorption are exchangeable. The specific adsorption involves forming inner-sphere complex with soil surface functional groups. The metal ions in this case are strongly held by ionic or covalent bonds. The adsorbed ions can hardly move from a surface site to another and are not easily removed from the surface.

In electrokinetic soil remediation, the hydrogen ions generated at the anode electrode cause the pH of the soil close to the anode to decrease forming an acidic medium. As the acid front migrates toward the cathode, it encounters soil at different locations and enhances the desorption and dissolution of metal ions from the soil particles. The extent of this mechanism was shown to be very crucial for the contaminants removal from soils (Puppala et al. 1997; Virkutyte et al. 2002; Darmawan and Wada 2002).

2.5.1.3 Precipitation/Dissolution

The precipitation and dissolution patterns of metal ions are highly pH dependant. They tend to precipitate as their hydroxides at a high pH and these hydroxides will then dissolve into metal ions when pH becomes low. The electrokinetic process, the acidic condition near the anode favors the dissolution of metal precipitates and oxides, while the base condition near the cathode can precipitate the metal ions in the soil solution.

2.5.1.4 Oxidation/Reduction

The speciation of metals in soil solution is also sensitive to redox condition. Some metals can exist in different valence state under different redox conditions (Reddy

et al. 2001; Reddy and Chinthamreddy 2003). Chromium is less mobile in trivalent state than in hexavalent state under a wide range of pH. Metalloid contaminants, such as arsenic, impose different environmental concern when they exist in different oxidation state. The arsenite, As (III), is more soluble, more mobile and more toxic than arsenate, As (V). The arsenic in different valence state also has different adsorption characteristics in soils (Lin and Puls 2000). The arsenic ions of different valence state could also migrate in different directions in an electric field.

2.5.2 Heavy Metal Speciation and Migration

Heavy metals in soil undergo many complicated physicochemical processes. At any given time, their forms and movements in the soil are controlled by various mechanisms. The sequential extraction technique is widely used to extract different fractions of metals present in soil using chemical reagents by following a certain procedure. It has been used to analyse various contaminated soils and sediments, and was found to have high reproducibility (Tessier et al. 1979; Chang et al. 1984; Clevenger 1990; Yong et al. 1993). The operationally defined fractions of metals in soils are listed below.

1. Exchangeable fraction

Metals exist as exchangeable ions and considered to be non-specifically adsorbed by soil particles such that they can be replaced by competing ions. The soil solids found to retain metals in this manner are clay minerals, organic materials, and amorphous materials.

2. Carbonate fraction

Metals in this fraction exist as precipitated or co-precipitated carbonate. This fraction of metal is sensitive to pH change and can be released by application of acids.

3. Oxide fraction

Metals that attach to amorphous Fe, Al, and Mn oxides belong to this fraction. The oxides formation is related to the redox condition in the soil solution. The metals in this fraction can be released under reducing condition.

4. Organic fraction

The metals considered here are those metals bind in association with organic matter through various mechanisms including complexation, adsorption, and chelating. The bind metals will be released once the organic matter is degraded under oxidizing condition.

5. Residual fraction

Metals in this fraction are generally believed to exist within the lattices of silicate minerals. The metals are very stable under the protection of the mineral crystal structure, and they are unlikely to be released under any of the conditions found in naturally occurring soils.

The speciation of a heavy metal in soils is highly dependent on the soil mineralogy, pH, and the type as well as the valence of the metal (Yong et al. 1993; Reddy et al. 2001; Darmawan and Wada 2002). In electrokinetic soil remediation, the exchangeable and carbonate fractions are generally more mobile and easier to remove than the other fractions. Depending on the buffer capacity of the soil, the advance of the acid front from anode to cathode reduces the pH of the soil and changes the distribution of metals among the fractions. The heavy metals near the anode tend to present as soluble and exchangeable fractions and migrate towards the cathode. The heavy metals at cathode, however, tend to precipitate due to high pH condition if no enhancement scheme is applied.

2.5.3 Organic Contaminants in Soil

Organic contaminants in the unsaturated zone exist in four phases: vapor in the pore spaces; sorbed to soil solids; dissolved in soil water; or as NAPL (non-aqueous phase liquid). Depending on its density, NAPL is divided into LNAPL (light non-aqueous phase liquid) and DNAPL (dense non-aqueous phase liquid). The nature and extent of organic contaminants migration in soil are determined by firstly their

physical/chemical properties such as density, vapor pressure, viscosity, and hydrophobicity. And secondly by the subsurface environment such as geology, aquifer mineralogy, soil microbiology and ground water hydrology.

2.6 Background of Electrokinetics Remediation

Electro-osmosis was first applied to dewater fine-grained soils by Casagrande (1949). The commercial application of this technology was then extended to stabilize soils under buildings and foundations (Zhinkin et al. 1965). Casagrande et al. (1983) later used electro-osmosis to stabilize slopes. Segal et al. (1980) studied the effluent from an electrokinetic experiment and find presence of Fe (III) and organic matters from the soil.

Many studies were since carried out to study the feasibility of using electrokinetics to extract contaminants, both organic and inorganic, from soils. This technology was also used in conjunction with other remediation technologies such as bioremediation, chelating agent and surfactances enhanced desorption to achieve better results. The comprehensive reviews of the past developments and status of the technology were presented by Virkutyte et al (2002) and Page and Page (2002).

2.6.1 Field Scale Studies

Lageman (1993) conducted a series of electrokinetic field tests in three sites that contain various heavy metals. The heavy metal removal in the first site was 80% for copper and 70% for lead in 43 days at an energy consumption of 65 kWh/m³. The concentration of zinc in the second site was reduced from 2410 ppm to 1620 ppm by using current density of 8 A/m² of soil and potential drop of 20-40 V/m. They found the soil resistivity decreased from 5 ohm per meter at beginning to 2.5 ohm per meter in two weeks. After 65 days of treatment, the arsenic concentration in three-quarters of the third site was reduced to 30 ppm with an average current strength of 4 A/m². A temperature rise from 7°C to 50°C was detected.

Ho et al. (1995) used 'Lasagna' to name his new electrokinetic remediation technology that involves creating treatment zones in contaminated soils. The

contaminants were transported back and forth by electrokinetics through the treatment zones where they were trapped and removed. A small field test and a big field test were later conducted to remove TCE from soil using the Lasagna technology (Ho et al. 1999a and Ho et al. 1999b). The small field test was reported to reduce TCE concentration in the soil to below 1 mg/kg and remove an overall 98.4% of TCE from the soil. In the large scale field test, iron fillings were used in the treatment zones to degrade TCE in-situ. The reported treatment period was 160 days and peak core temperature at center of the soil mass (hottest spot) was found be over 80°C. They concluded that the elevated temperature caused an increase in the TCE degradation with iron filings and resulted in accelerated TCE removal from the soil by electro-osmosis due to faster diffusion and dissolution of TCE in water. The TCE removal achieved in the full scale field test ranged from 95% to 98%.

The field scale studies are summarizes in Table 2.2.

Table 2.2 Field scale studies conducted using electrokinetics

References	Contaminants	Treatment duration	Initial concentration (ppm)	Removal efficiency (%)	Energy consumption/ cost
Lageman (1993)	Pb	43 days	300-5000	70-80	65 kWh/m ³
Lageman (1993)	Cu	43 days	500-1000	70-80	65 kWh/m ³
Lageman (1993)	Zn	8 weeks	2410	33	160 kWh/ton
Lageman (1993)	As	65 days	400-500	92-94	Not Available
Ho et al. (1999)	TCE	4 month	1-500	98	Not Available
Ho et al. (1999)	TCE	1 year	1-1500	95-99	\$80/yard ³

2.6.2 Laboratory Scale Studies

Runnells and Larson (1986) conducted laboratory scale experiments to remove Cu (II) from soil by electrokinetics. The reported removal efficiencies were ranged from 80% to 85%. However, they found that most of the extracted copper was transported from the region near the anode to the region near the cathode, and subsequently precipitated as Cu(OH)₂ due to the high pH condition near the cathode.

Lageman et al. (1989) investigated the electro-reclamation of different type of soils namely argillaceous sand and river mud contaminated with Pb (II), Cr (VI), Cd (II), and As. The energy consumption for the first type of soil was 30 kWh/ton of contaminated soil and the overall removing efficiency was 83%. For the second type of soil, the energy consumption was 100 kWh/ton of contaminated soil and an average 69% removal of the overall contaminants was achieved.

Hamed et al. (1991) studied electrokinetic removal of Pb (II) from Georgia kaolinite spiked by Pb (II) to a concentration of 145 µg/g clay. Their experimental results indicated there was no flow in the first 20 hours. The flow rate after the 20 hours increased rapidly and eventually decreased with time. They believed that the lack of saturation contributed to the absence of flow in the first 20 hours and the movement of acid front resulted the decrease of flow over the time period they observed. The strong acid condition in the region near the anode changed the soil particle surface charge and reversed the sign of zeta potential, causing the flow to decrease or even change direction. The results showed that 75-95% of the absorbed Pb (II) was removed. The reported power consumption was about 29-60 kWh/m³ of soil.

Segal and Bruell (1992) studied the removal of contaminants from saturated clay by one-dimensional and two-dimensional electro-kinetic extractions. The effects of pore water salinity and electrode material were also investigated. The soils used in the study were kaolin and a mixture of kaolin, glacial till and sand. Their findings from the experiments were as follows:

- 1) The saturated clay behaved as an electrochemical cell;
- 2) Electro-osmotic conductivity was proportional to soil porosity,
- 3) Increasing salinity had little effect on average flow rate but increased power consumption and gas generation;
- 4) Iron electrodes generated more hydrogen gas and larger flow rate than graphite electrode while the power consumption was the same; and
- 5) Electro-osmosis was showed to be effective in nitrogen transport, while the efficiency of transporting phosphates was very little.

They also concluded that the results of one-dimensional test could be used to predicate the results of three-dimensional systems.

Bruell and Segall (1992) performed laboratory scale experiments to investigate the feasibility of organic contaminants extraction by electrokinetics. Kaolin spiked by various organic substances including benzene, toluene, trichloroethylene (TCE), m-xylene, hexane, and isooctane was treated by electric gradient for certain durations. They confirmed that electro-osmosis behaved as hydraulic head in contaminant transport in kaolinite. And their results indicated that organic contaminants with high water solubility and low distribution coefficient (BTEX compounds, TCE, etc.) were easily removed from kaolin by electro-osmosis. However, chemicals with a low water solubility and high distribution coefficient such as hexane and isooctane were transported at a slower rate.

Acar et al. (1992) conducted laboratory tests to evaluate the feasibility of using electro-kinetic method to treat kaolinite contaminated by phenol. They hypothesized that the acid front generated at the anode will eventually reach the cathode and neutralized the base media produced by water electrolysis reactions. Their results showed that 85% to 95% of the phenol was removed from the kaolinite. The adsorbed phenol was efficiently extracted by electro-kinetic method. In addition they found that the soil electric conductivity, k_e and k_i value of the soil were decreased with time.

Shapiro and Probstein (1993) conducted experiments to investigate the effectiveness of removing organic compounds such as acetic acid and phenol from saturated clays using electrokinetic extraction. In their study, a numerical model to predict the cleanup and pH gradient was also developed. They found that the pH of the purging solution has a profound influence on the electro-osmotic flow. The experimental results indicated that the removal rate for phenol was 95%. They attributed the removal to electro-osmotic advection, ionic migration, chemical equilibrium, and electrochemical reactions.

Acar and Alshawabkeh (1993) summarized the theoretical background of electrokinetic technology and suggested some important aspects of this technology that affects the removal efficiency:

- 1) Electromigration is the major transport mechanism and plays important role in cleanup ionic contaminants,
- 2) The transference number is a function of ionic mobility and ionic concentration. The transport efficiencies of species under electric field largely depend on their transference numbers, and
- 3) The chemistry at the electrodes, especially the cathode, affects the cleanup of reactive contaminants. The heavy metals are accumulated in the region near the cathode by adsorption and precipitation due to the strong alkaline condition near the cathode. Use weak acid, such as acetic acid, to depolarize the cathode reactions can be an effective way to prevent hydroxyl ions from entering the soil.

Acar et al. (1994) investigated the removal of Cd (II) from kaolinite by electrokinetic extraction. Their results indicated that the samples with lower pH prior test achieved higher removal rate. And the higher removal rate was caused by electromigration rather than electro-osmosis. It was reported that up to 95% of the Cd (II) was removed from the kaolinite.

Hicks and Tondorf (1994) studied Zn removal from Georgia kaolin and developed mathematic model to simulate the electrokinetic extraction process and determine the optimum operation condition. Their study led to following conclusions:

- 1) The heavy metal extraction can be significantly affected by the naturally occurring matter and co-disposed substance,
- 2) The heavy metal speciation in complex aqueous mixtures can be determined by the equilibrium models, and can serve as guide to determine the optimum conditions, and
- 3) Isoelectric focusing can be prevented by rinsing away the hydroxyl ions generated at the cathode. Both experiment and the model showed more than 95% of the Zn was removal when rinsing was used.

Rødsand et al. (1995) conducted electrokinetic experiments on Pb (II) spiked (at 5000 mg/kg) Norwegian marine clay. They studied the effectiveness of different enhancement schemes including using acetic acid as depolarizing agent and using

ion selective membrane to prevent hydroxyl ion from moving into the specimen. The results of the experiments with no enhancement schemes showed that 40% of the total Pb (II) accumulated near the last 1cm of the specimen (cathode end). The same accumulation was found in experiments which used ion selective membrane. However, the amount accumulated near the last 1cm of specimen was only 8% when acetic acid was used to depolarizing the cathode reactions. They concluded that the extent of depolarizing using acetic acid had large impact on the cleanup efficiency.

Puppala et al. (1997) conducted experiments to determine the feasibility of treating soil with high buffer capacity by applying different enhancement methods. The soils used for this study were a mixture of illitic (40%), kaolinite (8%), Na-Montmorillonite (5%), and fine sand (47%). The two enhancement methods included using acetic acid to neutralize the cathode reactions and using ion selective membrane to prevent back-migration of hydroxyl ions at cathode. The reported experiment duration for certain batch was as long as 2400 hours due to very slow acid front formation in high buffer capacity soil. Their results showed that better removal efficiency was achieved compare to unenhanced tests. They found that the high buffer capacity soil required longer duration and higher energy expenditure than kaolinite. They concluded that it was feasible to extract metals from high sorption capacity soils.

Chung and Kang (1999) studied electrokinetic decontamination of lead spiked marine clay under laboratory conditions. They found that the efficiency of heavy metal removal from the contaminated soil increased with increases in treatment duration, the applied electrical current and the initial lead concentration. They found that electro-osmotic flow was larger at low Pb (II) concentrations was smaller at higher concentrations. They believed that the high concentration level had caused a less negative zeta potential which lead to reduction in electro-osmosis flow. Their experimental results showed that the electrical potential gradients across the electrodes increased with the increase in the operating duration and applied current, but decreased with the increase of lead concentration. The electric potential difference was found to decrease when nitric acid, acetic acid and ethylene di-amine

was introduced in the soil specimen as enhancement chemicals. They attributed the increase of electrical potential in the tests to the formation of a lead hydroxide which reduced ionic strength and soil pore space. All the tests with enhancement showed removal efficiency above 88%. They concluded that the enhancement chemicals used were efficient in removing lead from the soil.

Lee and Yang (2000) investigated the effect of controlling the pH at anode and cathode by circulating the anode electrolyte to cathode and then from cathode back to anode. Pb (II) spiked kaolinite was treated at a constant current of 0.46 mA/cm^2 for duration ranged from 22 days to 34 days. It was reported that the anode electrolyte pH could be increased to 4-6 and cathode electrolyte could be decreased to 6-8 with appropriate circulation rate. The removal efficient was reported to be 25.5-67.5%.

Li and Li (2000) studied the removal of Pb (II) using an electrokinetic system that had a layer that was continuously flushed with nitric acid at pH 3 near the cathode region and two reservoirs with 0.4 M NaOAc at pH 3.8 and acetic acid at pH 4 flushing the anode and cathode, respectively. It was reported that the system removed some 80% of Pb (II) from illite after 98 days of treatment. It was concluded that electrokinetic remediation was successful in soil with viable charge minerals like kaolinite, but it had difficulty with constant charge mineral such as carbonate-rich illite soils.

Reddy et al. (2001) studied heavy metal speciation and extent of migration in two different soils during electrokinetic extraction. The two soils, kaolin and glacial till were spiked by a mixture of either Cr (III) or Cr (VI), Ni (II) and Cd (II) at different concentrations and treated with voltage gradient of 1V/cm for over 200 hours. Sequential extraction analysis was performed on the contaminated soils before and after the treatment to provide information of the metal distribution and speciation. They noticed that the applied electric field transported Cr (VI) toward the anode, but transported Cr (III), Ni (II), and Cd (II) toward the cathode. They found considerably less soluble and exchangeable fractions of Cr, Ni, and Cd in glacial till than in kaolin. They also found that soluble and exchangeable fraction of these

metals in both soils were higher when Cr (VI) was included than in the case where Cr (III) was present. The results indicated that the contaminants existed in immobile fractions had low migration rates in both kaolin and glacial till. Based on the experiments, they drew these conclusions:

- 1) The initial speciation of contaminants affected the extent of migration under electrokinetics. Higher rates of contaminants migration occurred when the contaminants were in exchangeable form. The retardation of contaminants migration could be attributed to the presence of precipitates and complexes, and
- 2) Electrokinetic treatment significantly reduced the soluble and exchangeable fraction of contaminants in soils. However, the treatment had little effects on the contaminants existed in immobile complexes and precipitates.

Virkutyte et al. (2002) reviewed electrokinetic soil remediation and summarized the theoretical background and the past studies conducted in this field. They listed the drawbacks of electrokinetics as:

- 1) The process is highly dependant on acidic conditions which favors the release of the heavy metal contaminants into the solution phase. However, it can be very difficult to achieve acidic conditions in the soils possessing buffering capacity. In addition, acidification of soils may not be an environmentally acceptable approach,
- 2) The electrokinetic remediation can be a very time-consuming process. The overall treatment time may range from several days to a few years, and
- 3) The process can be affected by heterogeneity or anomalies found at sites, such as metal objects of certain size, large quantities iron or iron oxides, large rocks or gravel.

Nevertheless, they also concluded the advantages of electrokinetics as:

- 1) It is very targetable and can be applied in specified locations,
- 2) It can treat contaminants in-situ and avoid excavation,
- 3) It is most effective in clayey soils which have low hydraulic conductivity,
- 4) It has potential to treat both saturated and unsaturated soils,
- 5) It can treat both organic and inorganic contaminants, and

- 6) It is cost effective in many cases.

Saichek and Reddy (2003) investigated the removal of phenanthrene from kaolin by electrokinetic treatment. Phenanthrene was spiked into kaolin at a concentration of 500 ppm and the soil was treated with constant voltage gradient of 1 VDC/cm for durations up to 60 days. It was reported that the pH control and the subsequent changes in the soil and/or solution chemistry caused the overall removal efficiency to be very low.

Table 2.3 shows the comparison of some studies closely related to this research. Besides the studies listed above, many other studies was carried out to investigate various aspects of electrokinetic soil remediation (Acar et al. 1990; Jacobs et al; 1994; West et al. 1995; Acar and Alshawabkeh 1996; Alshawabkeh and Acar 1996; Murdoch and Chen 1997; Ho et al. 1997; Sah and Chen 1998; Alshawabkeh et al. 1999; Darmawan and Wada 2002; Reddy and Chinthamreddy 2003). It appears that most of the laboratory studies that yielded high removal efficiencies were conducted on commercial clay, such as kaolinite. These synthetically prepared/spiked soils have more or less uniform physicochemical properties. The results may not readily applicable to naturally occurring soils because the speciation and affinity of contaminants to the soil substances may be very different from those found in the synthetically prepared soils.

Electrokinetic remediation was generally reported to faces problems when it is applied in soils of high buffer capacity such as carbonate-rich illitic soil, humic-allophanic and allophonic soils. It usually requires significantly more energy and time to treat these soils than low buffer capacity soils like kaolin.

The reported energy consumption for total removal of heavy metals from contaminated soil was round 500 kWh/m³. Energy consumptions ranged from 18 to 4000 kWh/m³ were reported in other studies (Table 2.3). Lower energy expenditure can be achieved when cathode depolarization is used (Acar and Alshawabkeh 1996).

Table 2.3 Past studies related to this research

References	Soil type	Contaminants	Initial pH	Initial concentration	Current density/voltage	Duration (days)	Removal (%)	Energy kWh/m ³
Hamed et al. (1991)	Kaolinite	Pb	4.7-5.0	100-1064 mg/kg	0.012-0.123 mA/cm ²	4-52	75-95	29-60
Acar et al. (1992)	Kaolinite	Phenol	4.5-4.8	500 mg/kg	0.037 mA/cm ²	3-6	85-95	18-39
Acar et al. (1994)	Kaolinite	Cd	NA	100-140 mg/kg	0.037 mA/cm ²	20-67	92-100	50-120
	Kaolinite	Cr	NA				65-70	
Shapiro and Probststein (1993)	Kaolinite	Acetic Acid	NA	0.1 M	25 V	20-100	45	3.7 kWh/t
			NA	0.5 M			95	
Probststein and Hicks (1993)	Kaolinite	Phenol	NA	450 mg/kg	0.62 V/cm	up to 60	95	5.3-260 kWh/t
				45 mg/kg			75	
Yeung et al. (1996)	Kaolinite	Pb	4.2-5.3	1.5 mg/g	1.5-3.1 V/cm	12-50	NA	NA
Acar and Alshawabkeh (1996)	Kaolinite	Pb	4.7	856-5322 mg/kg	0.133 mA/cm ²	54-123	80-90	60-700
Puppala et al. (1997)	Mixture of illitic, Kaolinite, sodium montmorillonite and fine sand	Pb	NA	2330 and 18000 mg/kg	0.05-0.25 mA/cm ²	up to 98	0-40	49-9958
Chung and Kang (1999)	Marine Clay	Pb	6.5-7.13	500-50000 mg/kg	0.064-0.382 mA/cm ²	5-30	> 88	NA
Lee and Yang (2000)	Kaolinite	Pb	4.5	141-143 mg/kg	0.47 mA/cm ²	20-35	25.5-50.6	NA
	Kaolinite	Pb	3.7	110-1000 mg/kg	0.022-0.111 mA/cm ²	23-31	20-70	NA
Li and Li (2000)	Illitic Soil	Pb	8.5	1000-5000 mg/kg	0.022-0.222 mA/cm ²	44-98	10-80	NA
Saichek and Reddy (2003)	Kaolinite	Phenanthrene	4.9	500 mg/kg	1 V/cm	up to 60	No Obvious Removal	NA

Note: NA = Not Available

Chapter 3 Materials and Methodology

3.1 Introduction

This study aimed to develop and evaluate an electrokinetic system that vertically transports contaminants, both heavy metals and organic contaminants. The first section of this chapter illustrates the electrokinetic reactor setup and the working principles of the upward electrokinetic soil remedial system (UESR). The experimental methodologies such as materials used and the experimental procedures are presented thereafter.

3.2 The Proposed Electrokinetic System: UESR

3.2.1 Electric Fields in UESR

Unlike the horizontally orientated reactors, which have been commonly adopted in electrokinetic remediation studies, the proposed UESR system was vertically orientated. The cathode electrode was placed on the surface of soils while the anode electrode was embedded at bottom of the contaminated soils, generating an overall vertical electric field pointing upwards in the soil as illustrated in Figure 3.1.

Figure 3.1 Vertical electric fields by pairs of point charges at different spacing

3.2.2 Progressive Migration of Contaminants

As shown in Figure 3.1(a)-(d), the electric field generated by a pair of point electrodes deforms as the anode being moved closer to the cathode. When the electrodes are separated at a further distance, a larger area in the soil is covered by the electric field but the average field strength decreases according to Gauss' Law. Reversely, the electric field covers a smaller area but with larger average field strength when the anode is moved closer to the cathode.

The proposed UESR process can progressively transport contaminants in the soil towards the soil surface by raising the anode to a higher position and concentrating the energy (i.e., electric field) on the zones with accumulated contaminants. Once the contaminants at deeper locations are moved to the shallower layers and the region near the anode is cleaned, there is no need to include this cleaned region in the treatment zone anymore. Furthermore, due to the rise of anode, the hydrogen ions generated at anode thereafter travel a shorter distance to reach the high pH region. By applying this procedure, the contaminants can be progressively lifted to the soil surface with reduced energy cost.

3.2.3 Organic Contaminants Removal Using UESR

Electro-osmosis was found to be the main process responsible for transporting organic contaminants in clayey soils (Segall and Bruell 1992; Acar et al. 1992; Ho et al. 1995, 1999). Segall and Bruell (1992) concluded that the purging of organic contaminants in clayey soils was more efficient when the organic substances had higher water solubility.

The UESR also generates electro-osmotic flow of soil water towards the cathode. Organic substances dissolved in the pore water are transported to the soil surface (cathode side) along with the electro-osmosis flow. In addition to transporting the dissolved organic contaminants, the UESR could provide an additional purging force to the organic substances existing as light non-aqueous phase liquid (LNAPL) in the soil capillary. As LNAPLs tend to exist on top of pore water surface due to its light density and low solubility in water, the pore water traveling upward could lift the LNAPLs in the same direction by pushing them upwards. The flushing of pore

water through clay capillaries can also assist the cleaning of organic contaminants sorbed to soil particles in the soil capillaries. The transporting efficiency in this case is likely to be high if LNAPLs have low affinity to the soil particles and the capillaries exert small resistance (due to friction) forces to the pore water flow.

3.2.4 Effect of Gas Generation

H₂ is generated at cathode, and O₂ is generated at anode due to water electrolysis at the electrodes (Equation 2.26). The oxygen produced at the anode electrode can be used to enhance biodegradation of organic contaminants in UESR. Since the anode is embedded in the soil and the oxygen generated is accumulated in a confined space at the anode, the dissolved oxygen (DO) level increases in the anode region during the treatment process. The electro-osmosis flow can then bring the pore water with high DO to the other parts of the soil to replenish the oxygen that is necessary to stimulate biodegradation of organic contaminants by indigenous bacteria. Moreover, the nutrients and TEAs (terminal electron acceptors) can also be injected to the soil to boost the bacteria population by electromigration and/or electroosmosis.

3.2.5 Factors Affecting the Performance of UESR

With cathode electrode on the top of the soil, the UESR will only be efficient for transporting cationic contaminants, dissolved no-ionic substances as well as LNAPLs. The extraction of anionic contaminants, such as certain arsenic compounds, requires a reverse of polarities of the two electrodes such that the anode is on the surface of soil. The reverse of polarity also results the reverse of electro-osmotic flow.

When the anode electrodes are raised to concentrate the electric field on the upper portion of the soil, the lateral area influenced by the electric field of each individual pair is reduced and give rise to some dead zones between the electrodes where electric fields are relatively weak. Additional electrodes need to be inserted in these zones to maintain a sufficient uniform electric field.

3.3 Reactor Setup

As shown in Figure 3.2, an UESR reactor contains a vertical cylindrical cell, anode and cathode electrodes, a DC power supply, pumps, liquid circulating pipes, and cathode chamber influent and effluent reservoirs. The pH in the cathode chamber was controlled using cathode chamber influents. During the experiments, the cathode chamber influents were pumped into the cathode chamber while the cathode chamber effluent was pumped out at the same flow rate through silicon tubing by peristaltic pumps. Specially designed voltage detecting probes were used to measure the electric potentials at various locations in the cell.

Figure 3.2 Schematically UESR reactor setup

3.3.1 Electrokinetic Cell

Most of the electrokinetic cells used in the previous laboratory scale studies were cylindrical tubes made of acrylic or equivalent materials. Many studies used cells with diameters ranged from 50 to 100 mm. The lengths of cells varied from 70 to

200 mm, with occasionally up to 55 cm, in most studies (Acar et al. 1990; Hamed et al. 1991; Acar et al. 1992; Segal and Bruell 1992; Hicks and Tondorf 1994; Acar et al. 1994; Yeung et al. 1996; Puppala et al. 1997; Alshawabkeh et al. 1999; Chung and Kang 1999; Reddy et al. 2001). Box-shaped container with size of 91.4 cm x 182.9 cm x 91.4 cm was used by Acar and Alshawabkeh (1996) in a pilot scale test. The material for the box in that study was plywood.

In the UESR setup (Figure 3.2), the electrokinetic cell, containing contaminated soil sample, stood vertically during treatment. Vertical electric fields were established in the cells. Cells with different diameter and length were used to study the effect of specimen size. Their diameters included 70, 100, and 140 mm. The length varied from 100 to 300 mm. Each cell has a cap with orifices drilled at designed locations for tubing (Master Flex) and wires.

3.3.2 Electrodes and DC Power Supply

The electrodes adopted in the past studies were mainly perforated circular graphite plates, stainless steel and platinum plated materials were occasionally used (Hamed et al. 1991; Acar et al. 1992; Segal and Bruell 1992; Bruell and Segall 1992; Hicks and Tondorf 1994; Acar et al. 1994; Yeung et al. 1996; Puppala et al. 1997; Alshawabkeh et al. 1999; Chung and Kang 1999; Reddy et al. 2001). The plate-shaped electrodes were used to create 1-dimensional electric fields between the electrodes, and graphite was preferred because it's stable chemical properties.

The electrodes used in this study (Figure 3.3) were designed to generate non-uniform vertical electric fields (Figure 3.1). The anode electrode was rod-shaped ($\varnothing 8.5$ mm) with an insulating tube such that it could be inserted into the contaminated area up to the desired depth with minimal site disturbance. Perforated stainless steel rings were used as cathode electrodes and graphite was selected as the anode electrode material. The insulating tube ($\varnothing 12.5$ mm) prevented direct contact between anode and cathode, and ensured the anode would only be exposed to the soil at the tip. The small geometry of the electrodes was designed to simulate the electric field of two point charges as shown in Figure 3.1. As described in Section 2.4.1, the electric field generated by two point electrodes in the soil is non-

uniform and three-dimensional. However, the electric field superimposed on the adjacent electric fields such that a relatively uniform electric field would be generated when the electrode pairs were placed close to each other as demonstrated by Segall and Bruell (1992).

The DC power supply (Nemic Lambda, Model GEN300-2.5, USA) was able to deliver a maximum voltage of 300 VDC, or a current of 2.5 A. Configurations with both constant current and constant voltage were investigated. The voltage gradients in soil were measured by a fabricated voltage detecting probes.

Figure 3.3 Anode electrode in UESR

3.3.3 Experimental Program and Parameters

Nineteen electrokinetic experiments were carried out with different operating conditions. Seven heavy metals, including Arsenic (III), Chromium (III), Nickel (II), Copper (II), Zinc (II), Lead (II), and Cadmium (II), as well as two organic compounds, p-xylene and phenanthrene, were investigated in this study. The

effects of different specimen diameters, specimen heights, cathode chamber influents, and treatment durations were examined by T1 and T2 series. The T7 and T8 series were focused on the usage of different voltage gradients, current densities, soil types, as well as contaminants mixtures. The experimental parameters of the experiments are summarized in Table 3.1

Table 3.1 Parameters of tests performed

Test	Specimen diameter (mm)	Specimen height (mm)	Current /voltage	Test duration (days)	Cathode chamber influent	Contaminant compositions
T1D1	100	100	15 mA	9	Distilled water	As, Cr, Ni, Cu, Zn, Pb, Cd
T1S1	70	100	15 mA	6	Distilled water	As, Cr, Ni, Cu, Zn, Pb, Cd
T1D2	100	100	15 mA	6	Distilled water	As, Cr, Ni, Cu, Zn, Pb, Cd
T1D3	100	100	15 mA	4	Distilled water	As, Cr, Ni, Cu, Zn, Pb, Cd
T1S4	140	100	15 mA	6	Distilled water	As, Cr, Ni, Cu, Zn, Pb, Cd
T1F1	100	100	15 mA	6	10^{-2} N HNO_3	As, Cr, Ni, Cu, Zn, Pb, Cd
T2S2	70	300	15 mA	18	10^{-2} N HNO_3	As, Cr, Ni, Cu, Zn, Pb, Cd
T2S1	140	300	15 mA	18	10^{-2} N HNO_3	As, Cr, Ni, Cu, Zn, Pb, Cd
T7M2	100	100	15 mA	6	10^{-2} N HNO_3	As, Cr, Ni, Cu, Zn, Pb, Cd
T7M3	100	100	15 mA	6	10^{-2} N HNO_3	Cu, Pb, p-xylene, phenanthrene
T7M4	100	100	15 mA	6	Distilled water	Cu, Pb, p-xylene, phenanthrene
T7M5	70	100	15 mA	6	10^{-2} N HNO_3	Cu, Pb, phenanthrene
T7M6	70	160	15 mA	6	10^{-2} N HNO_3	Cu, Pb, phenanthrene
T8V1	100	100	3.5 V	18	10^{-2} N HNO_3	As, Cr, Ni, Cu, Zn, Pb, Cd
T8V2	100	100	3.5 V	6	10^{-2} N HNO_3	As, Cr, Ni, Cu, Zn, Pb, Cd
T8V3	140	100	3.5 V	18	10^{-2} N HNO_3	As, Cr, Ni, Cu, Zn, Pb, Cd
T8S1	140	200	20 V	30	10^{-2} N HNO_3	Pb, phenanthrene
T8S2	140	200	20 V	30	10^{-2} N HNO_3	Pb, phenanthrene
T8S3	140	200	20 V	30	10^{-2} N HNO_3	Pb, phenanthrene

The tests, namely T7M3, T7M4, T7M5, and T7M6, were conducted with control cells. Control cells were used to count for the lost of p-xylene due to evaporation. The control cells were prepared in the same procedure as their respective treating cell except it was not connected to DC power or pumps.

3.4 Soil Characterization

Two types of kaolins were used for this study due to their low buffer capacity and it has been well characterized in many studies (Hamed et al. 1991; Acar et al. 1992; Acar et al. 1994; Yeung et al. 1996, etc.). The first type of kaolin (Kaolin I) was supplied by Kaolin (Malaysia) Sdn Bhd. The chemical properties obtained from the supplier were listed in Table 3.2. The other type of kaolin (kaolin, Hydrated Aluminum Silicate, USA) (Kaolin II) was supplied by Sigma.

Table 3.2 Chemical properties of kaolin 1

Chemical composition (%)	
Alumina	33-39
Silica	45-50
Iron	below 1.0
Potassium	below 1.0
Magnesia	below 1.0

The kaolins were tested for heavy metals using acid digestion by a High Pressure Asher (Anton Parr; Model HPA-S, Austria) and subsequent quantification by an Inductively Coupled Plasma (ICP) emission spectrometry (Perkin-Elmer; Model Optima 2000DV). The kaolin clays were also tested for zeta potential, particle sizes, and conductivity.

3.5 Contaminated Kaolin Preparation

3.5.1 Spiking of Kaolins with Heavy Metals

Heavy metals in their nitrates form (analytical grade) were carefully weighed and dissolved into distilled water to obtain solutions of known concentrations. The amount of dry kaolin powder and the solution needed were calculated to yield the targeted contaminant contents. The dry kaolin powder and the solution were then thoroughly mixed in a motor driven mixer. After that, the mixture was allowed to

reach equilibrium for 24 hours before it was stored in a refrigerator. The moisture content for the contaminated kaolin ranged from around 50% to 70%.

3.5.2 Spiking of Kaolins with Organic Compounds

Analytical grade phenanthrene were measured and then dissolved into 600 ml of dichloromethane (DCM). The DCM-phenanthrene mixture was mixed with a calculated amount of dry kaolin in a motor driven mixer for 1 hour to obtain homogeneous distribution of phenanthrene. The kaolin-DCM-phenanthrene mixture was then placed in a ventilation hood for 7 days for DCM to evaporate. Two samples were taken to determine the actual concentration at the end of day 7. This kaolin was finally mixed with heavy metal containing solution to obtain the contaminated kaolin using the same procedure as described in Section 3.5.1.

P-xylene was measured and directly dissolved in the heavy metal solution. The solution was immediately used to spike clean dry kaolins or phenanthrene spiked kaolins using the procedure described in Section 3.5.1. Two samples were taken before the kaolin was packed into reactor cell to determine the initial concentrations of p-xylene as part of the p-xylene evaporated during mixing and storage.

3.6 Experimental Procedures

3.6.1 Reactor Packing and Monitoring

The prepared kaolin specimen was placed into the cell layer by layer. The specimen in each layer was uniformly compacted using a 2.7 kg steel hammer by dropping it from a height of 10 cm for about 25 times before the next layer was added. Depending on the amount of soil used, the number of layers put in the cell varied from 5 layers to 15 layers. The sample in the cell was cured overnight at room temperature (25°C) to attain equilibrium before the experiment started. Samples were taken at different layers during packing to determine the initial soil pH, moisture content, and contents of heavy metals and organic contaminants.

The anode (including the insulating tube) was inserted up to the bottom. After the anode electrode system was installed, the cathode (the stainless steel ring) was

placed on the top center of the clay. The electric wiring and tubing were then connected and arranged through the holes on the cap plate. The cell was finally capped and the pumps turned to deliver cathode chamber influent. The DC power supply was turned on 1 hour later to supply direct current. The experiments were conducted either under constant voltage gradients or constant current densities.

While the cathode electrode was continuously flushed by distilled water or 10^{-2} N HNO_3 , the liquid in cathode chamber was continuously pumped out from the cathode chamber at the same flow rate (1.1-1.6 ml/min) to maintain the water level. The voltage and current, as well as the pH values of the pumped effluent were recorded two times a day. Effluent samples were taken at a constant interval to monitor the amount of contaminants in the collected effluent.

3.6.2 Sampling Procedures

The power was turned off after planned duration. The reactors were disassembled and the soils were taken out. The specimens were immediately sliced into layers of 2 cm each, and then two samples were taken from the inner zone (inner ring) of each layer and the two other from the outer zone (outer ring) (Figure 3.4). The samples were then analyzed for pH, water content, and contaminant concentrations.

Figure 3.4 Sampling procedure of treated soil

3.7 Analytical Methods

3.7.1 Measuring pH

The pH values of the cathode effluent were measured by directly inserting the electrode probe of a pH meter (Orion; Model 710A) into the collected effluent sample. The pH meter was calibrated daily.

For kaolin samples, a slurry form mixture was firstly made by adding approximately 2 grams of kaolin into 20 ml of distilled water. The mixture was stirred and the pH probe was inserted into the slurry.

3.7.2 Measuring Moisture Content

The moisture content was measured by mass reduction in oven (103°C). A soil sample was weighed (M_1) in a pre-weighed aluminum dish (M_2). The sample was put in oven for 24 hours and weighed again to determine the dry mass (M_3). The moisture content, w , was given by

$$w = \frac{M_1 - M_3}{M_3 - M_2} \times 100\% \quad (3.1)$$

3.7.3 Measuring Zeta Potential

The samples were prepared using the procedures described by Vane and Zang (1997) and the zeta potential measurement was performed with a Malvern Zetasizer (Model Zetasizer 3000). The clay concentration used was 0.1 g/l. A series of samples were prepared and adjusted to different pH (ranged from 2 to 11).

Two 10 ml samples aliquot replicates were injected into the Zetasizer cell and analyzed for zeta potential. The average value was reported.

3.7.4 Measuring Particle Size

Slurry of kaolin powder in distilled water was slowly dropped and diluted into the sample chamber of a HYDRO Masterziser (Model 2000S). The mixture was continuously stirred and particle sizes of the added sample was automatically

measured. The measurements were in triplicates and the averaged values were reported.

3.7.5 Measuring Conductivity

Slurries were made by mixing 6 g of dry kaolins with 30 ml deionized water in 60 ml polyethylene (PE) centrifuge bottles. The bottles were then capped and put on a shaker for 24 hours at 250 rpm. Next, the mixtures were centrifuged at 2500 rpm for 30 minutes and the supernatant was transferred to a 30 ml glass via for conductivity measurements. The conductivity was measured using a conductivity meter (Horiba; Model ES-14).

3.7.6 Measuring Heavy Metal Concentrations

The samples taken from kaolin specimens were digested and analyzed for heavy metal concentrations using ICP (Perkin-Elmer; Model Optima 2000DV).

The acid digestion and heavy metal determination of a soil samples involved the following steps:

- 1) The soil sample was oven dried for 24 hours to determine its moisture content,
- 2) The dried soil sample was grounded into fine particles by a Fritsch brand grinder,
- 3) Approximately 0.1 g of the sample (in powder form) was weighed to the nearest 0.001 g and mixed with 3 ml nitrate acid in a 15 ml quartz vessel,
- 4) The mixture was sonicated for 20 minutes in a sonicator (Branson; Model 1510) before it was digested under elevated temperature (300°C) and high pressure (90 bars) in a High Pressure Asher (Anton Paar; Model HPA-S) for 160 minutes,
- 5) The digested mixture was diluted to 25 ml and filtered using a 45 µm pore size Whatman membrane filter, and
- 6) The filtrate was then detected for heavy metals by the ICP.

3.7.7 Measuring Xylene and Phenanthrene Concentrations

After sampling, the kaolin samples (approximately 2 g each) were immediately placed in pre-weighed 40ml brown glass vials to minimize the loss of p-xylene during sample transfer. Clean tissue was used to wipe off the soil samples adhered on the surface of the glass vials as well as the vial openings. The glass vials were then immediately capped to air tight and weighed to the nearest 0.001 g. Approximately 2.5 g of drying agent (anhydrous sodium sulfate) were weighed and put into each sample containing vial. A stainless steel spoon was used to mix the sample and the drying agent. After that, 10 ml of DCM was added into each vial and the mixture was sonicated for 1 hour and subsequently shaken at 250 rpm for 12 hours to extract p-xylene from the soil. The samples were finally centrifuged at 2000 rpm for 20 minutes. 1.5 ml from the supernatant in each vial was transferred to a HPLC vial and analyzed for p-xylene. The concentration of p-xylene in the soil sample was back calculated as in μl p-xylene per kg of wet soil.

The measurement of phenanthrene concentration was also conducted with a HPLC (Perkin Elmer; Model Series 200). The soil samples were first air dried for 7 days and then ground into powder. The samples were put into pre-weighed 40 ml brown glass vials and the total masses of samples and glass vials were measured. 10 ml of acetonitrile was then added into each vial and the mixture was sonicated, shaken and centrifuged in the same manner as for p-xylene extraction. For each sample, 1.5 ml of the supernatant was transferred to a HPLC vial and analyzed by HPLC.

The mobile phase used was acetonitrile and DI water at volume ratio of 70:30. The column used was PAH column and the wave length of 280 nm was used in the uv/vis detector.

Chapter 4 Results and Discussion

4.1 Soil Characterization

4.1.1 Kaolin Particle Size

The results of particle size analyses, pH, and conductivity are presented in Table 4.1. Detailed analysis results can be found in Appendix A. Both kaolin I and kaolin II had predominantly fine particles (99% under 30 μm). The Georgia kaolinite used in other studies was reported to have over 90% particle below 2 μm (Hamed et al. 1991, Acar et al. 1992, Acar et al. 1994). Both two kaolin soils used in this study had larger particle size and therefore higher hydraulic conductivity than the Georgia kaolinite. Kaolin I had slightly larger particle size than kaolin II. The obvious difference between the two soils was that kaolin I had a much larger conductivity than that of kaolin II.

Table 4.1 Properties of kaolin I and kaolin II

	Kaolin I	Kaolin II
Mean particle size (μm)	8.75	8.25
Percentage under 26 μm (%)	98.1	99
Percentage under 10 μm (%)	68.3	67.6
pH	4.8-5.1	4.9-5.1
Conductivity ($\mu\text{S}/\text{cm}$)	293	160.3

4.1.2 Kaolin Zeta Potential

Zeta potential for the two kaolin soils under various pH conditions is presented in Figure 4.1. Zeta potential of the two soils were almost identical in the pH range of 2 to 4, where they both gradually decreased from 10 mV at pH 2 to -10 mV at pH 4. The points of zero potential for both kaolins were found to be approximately at pH 3.5-3.6. The zeta potential of the two soils were found to have different trend at pH value larger than 4. Similar results were reported by Vane and Zang (1997) for Georgia kaolinite.

Figure 4.1 Zeta potential of the kaolin soils

4.2 Concentration of Spiked Contaminants

The actual contamination concentrations were determined after the kaolin specimen preparation processes. As shown in Table 4.2, the level of heavy metals in contaminated kaolin varied from near 100 mg/kg dry soil to near 1000 mg/kg dry soil. And the level of organic contaminants (p-xylene and phenanthrene) in contaminated kaolin varied from near 300 mg/kg dry soil to near 900 mg/kg dry soil. All heavy metals and phenanthrene were expressed in mg/kg dry mass. The initial moisture contents and pH of contaminated kaolin specimens were determined before the contaminated kaolins were packed into reactors. As shown in Table 4.3, the pH values varied from 2.5 to 4.9 and moisture contents were in a range from 49% to 72%. The initial contaminant concentrations, soil pH, and moisture content used by different researchers were largely different among the past studies conducted to investigate electrokinetic soil remediation (Table 2.3). The heavy metal concentrations in the range of 45-5000 mg/kg and initial pH in the range of 3.7-8.5 were reported in relevant studies (Hamed et al. 1991; Acar et al. 1992;

Segall and Bruell 1992; Shapiro and Probststein 1993; Hicks and Tondorf; 1994; Chung and Kang 1999; Li and Li 2000; Saichek and Reddy 2003).

Table 4.2 Concentration of contaminants before treatment (mg/kg)

Test	As	Cr	Ni	Cu	Zn	Pb	Cd	p-Xylene	Phenanthrene
T1D1	164	233	86	286	280	472	287	-	-
T1D2	165	289	107	338	363	514	359	-	-
T1S1	165	289	107	338	363	514	359	-	-
T1D3	165	206	102	362	402	538	353	-	-
T1S4	277	286	293	312	308	347	286	-	-
T1F1	605	308	282	341	306	338	312	-	-
T2S2	540	982	644	739	764	761	721	-	-
T2S1	409	248	321	338	355	402	330	-	-
T7M2	154	-	134	165	159	206	139	-	-
T7M3	-	-	-	740	-	820	-	895	875
T7M4	-	-	-	740	-	820	-	895	875
T7M5	-	-	-	740	-	820	-	-	875
T7M6	-	-	-	740	-	820	-	-	875
T8V1	169	-	180	216	210	241	188	-	-
T8V2	169	-	180	216	210	241	188	-	-
T8V3	169	-	180	216	210	241	188	-	-
T8S1	-	-	-	-	-	220	-	-	408
T8S2	-	-	-	-	-	226	-	-	402
T8S3	-	-	-	-	-	201	-	-	380

Table 4.3 Moisture contents and pH of soil before treatment

Test	pH	Moisture content (%)	Test	pH	Moisture content (%)
T1D1	3.0	63	T7M3	2.6	61
T1D2	2.8	72	T7M4	2.6	61
T1S1	3.0	63	T7M5	3.6	61
T1D3	2.8	65	T7M6	3.6	61
T1S4	2.5	59	T8V1	2.6	61
T1F1	2.8	62	T8V2	2.6	61
T2S2	3.0	60	T8V3	3.0	61
T2S1	3.1	53	T8S1	4.6	60
T7M2	3.0	50	T8S2	4.9	53
			T8S3	4.9	49

4.3 Accumulation of metals on cathode and cracks development

4.3.1 Accumulation of Metals on Cathode

Metal ions transported to the surface via electromigration and eventually deposited on the stainless steel cathode. Visible metal deposits were first observed on the bottom of the cathode surface, and then propagated to the whole surface submerged in the cathode chamber fluid. Within 24 hours of treatment, heavy metal precipitates accumulated on top of the soil close to the cathode electrode.

The amount of such matter (deposits and precipitates) formed at the end of the tests varied with the type of cathode chamber influent. When distilled water was used as the cathode chamber influent to flush the cathode electrode, such as in T1D1, T1D2, and T1S1, there were usually large amount of such accumulated matter and the cathode electrode was completely covered by it. The amount was much less when 10^{-2} N HNO₃ was cathode chamber influent. This could be due to the metals migrated to the top were kept in soluble phase when the pH at cathode was low. These metal ions in solution were then pumped out along with cathode effluent.

4.3.2 Development of Cracks in the Soil

Cracks were usually developed in soils and could be observed from the side of column after a few days of treatment (Table 4.4). The cracks could become wider and longer as the experiments proceeded. It was found that the cracks appeared faster in soil specimens with smaller diameter. Cracks were mostly resulted from unbalanced strains developed in soils at different locations when soil pore water was drawn off. Other factors could contribute to development of cracks include the weight of soil specimen, electric field distribution, usage of different cathode chamber influent, and soil electroosmotic permeability. The development of crack in soils during electrokinetic treatment was also reported in studies where horizontal electric fields were used (Acar and Alshawabkeh 1996). The effects of the development of cracks on the removal of contaminants were not well understood.

Table 4.4 Cracks development in soils

Test	Specimen diameter (mm)	Flushing liquid	Cracks appear time (days)
T1D2	100	Distilled Water	≈ 4
T1S1	70	Distilled Water	≈ 1
T1D3	100	Distilled Water	> 4
T1S4	140	Distilled Water	> 6
T2S1	140	10 ⁻² N HNO ₃	> 10
T2S2	70	10 ⁻² N HNO ₃	≈ 3
T1F1	100	10 ⁻² N HNO ₃	≈ 2
T7M2	100	10 ⁻² N HNO ₃	> 6

4.4 Soil Water Content after UESR Treatment

The final water content of kaolin treated in T1D2 (Ø100 mm), T1S1 (Ø70 mm), and T1S4 (Ø140 mm) under the same conditions (current density 15 mA and treatment duration 6 days) are presented in Figure 4.2 (a). The final water content results of test T8V1 (Ø100 mm) and T8V3 (Ø140 mm), both treated under constant voltage 3.5 V and for 18 days, were shown in Figure 4.2 (b).

(a)

(b)

Figure 4.2 Water Content of samples with different diameter for 6 days under constant current (a) and for 18 days under constant voltage (b)

When the height of soil specimen was 100 mm, the diameter of the soil specimen seemed to have limited effect on the movement of soil pore water under electrokinetic treatment. As shown in Figure 4.2 (a), the reduction of moisture content due to electroosmosis was not obvious for the four tests that used distilled water as cathode chamber influent and were treated for 6 days. However, the two tests (T8V1 and T8V3), which were treated for 18 days using 10^{-2} N HNO₃ to control cathode pH, as shown in Figure 4.2 (b) were observed a reduction of moisture content up to 6% compared to the initial moisture content.

The moisture content results for T8S1, T8S2, and T8S3 are presented in Figure 4.3. All the three tests were treated under a constant voltage of 20 V (or voltage gradient of 1 V/cm) for 30 days. T8S1 and T8S2 used kaolin I while T8S3 used kaolin II. The electroosmotic transportation of pore water was reflected by the difference of moisture content between the top layer and bottom layers. Such differences were approximately 5%, 3% and 7% for T8S1, T8S2 and T8S3, respectively. The results indicated that Kaolin II had slightly higher electroosmotic permeability than that of kaolin I.

The results also indicated that the treatment duration affected the electroosmotic pore water flow in the soils. Similar results were reported in the study conducted by Thevanayagan and Rishindran (1998). However, much higher moisture content reductions (13-20%) were also reported (Segall and Bruell 1992; Acar and Alshawabkeh 1996). It was expected that electroosmotic flow would be lower in UESR since the migration of pore water upward had to overcome to gravitational force acting upon the pore water.

Figure 4.3 Water content change in T8S1, T8S2, and T8S3

4.5 Soil pH after UESR Treatment

The electrolysis reactions on anode and cathode produced an acidic region near anode (the bottom of the specimen) and a base region near the cathode (the surface of the specimen). The pH value of the three experiments, namely T1D2 (Ø100 mm), T1S1 (Ø70 mm), and T1S4 (Ø140 mm), at different depth are presented in Figure 4.4 (a).

All three tests showed that the soil at the bottom had lower pH (2.1-2.2) than the initial value, while the pH values of soils of top layers were higher than the initial pH. It proved that the hydrogen ions in these tests were transported upward by the vertical electric field.

Figure 4.4 (b) presents the pH results obtained for the inner zone and outer zone of test T1D2 as well as the average of T1F1. The results showed that the inner zone of T1D2 was acidified faster than the outer zone. This could be due to the difference in

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Figure 4.4 (b) presents the pH results obtained for the inner zone and outer zone of test T1D2 as well as the average of T1F1. The results showed that the inner zone of T1D2 was acidified faster than the outer zone. This could be due to the difference in

electric field strength between the inner zone and the outer zone as the electric field generated was not uniform. The electric field strength in the inner zone was higher and the hydrogen ions migrated at a faster rate. As shown in Figure 4.4 (b), the soil in T1F1 had a relatively uniform pH in all depth. The operating conditions for T1D2 and T1F1 were the same except that T1D1 used distilled water as cathode chamber influent, while T1F1 used 10^{-2} N HNO_3 . Application of 10^{-2} N HNO_3 therefore was effective in neutralizing the hydroxyl ions generated at cathode so that the entire soil was in acidic condition.

(a)

(b)

Figure 4.4 Soil pH after treatment

The pH results of T8S1, T8S2, and T8S3 are shown in Figure 4.5. The three tests were conducted with an overall voltage gradient of 1 V/cm using 10⁻² N HNO₃ as cathode chamber influent for 30 days. The initial pH for the specimens was 4.6-4.9 and the final pH of the treated soils was within a range of 2.8-3.1.

Figure 4.5 T8S1, T8S2, and T8S3 treated sample pH

4.6 Heavy Metal Removal after UESR Treatment

4.6.1 Effect of Reactor Size

Figure 4.6 (a) shows the removal of heavy metals for T1S1 (Ø70 mm), T1D2 (Ø100 mm), and T1S4 (Ø140 mm) after 6 days of treatment under a constant current of 15 mA. T1S1 had the smallest diameter among the three reactors but it achieved higher removal than those of T1D2 and T1S4 for all the heavy metals investigated.

(a)

(b)

Figure 4.6 Heavy metal removal for different cell diameter

Figure 4.6 (b) shows the heavy metal removal for T8V1 ($\varnothing 100$ mm, height 100 mm) and T8V3 ($\varnothing 140$ mm, height 100 mm) after 18 days of treatment under a constant voltage of 3.5 V. T8V1 and T8V3 had different diameters but were tested in parallel using 10^{-2} N HNO_3 as the cathode chamber influent. There was, however, no significant difference between the heavy metal removal efficiencies of T8V1 and T8V3 (Figure 4.6 (b)). The strength of the electric field generated in the specimen was measured by either the current density (when the current was fixed) or the voltage gradient (when the voltage was fixed). When the experiments were conducted in constant current mode, the current density was inversely proportional to the cross sectional area or the square of cell radius. However, the voltage gradient was independent of the cell diameter when experiment was conducted with constant voltage mode. There was therefore no obvious difference between the removal efficiencies of the heavy metals in the two tests.

The correlations between removal efficiency and cell diameter are presented in Figure 4.7 for experiments conducted using distilled water as cathode chamber influent. It showed that removal for all metals were inversely related to the reactor diameter. Based on the gradients of the curves in Figure 4.7, it was clear that the heavy metal removal efficiencies were largely affected by the reactor diameter in the range of 100-140 mm.

Figure 4.7 Correlations between removal rate and cell diameter

4.6.2 Effect of Cathode Chamber Influent

Table 4.5 compares the results obtained from the experiments that flushed with distilled water and those flushed with 10^{-2} N HNO_3 . As shown in Table 4.5, the effect on metal removal by using different types of cathode chamber influent varied significantly with different heavy metals. T1D2 showed higher removal of As and Pb than T7M2, while T7M2 showed higher removal of Ni, Cu, Zn, and Cd than T1D2. The removal of Cu in both T7M3 and T7M5 was higher than their counterparts that used distilled water (Table 4.5). The effects of applying 10^{-2} N HNO_3 solutions at cathode on the heavy metals concentration in cathode effluent and on treatment energy consumptions are discussed in Sections 4.8 and 4.9.

Table 4.5 Metal removal for tests using different cathode chamber influent (%)

	100 mm				70 mm	
	Distilled water	10^{-2} N HNO_3	Distilled water	10^{-2} N HNO_3	Distilled water	10^{-2} N HNO_3
	T1D2	T7M2	T7M4	T7M3	T1S1	T7M5
As	26.0	23.2			43.1	
Cr	45.6				52.3	
Ni	50.0	57.2			56.6	
Cu	33.8	56.2	44.0	51.8	45.9	71.5
Zn	51.6	53.2			59.3	
Pb	42.1	35.7	25.4	38.4	48.4	43.5
Cd	42.8	56.4			50.5	

4.6.3 Effect of Treatment Duration

The metal removal rates of T1D3 (4 days), T1D2 (6 days), and T1D1 (9 days) are shown in Figure 4.8 (a). All the three tests were conducted under 15 mA with distilled water as cathode chamber influent. Figure 4.8 (b) presents two tests, T8V2 (6 days) and T8V1 (18 days), which were treated under constant voltage of 3.5 V and with 10^{-2} N HNO₃ as cathode chamber influent. As shown in Figure 4.8 (a)-(b), heavy metal removal efficiencies were higher for experiments conducted with longer durations. For different heavy metals, the removal rates increased with different patterns. As illustrated in Figure 4.9, the removal efficiencies of Cu, Cd, and Ni had small increments from 4 to 6 days and relatively larger increments from 6 to 9 days. The removal rates of Zn, As, Cr, and Pb had much larger increments from 4 to 6 days but little increase from 6 to 9 days. These patterns were correlated with their mobility as discussed in Section 4.6.4. Ni, Cd, and Cu generally have higher mobility than the other 4 metals and were transported faster than the other four metals (As, Cr, Zn, and Pb) when the duration was only 4 days. After the Ni, Cd, and Cu ions had migrated to the cathode region, the other four contaminants became dominate ions in the soil pore solution and were transported at a faster rate. These probably caused the rapid increase of removal efficiencies of As, Cr, Zn, and Pb from 4 to 6 days.

(a)

(b)

Figure 4.8 Effect of treatment duration on metal removal for experiment conducted on constant current (a) and constant voltage (b)

Figure 4.9 Correlations between removal efficiencies and treatment durations

4.6.4 Mobility of Heavy Metals

The removal efficiencies of the seven heavy metals investigated were summarized in Table 4.6 for the 10 tests conducted. As shown in Table 4.6, the highest removal rates obtained were for Ni (27.2-68.3%), Cd (24.7-67.2%), and Zn (14.4-61%), while the lowest removal efficiencies were observed for As (1.8-43.1%) and Cr (1.9-52.3%).

Table 4.6 Removal efficiencies of different types of metals (%)

	Cathode chamber influent : 10^{-2} N HNO ₃						Cathode chamber influent: distilled water			
	T2S1	T2S2	T7M2	T8V2	T8V3	T8V1	T1S1	T1D1	T1D2	T1D3
As	13.9	3.0	23.2	15.4	17.7	12.9	43.1	27.0	26.0	1.8
Cr	1.9	13.0	-	-	-	-	52.3	49.7	45.6	16.0
Ni	27.2	37.7	57.2	32.8	64.3	65.3	56.6	68.3	50.0	43.9
Cu	24.1	38.3	56.2	32.2	63.3	62.5	45.9	51.2	33.8	27.7
Zn	25.5	37.3	53.2	30.6	60.4	61.0	59.3	49.6	51.6	14.4
Pb	18.2	20.1	35.7	25.9	43.9	44.9	48.4	52.5	42.1	6.4
Cd	24.7	34.3	56.4	32.0	62.8	61.3	50.5	67.2	42.8	31.3

Table 4.6 shows that As is the least mobile metal and Ni is generally the most mobile metal in tests using distilled water as cathode chamber influent. Mobility of the other five metals are generally in the range between that of As and Ni and varied in different experiments. For the experiments conducted with 10^{-2} N HNO₃ as cathode chamber influent, the differences in mobility of the seven metals were more obvious. The order of mobility is Ni > Cd > Zn $\approx$ Cu > Pb > As > Cr. It seemed that the gravity did not play any significant role since Cd has higher atomic weight than Zn and Cu, while As and Cr have lower atomic weight than Pb. Other factors including diffusion constant, the radius of the hydrated metal ions, and affinity of metals to the kaolin particle surface probably had larger influence on the mobility of a heavy metal. The results of Cd, Pb, and Cr are in good agreement with the reported effective mobility of the three metals (Cd > Pb > Cr) (Acar and Alshawabkeh 1993). Cr(III) and Cr(VI) are the two prevailing valance states for chromium commonly found in subsurface. Cr(III) exists as cationic ions/complexes

such as Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$, while Cr(VI) exists as anions, such as HCrO_4^- (Virkutyte et al. 2002 and Reddy and Chinthamreddy 2003). In electrokinetic process, Cr(III) in soil solution migrates toward the cathode but Cr (VI) migrates to the anode. The migration of chromium could be retarded when part of Cr(III) was oxidized to Cr(VI) at anode where strong oxidizing condition presented. Similar to chromium, the migration and speciation of arsenic were also affected by the condition in contaminated kaolin as well as at anode electrode (Virkutyte et al. 2002).

4.6.5 Effect of Soil Types on Heavy Metal Removal

The three tests, namely T8S1, T8S2, and T8S3, were conducted to investigate the contaminants removal from two different soils namely Kaolin I and Kaolin II. T8S1 and T8S2 were packed with Pb contaminated Kaolin I while T8S3 was packed with Pb contaminated Kaolin II. The three tests were carried out in parallel for 30 days with the same specimen size, voltage, and cathode chamber influent. The removal efficiencies of Pb for T8S1, T8S2, and T8S3 were 68%, 62%, and 78%, respectively (Figure 4.10). As reported in Table 4.1, the two kaolin soils had different conductivity values, which were 293 and 160.3 $\mu\text{S}/\text{cm}$ for Kaolin I and Kaolin II, respectively. Therefore the amount of dissolved salts in pore water may have affected the removal efficiencies during electrokinetic treatment. It was reported by Acar and Alshawabkeh (1993) that transference number could affect the removal efficiency of heavy metals in soils. The transference number of an individual ion depends on the ionic mobility, concentration, and the total electrolyte concentration in the pore fluid. It will increase as the ionic concentration of that specific species increase. The dominant species in the soil pore water has the largest transference number and is migrated by electromigration to a larger extent than the other ions. The transference numbers of contaminant ions decrease when larger amount of background ions are present in the pore fluid. Due to the much higher electrolyte concentration (as indicated by conductivity) of Kaolin I. The Pb ions in contaminated Kaolin I therefore had smaller transference number than the Pb ions in contaminated Kaolin II even they were presented at the same concentration. The difference in transference number probably caused the removal efficiency in Kaolin II to be higher than Kaolin I after 30 days of treatment.

Figure 4.10 Removal efficiencies of Pb in test T8S1, T8S2, and T8S3

4.6.6 Effect of Current Density and Voltage Gradient

Figure 4.11 shows the heavy metal removal efficiencies for T1S1 ($\varnothing$ 70 mm, constant current density 0.39 mA/cm^2), T1D2 ($\varnothing$ 100 mm, constant current density 0.191 mA/cm^2), and T1S4 ($\varnothing$ 140 mm, constant current density 0.097 mA/cm^2) which were treated for 6 days. When the current density was raised from 0.097 to 0.191 mA/cm^2 , the heavy metal removal efficiencies increased 2 to 5 times depending on the type of metal. The slopes of the curves (Figure 4.11) varied for each heavy metal. Zn(II) and Ni(II) had curves with larger gradients therefore the change in current density had stronger influence on their removal. The influence was much smaller for As(III). The increments for all heavy metals gradually reduced when current density further increased from 0.191 to 0.39 mA/cm^2 (Figure 4.11). This could be due to the excess amount of hydroxyl ions generated at the cathode for experiments with higher current density, while the distilled water was supplied at a constant flow rate for all the experiments. Flushing the cathode electrode with distilled water became less effective in controlling the cathode pH from rising as current density increased (Figure 4.12). The migration of heavy metals in the tests with high current density could be eventually impeded by the raise of pH at cathode chamber as well as in the kaolin near the cathode.

The two tests T8V1 ($\varnothing$ 100 mm, voltage gradient 0.35 V/cm) and T8V3 ($\varnothing$ 140 mm, voltage gradient 0.35 V/cm) were treated by UESR for 18 days under the same

condition. As shown in Table 4.6, the two tests had the same level of removal efficiencies for all the heavy metals investigated despite the difference in their reactor cross sectional area as well as the amount of contaminated kaolin treated. It was the primarily because the same voltage gradients was applied during treatment.

Figure 4.11 Correlation of heavy metal removal and current density

Figure 4.12 Change in pH of soil specimen after treatment

4.6.7 Effect of Contaminant Composition

The effect of the presence of organic contaminants in the soil on the removal efficiency of metals was found to be complicated and dependant on each specific metal. As shown in Table 4.7, the removal efficiency of Pb was 43.1% in test T1D2 when all the contaminants were heavy metals, while Pb removal efficiency was only 25.4% in test T7M4 when organic compounds existed as co-contaminants. Nevertheless, this was not the case for Cu, which had lower removal efficiency (32.5%) in T1D2 and higher removal efficiency in T7M4 (44.0%). The effect of contaminant composition on the heavy metal removal was even more complicated by the use of different cathode chamber influent. The removal of Pb and Cu in the two tests T7M2 and T7M3, which used 10^{-2} N HNO₃ as the cathode chamber influent, were found to be similar.

Table 4.7 Effect of different contaminants compositions

Test	T1D2	T7M4	T7M2	T7M3
Cell diameter (mm)	100	100	100	100
Cathode chamber influent	H ₂ O	H ₂ O	10^{-2} M HNO ₃	10^{-2} M HNO ₃
As removal (%)	24.4		23.2	
Cr removal (%)	44.3			
Ni removal (%)	49.1		57.2	
Cu removal (%)	32.5	44.0	56.2	51.8
Zn removal (%)	50.9		53.2	
Pb removal (%)	41.3	25.4	35.7	38.4
Cd removal (%)	41.5		56.4	

Studies on simultaneous removal of mixed organic contaminants and heavy metals in electric field are very limited. The application of electric fields on contaminated soils gives rise to complicated physiochemical and hydrodynamic changes in the soil solutions (Hamed et al., 1991; Acar and Alshawabkeh 1993). The understanding of the adsorption and speciation of those contaminants in subsurface is not sufficient for any comprehensive analysis of the removal of mixed contaminants observed in this study. The change in removal efficiencies of Pb and Cu in T7M4 could also be attributed to the absence of the other heavy metals in the contaminated kaolin.

It is probably reasonable to say that the heavy metals and organic contaminants in soils to a certain extent have negligible effect on the removal efficiencies of one another since the main mechanisms responsible for transporting heavy metals and organic contaminants were electromigration and electroosmosis, respectively. The results of T7M2 and T7M3 (Table 4.7) showed that the difference was not obvious when organic contaminants were present and experiments were conducted using 10^{-2} N HNO_3 as cathode chamber influent. The effect of contaminant composition on the cathode effluent pH and the amount of dissolved contaminants were discussed in Section 4.8.

4.6.8 Distribution of Heavy Metals after UESR Treatment

The distribution of heavy metals after treatment is presented in Table 4.8 for the four experiments T1D2, T7M2, T8V1, and T8V3. After treatment, the heavy metals were distributed among the four fractions namely

- 1) Remained in treated kaolin,
- 2) Precipitated on the top surface of kaolin,
- 3) Deposited on cathode, and
- 4) Dissolved in cathode chamber effluent.

Amounts of metals precipitated on the top surface of kaolin, deposited on cathode and dissolved in cathode effluent were considered as metals removed from kaolin. As shown in Table 4.8, most of removed heavy metals were in the fractions 2 and 3 while the fraction 4 only counted less than 1%, when distilled water was used as cathode chamber influent (T1D2). Amounts of removed metals in the cathode chamber effluent significantly increased; meanwhile the amounts of heavy metals deposited on cathode and precipitated on top of kaolin, as well as remained in kaolin, decreased for the tests using 10^{-2} N HNO_3 as cathode chamber influent (T7M2). The higher removal of heavy metals with cathode chamber effluent and lower percentage of heavy metals remained in kaolin were observed when constant current density was applied (T7M2) in comparison with constant voltage gradient (T8V2). The extension of duration from 6 (T8V2) to 18 (T8V1) days improved the process of heavy metals removal with cathode chamber effluent and diminished the

amounts of heavy metals remained in kaolin. Table 4.8 suggests that the influent/effluent pH and the ability for a metal to dissolve in the effluent significantly influenced the total removal.

Table 4.8 Distribution of heavy metals after UESR treatment

Heavy metal	Test	Distribution, %			
		fraction 1, remained in kaolin	fraction 2, deposited on cathode	fraction 3, precipitated on top of kaolin	fraction 4, dissolved in cathode effluent
As	T1D2	70.1	26.3	3.6	< 1
	T7M2	78.9	0.7	3.8	16.6
	T8V2	85.2	0.4	3.5	10.9
	T8V1	81.8	1.0	2.1	15.0
Ni	T1D2	52.8	26.4	20.8	< 1
	T7M2	38.1	2.9	9.1	49.9
	T8V2	63.3	0.7	7.6	28.4
	T8V1	33.6	4.3	1.6	60.6
Cu	T1D2	61.8	17.9	20.4	< 1
	T7M2	40.7	5.5	8.3	45.5
	T8V2	65.2	0.9	7.4	26.5
	T8V1	37.7	5.3	2.3	54.7
Zn	T1D2	49.8	32.8	17.4	< 1
	T7M2	41.8	3.6	8.1	46.5
	T8V2	64.8	0.6	7.1	27.4
	T8V1	36.6	3.7	1.6	58.1
Pb	T1D2	51.9	36.8	11.3	< 1
	T7M2	63.0	2.6	6.1	28.4
	T8V2	72.4	0.9	6.5	20.2
	T8V1	52.7	4.4	2.5	40.5
Cd	T1D2	58.4	21.5	20.1	< 1
	T7M2	39.9	4.3	7.9	47.9
	T8V2	64.4	0.8	6.6	28.2
	T8V1	37.0	3.7	1.8	57.5

Note:

T1D2 (distilled water, constant current 15 mA, 6 days, cell diameter 100 mm)

T7M2 (10^{-2} N nitric acid, constant current 15 mA, 6 days, cell diameter 100 mm)

T8V2 (10^{-2} N nitric acid, constant voltage 3.5 V, 6 days, cell diameter 100 mm)

T8V1 (10^{-2} N nitric acid, constant voltage 3.5 V, 18 days, cell diameter 100 mm)

Figure 4.13 Distribution of heavy metals as ratio of final content over initial content in inner and outer zone of treated kaolin in test T1D1 (a) and T8V1 (b)

Content ratios as ratios of final contents of heavy metals, As, Ni, Cu, Zn, Pb, and Cd, to their initial contents were determined in kaolin after UESR treatment at different distance to cathode (Figure 4.13). The pattern of heavy metals distribution

in the soil after treatment was strongly affected by the type of cathode flushing liquid. As shown in Figure 4.13, the tests using distilled water as cathode chamber influent had large amount of metal accumulated in the top 1-2 layers of soils and less metal in the bottom layers after treatment. The concentrations of metals in the inner zone (inner ring) of soils were usually much higher metal than the soils of outer zone (outer ring). This was probably due to the non-uniform electric field generated by UESR. Nevertheless, the tests using 10^{-2} N HNO₃ had relatively uniform distribution of metals among the layers from bottom to top. In additional, the concentrations of metals in the inner zone of soils were very close to those in the outer zone.

4.7 Organic Contaminants Removal after UESR Treatment

The results of tests with organic contaminants are presented in Table 4.9. The removal efficiencies of p-xylene, ranged from 82.8% to 92.8%, were generally much higher than those of phenanthrene, which ranged from 38.5% to 66.9%. Bruell and Segal (1992) concluded that the organic compounds with high water solubility and low distribution coefficient, like BTEX and TCE, were easily removed from kaolin by electroosmosis. Chemicals with low water solubility and high distribution coefficient were transported at a slower rate. The study conducted by Acar et al. (1992) and the study carried out by Shapiro and Probstein (1993) both found that up to 95% of phenol could be removed from kaolin soils. Saichek and Reddy (2003) conducted electrokinetic experiments to remove phenanthrene from kaolin. They found that the phenanthrene at anode side migrated toward cathode and accumulated in the kaolin near cathode but there was little overall removal. The removal of p-xylene obtained in T7M3 and T7M4 (Table 4.9) was therefore mainly due to electroosmosis. However, the removal of phenanthrene could not be attributed to electroosmosis alone because phenanthrene has very low solubility in water and electroosmosis was not effective in transporting such a compound. The upward lifting effects, as described in Section 3.2.3, as well as dielectrophoresis, described in Section 2.4.5 might contributed significantly to the removal of phenanthrene.

Table 4.9 Organic contaminants removal after UESR treatment

	T7M3	T7M4	T7M5	T7M6	T8S1	T8S2	T8S3
Cell diameter (mm)	100	100	70	70	140	140	140
Cell height (mm)	100	100	100	160	200	200	200
Current/Voltage	15 mA	15 mA	15 mA	15 mA	20 V	20 V	20 V
Duration (days)	6	6	6	6	30	30	30
Cathode chamber influent	10^{-2} N HNO ₃	Distilled water	10^{-2} N HNO ₃	10^{-2} N HNO ₃	10^{-2} N HNO ₃	10^{-2} N HNO ₃	10^{-2} N HNO ₃
Cu removal (%)	51.8	44.0	71.5	62.1	-	-	-
Pb removal (%)	38.4	25.4	43.5	35.2	68.6	62.2	78.1
P-Xylene removal (%)	82.8	92.8	-	-	-	-	-
Phenanthrene removal (%)	38.5	55.2	40.0	66.9	47.3	48.5	52.0

4.7.1 Effect of Reactor Size

As shown in Table 4.9, the removal rate for phenanthrene in T7M5 ($\varnothing$ 70mm, constant current 15 mA, and 6 days) was slightly higher than the removal rate obtained in T7M3 ($\varnothing$ 100mm, constant current 15 mA, and 6 days). It suggested the reactor diameter affected the removal efficiencies of organic compounds in the same way as for heavy metals. T7M5 and T7M6 were packed with contaminated kaolin specimen of the same diameter but with heights of 100 mm and 160 mm, respectively. The results revealed that the effects of kaolin specimen height to the removal efficiencies of heavy metals and phenanthrene were very different. The removal efficiencies of phenanthrene were positively related to the heights of the kaolin specimen while the removal efficiencies of Cu and Pb were negative correlated with the height. The different pH profile of the specimen in T7M5 ($\varnothing$ 70mm; height 100 mm) and T7M6 ($\varnothing$ 70mm; height 160 mm), shown in Appendix B, suggested that T7M6 probably had larger electroosmotic pore water flow than T7M5.

4.7.2 Effect of Cathode Chamber Influent

As shown in Table 4.9, higher removal efficiencies for both p-xylene and phenanthrene were obtained in T7M4 ($\varnothing$ 100mm, constant current 15 mA, 6 days, using distilled water to flush cathode) than T7M3 ($\varnothing$ 100mm, constant current 15 mA, 6, using 10^{-2} N HNO₃ to flush cathode).

Figure 4.14 pH profile of T7M3 and T7M4 after UESR treatment

As the organic compounds were presented as co-contaminants with heavy metals, the interactions between the inorganic and organic contaminants in the soils shall be considered. The use of different cathode chamber influent might cause them to interact differently as the contaminants were transported by the applied electric fields. The cathode chamber influent also significantly affected the pH profile of the soil specimen in UESR treatment (Figure 4.4-4.5, and Figure 4.14). As zeta potential is pH dependent (Figure 4.1), the contaminated kaolin in T7M3 and T7M4 would develop different zeta potential in their capillaries in the kaolin specimens under treatment as they had different pH. T7M3, which used 10^{-2} N HNO_3 as the cathode chamber influent, was found to have lower pH than T7M4, which used distilled water (Figure 4.14). As shown in Figure 4.1, the lower pH in the kaolin would diminish the value of zeta potential and consequently reduce the flux of electroosmotic flow. Therefore, less electroosmotic flow in T7M3 probably caused the removal efficiencies of both p-xylene and phenanthrene to be lower than that of T7M4. Furthermore, electric fields in the specimen were found to distribute more uniformly when 10^{-2} N HNO_3 was the cathode chamber influent. The effect of dielectrophoresis was therefore less since the electric fields were more uniform.

4.7.3 Effect of Soil Type

The test T8S3 (Kaolin II, constant voltage 20 V, and 30 days) had higher removal efficiencies of phenanthrene than the two tests T8S1 and T8S2 (Kaolin I, constant

voltage 20 V, and 30 days), which were conducted with kaolin I. As shown in Table 4.1, , the two kaolin soils had different conductivity values, which were 293 and 160.3 $\mu\text{S}/\text{cm}$ for Kaolin I and Kaolin II, respectively. The value of zeta potential reduces when the total concentration of electrolyte increases (Mitchell 1993; Acar and Alshawabkeh 1993; and Vane and Zang 1997). Meanwhile, the electroosmotic flow flux is proportional to the electric field as well as the electroosmotic permeability, which is positively related to the zeta potential. The higher dissolved salt content in kaolin I probably made it less effective in transporting phenanthrene than Kaolin II, since electroosmosis was found to be one of the significant, if not the only, mechanism that transported the phenanthrene in both kaolins.

4.7.4 Distribution of Organic Compounds after UESR Treatment

The amount of p-xylene and phenanthrene detected in the effluent did not reflect their actual amount removed from the soil because p-xylene is volatile while phenanthrene has very slow water solubility. The total amount of p-xylene in effluent was less than 10% of the initially mixed amount. The removal efficiency was calculated by comparing the mass of the organic compound left in the kaolin with the final mass in a control column, which had the same size, packed with the same contaminated kaolin, and placed at one side for the same duration without electrokinetic treatment.

As shown in Table 4.10, the final concentrations of both p-xylene and phenanthrene in the kaolin of top layers (2-4 cm) were lower than those of the bottom layers (6-10 cm). The amount of p-xylene and phenanthrene left in the kaolin specimen after treatment for T7M3 were 8.7-15.3% and 39.8-69% of the initial concentration, respectively. In T7M4, there were 2.3-9.8% initial p-xylene and 21.4-61.9% initial phenanthrene left after treatment. The concentrations of both p-xylene and phenanthrene in the inner zone of the kaolin specimen were usually lower than the outer zone. It suggested that the organic contaminants in the inner zone were removed faster than in outer zone. It was noticed that the use of different cathode chamber influent had little effect on the distribution of organic compounds in the kaolin specimen after treatment.

Table 4.10 P-xylene and phenanthrene concentration after treatment (mg/kg)

Distance to cathode	Inner/Outer zone	T7M3		T7M4	
		p-xylene	phenanthrene	p-xylene	phenanthrene
2 cm	Inner zone	116	554	70	528
	Outer zone	137	348	88	542
4 cm	Inner zone	78	453	43	290
	Outer zone	137	345	33	246
6 cm	Inner zone	95	585	21	187
	Outer zone	130	604	47	298
8 cm	Inner zone	136	577	30	227
	Outer zone	217	598	62	422
10 cm	Inner zone	129	531	76	494
	Outer zone	106	546	82	490

4.8 Cathode Effluent in UESR

4.8.1 Effluent pH

Samples of the cathode effluent were taken at constant interval during the experiments. The pH of the effluent samples was measured immediately after sampling. Figure 4.15 presents the pH of the effluent for 7 tests, including 3 tests that used distilled water as cathode chamber influent (T1D2, T1S1, and T7M4) and 4 tests that used 10⁻² N HNO₃ as cathode chamber influent (T2S1, T7M3, T8V1, and T8V2). The pH of the first effluent samples, which were taken a few hours after experiments commenced, was about 4 for all three tests using distilled water as cathode chamber influent. The pH of all the subsequent effluent samples were in the range from 4 to 7 for T1D2 (Ø 100mm; contaminated by As, Cr, Ni, Cd, Zn, Cu, and Pb; 6 days) and T1S1 (Ø 70mm; contaminated by As, Cr, Ni, Cd, Zn, Cu, and Pb; 6 days), while it was from 8 to 9 for T7M4 (Ø 100mm; contaminated by Cu, Pb, p-xylene, and phenanthrene; 6 days). It was noticed that the composition of the contaminants also affected the effluent pH. The higher pH in T7M4 effluent was probably due to the kaolin specimens had been contaminated by less heavy metal contaminants than those in T1D2 and T1S1. The reason could be the hydroxyl ions in the cathode chamber, for the latter two tests, were consumed faster since a large

fraction of the heavy metals were precipitated as metal hydroxyls near the cathode area (Table 4.8).

As shown in Figure 4.15, the effluent pH remained relatively stable (pH 1.9-2.3) throughout the experiment duration for tests using 10^{-2} N HNO₃ as cathode chamber influent. Heavy metals were predominantly dissolved in the cathode chamber effluent and subsequently removed from the contaminated kaolin.

Figure 4.15 Change of cathode effluent pH with treatment time

4.8.2 Contaminants in Cathode Effluent

The effluent samples were analyzed to determine the amount of heavy metals as well as organic compounds. It was found that only the first one or two effluent samples contained certain level of heavy metals when experiments were conducted using distilled water as cathode chamber influent. All the effluent samples taken thereafter contained negligible amount of heavy metals most probably due to the high pH of the effluent (Figure 4.15). The effluent samples for the tests that used 10^{-2} N HNO₃ as cathode chamber influent, nevertheless, had appreciable amount of heavy metals throughout the treatment period as shown for T8V3 in Figure 4.16.

The initial content of the heavy metals in the contaminated kaolin of T8V3 were: As, 170 mg/kg; Ni, 180 mg/kg; Cu, 216 mg/kg; Zn, 210 mg/kg; Pb, 241 mg/kg; and Cd, 188 mg/kg (Table 4.2). Figure 4.16 also suggested that the amount of heavy metals

existed in the effluent was rather dependant on the specific metal than its initial concentration. Zn, Ni, Cu, Cd and Pb were generally present in effluent at higher quantity, while the amount of As was found to be less.

Figure 4.16 Heavy metals in effluent for test T8V3

The concentrations of p-xylene in effluents for test T7M3 (using 10^{-2} N HNO₃ as cathode chamber influent) and T7M4 (using distilled water as cathode chamber influent) are presented in Figure 4.17. The average concentrations of p-xylene in effluent samples of T7M3 and T7M4 were 5.35 and 8.14 mg/L, respectively. More p-xylene was removed via the effluent from the contaminated kaolin in T7M4 than T7M3.

Effluent samples were in acidic condition (approximately pH 2) for T7M3, and were in alkaline condition (approximately pH 8) for T7M4 as discussed in Section 4.8.1. The results suggested that the use of 10^{-2} N HNO₃ solution to control the pH at cathode, though it was effective in developing acidic condition throughout the kaolin specimen, impeded the transportation of p-xylene from contaminated kaolin into the cathode effluent. As discussed in Section 4.1.2, the zeta potential of kaolin can be diminished toward a value of zero when the pH approaches the point of zero potential. The weaker zeta potential caused by low pH condition in kaolin specimen of T7M3 gave rise to lower electroosmotic permeability as well as less electroosmosis flow.

Figure 4.17 Concentration of p-xylene in effluent for T7M3 and T7M4

Phenanthrene was detected to have concentrations near 1 mg/L for most of the effluent samples. Since the solubility for phenanthrene in water is 1.1 mg/L at normal condition. Little phenanthrene could have been transported by effluent in dissolved phase. The free phase phenanthrene, if formed in the cathode chamber, was most likely to attach to cathode electrode surface or float on the surface of the cathode chamber liquid due to its low density (less than water at normal condition). The possibility of it being adhered to the tubing walls and its low solubility in water made the quantification of the amount of phenanthrene removal via effluent impractical.

4.9 Soil Resistance and Energy Consumption

4.9.1 Current and Voltage Variation during UESR Treatment

When current was kept constant (15 mA) and cathode chamber influent was distilled water, the voltage rapidly increased to some 80-100 V in the first 2-3 days and steadily increased at a slower rate to some 140-160 V after 6-9 days as shown in Figure 4.18 (a). The increase of reactor electric potential drop, i.e. reactor apparent resistance building up, was mainly due to the deposition/precipitation of heavy metals on the cathode as well as in the soils on top 2 cm. Further examination of the voltage drop across the soil revealed that the majority part of the electric

potential drop was concentrated in the top 2 cm of the kaolin. It caused the electric fields distribution in the kaolin specimen to be more heterotrophic.

(a)

(b)

Figure 4.18 Change of reactor voltage for experiments conducted with constant current 15 mA and used (a) distilled water and (b) 10^{-2} N HNO_3

The changes of reactor voltage with time for three tests namely T7M3 ($\varnothing 100$ mm, height 100 mm), T7M5 ($\varnothing 70$ mm, height 100 mm), and T7M6 ($\varnothing 70$ mm, height 160 mm) conducted with constant current 15 mA using 10^{-2} N HNO_3 as cathode chamber influent are presented in Figure 4.18 (b). The reactor voltage initially

increased for a few volts but eventually started to decrease with time. Figure 4.18 (b) also suggested that smaller specimen diameter and larger specimen height gave rise to large electrical potential drops across the kaolin specimen being treated. The formation of metal hydroxides in the kaolin on the top and hence forming a zone of high apparent electric resistance were effectively controlled by lowering the pH at cathode. Lower voltage would cause the overall energy expenditure to be smaller since the current was fixed.

Sah and Chen (1998) conducted electrokinetic remediation experiments with natural soils and observed the apparent soil resistance increased sharply in the first 2-3 days of treatment. The apparent soils resistance was reported to be rather stable after 3 days. The increase in resistance was attributed to activation polarization, resistance polarization and concentration polarization. Similar findings were also reported in a number of other studies (Lee and Yang 2000; Darmawan and Wada 2002; Reddy and Chinthamreddy 2003).

The current variation for tests conducted with constant voltage of 3.5 V and 20 V are presented in Figure 4.19 (a) and Figure 4.19 (b), respectively. The current in experiment T8V2 showed an overall decrease during the 6-day treatment by UESR. The current dropped to below 5 mA at the end of 6th day. It was observed that the cathode electrode surface was coated with a thin layer of metal deposits after treatment. This layer of deposit could increase the electrical potential drop across the interface between the cathode electrode and the cathode chamber electrolyte. Cathode electrodes in experiments T8V1 and T8V3 were replaced with new cathode electrodes after 264 hours of treatment when the current dropped to approximately 10 mA. The cathode electrodes were also replaced for T8S2 and T8S3 after 354 hours and for T8S1 after 464 hours when current dropped a significant amount. Sharp increase of current was observed immediately after cathode electrode replacement (Figure 4.19 (a)-(b)). Replacing the cathode electrode after certain duration was therefore effective in minimizing the voltage drop across the electrolyte-electrode interface at cathode and restoring the reactor current in the contaminated kaolin to maintain the rate of electrokinetic remediation.

(a)

(b)

Figure 4.19 Change of reactor current for experiments conducted with (a) constant voltage of 3.5 V and diameter 100 mm, and (b) constant voltage 20 V and diameter 140 mm

4.9.2 Energy Expenditure

As shown in Table 4.11, experiments using 10^{-2} N HNO₃ as cathode chamber influent were found to consume far more less energy than the experiments using distilled water. Generally speaking, higher unit energy expenditure was observed for experiments conducted with cells of smaller diameter, longer treatment duration, and higher voltage. The energy costs were determined based on a rate of 16.35 cents/kWh.

Table 4.11 Energy consumption and cost

Test	Diameter (mm)	Height (mm)	Cathode chamber influent	Test duration (days)	Unit energy (kWh/m ³)	Unit cost (S\$/m ³)
T1D1	100	100	Distilled Water	9	349.7	57.18
T1S1	70	100	Distilled Water	6	499.8	81.71
T1D2	100	100	Distilled Water	6	263.1	43.02
T1D3	100	100	Distilled Water	4	101.7	16.63
T1F1	100	100	10^{-2} N HNO ₃	6	10.9	1.78
T2S2	70	300	10^{-2} N HNO ₃	18	96.9	15.84
T2S1	140	300	10^{-2} N HNO ₃	18	7.9	1.29
T7M2	100	100	10^{-2} N HNO ₃	6	19.1	3.13
T7M3	100	100	10^{-2} N HNO ₃	6	14.7	2.41
T7M4	100	100	Distilled Water	6	304.7	49.82
T7M5	70	100	10^{-2} N HNO ₃	6	32.4	5.29
T7M6	70	160	10^{-2} N HNO ₃	6	29.0	4.74
T8V1	100	100	10^{-2} N HNO ₃	18	19.7	3.23
T8V2	100	100	10^{-2} N HNO ₃	6	8.5	1.39
T8V3	140	100	10^{-2} N HNO ₃	18	14.6	2.39
T8S1	140	200	10^{-2} N HNO ₃	30	281.9	46.09
T8S2	140	200	10^{-2} N HNO ₃	30	263.4	43.07
T8S3	140	200	10^{-2} N HNO ₃	30	273.0	44.63

The energy expenditure reported in the past studies ranged from 18 to more than 4000 kWh/m³ (Acar et al. 1990; Hamed et al. 1991; Acar et al. 1992; Segal and Bruell 1992; Hicks and Tondorf 1994; Acar et al. 1994; Yeung et al. 1996; Puppala et al. 1997; Alshawabkeh et al. 1999; Chung and Kang 1999; Reddy et al. 2001). The normal energy consumption for total removal of metals from contaminated soils was believed to be 500 kWh/m³ (Acar and Alshawabakeh 1996). The highest energy consumption in this study was observed to be 499.8 kWh/m³ and the lowest energy consumption was observed to be 7.9 kWh/m³.

4.10 Electric Fields in Soil

The electrical potential distribution in the kaolin under treatment was measured with a fabricated voltage detecting probe. The potential contours were sketched based on the measured potential distribution at the 18th day for experiment T8V3 (constant voltage 3.5 V, 18 days) and at the 15th day for T8S1 and T8S3 (constant voltage 20 V, 30 days) as shown in Figure 4.20. It was found that a considerable portion of the applied total electrical potential was lost at the electrodes. 1.35 V out of the supplied 3.5 V, or 39% of total, was delivered to the kaolin for T8V3 at the time of measurement. 61% of the total voltage was lost at the electrodes. The losses measured at the 15th day for T8S1 and T8S3 were 93% and 89%, respectively. Figure 4.20 also indicated that the majority of the electric potential losses went to anode electrode. It was reported that rod-like electrodes could suffer large potential losses as the electric field converges in the vicinity of the electrodes (Murdoch and Chen, 1997).

Experiment T8S3 (constant voltage 20 V, 30 days) used a piece of filter paper to prevent the fine kaolin particles from being taken into the effluent tubing. As shown in Figure 4.20, approximately 1 V of the electrical potential was lost across the filter paper. Nevertheless, the presence of the filter paper between the cathode electrode and the kaolin underneath in was not found to affect the overall distribution of the electric field.

As shown in Figure 4.20, the electric fields were non-uniform, especially at locations near the electrodes. Larger electrical potential was concentrated at the upper layers of the kaolin (the kaolin near the cathodes) than the layer at lower half. The electric fields became stronger when the measured locations were closer to electrodes; meanwhile the electric fields were stronger in the inner zone than in the outer zone of the kaolin in the same reactor. However, the distribution pattern of the contaminants left in the kaolin after treatment was not found to correlate closely with the distribution of the electric field as discussed in the Section 4.6.8 for heavy metals and Section 4.7.4 for organic contaminants.

Figure 4.20 Electric fields for T8V3 (constant voltage 3.5 V), T8S1(constant voltage 20 V) and T8S1 (constant voltage 20 V)

outer zone (outer ring) (Figure 4.21). The stronger electric fields in the inner zone of the kaolin under treatment (Figure 4.20) were believed to transport heavy metal ions faster than in outer zone. Meanwhile, organic contaminants, including phenanthrene, in the inner zone were also found to be removed faster than that of outer zone of the same layer as discussed in Section 4.7.4 (Figure 4.22).

Figure 4.21 Pb concentration in kaolin after UESR treatment in T8S1, T8S2, and T8S3

Figure 4.22 Phenanthrene concentration in kaolin after UESR treatment in T8S1, T8S2, and T8S3

Nonetheless, Figure 4.23 and Figure 4.24 revealed that moisture contents in the inner zone of treated kaolin were, in most cases, higher than that of the corresponding outer zone. Therefore the kaolin in outer zone under treatment in fact had higher average moisture content reductions and hence higher electroosmotic pore water flows than the kaolin in inner zone. It strongly suggested that the mechanism that transported the pore water might not be the same as that worked with phenanthrene. There might also be a mechanism that transported pore water and phenanthrene but in different direction.

Figure 4.23 Moisture content of kaolin after UESR treatment in T7M3 and T7M4

Figure 4.24 Moisture content of kaolin after UESR treatment in T8S1, T8S2, and T8S3

It was clear that dielectrophoresis transported certain amount of pore water as well as phenanthrene in the contaminated kaolin during the UESR treatment. Pore water had the highest dielectric constant (around 79) and phenanthrene had the lowest dielectric constant (2.8) among the components of the contaminated kaolin mixture (Lide 2003). Dielectrophoretic migration of pore water and phenanthrene in the soil medium due to the non-uniform electric field was therefore in opposite directions (equation 2.20). Having a higher dielectric constant than the surrounding kaolin, the pore water moved towards places of higher electric field strength (inner zone). Phenanthrene, on the other hand, moved toward the places of lower electric field strength (outer zone). Nevertheless, dielectrophoresis might not be the main mechanism that removed phenanthrene from the soils as the effect of dielectrophoresis was reported to be much less than electroosmosis when conducting electrodes were used (Shang 1997; Shang and Lo 1997).

It was evident that dielectrophoresis played a part in the UESR treatment investigated in this study; however, it remained unclear whether dielectrophoresis significantly enhanced the removal of phenanthrene.

Chapter 5 Conclusions and Recommendations

In this research, an innovative soil remediation technology, upward electrokinetic soil remedial (UESR) technology, was proposed and verified by 19 lab-scale experiments. UESR was demonstrated capable of simultaneously removing heavy metals, p-xylene, and phenanthrene from kaolins. The removal efficiencies obtained were 43.1% for As, 49.7% for Cr, 68.3% for Ni, 71.5% for Cu, 59.3% for Zn, 52.5% for Pb, 67.2% for Cd, 92.8% for p-xylene, and 66.9% for phenanthrene after 6-9 days of UESR treatment. Higher removal efficiencies could be achieved if longer durations were used.

5.1 Conclusions on Heavy Metal Removal in UESR

Based on the results obtained, the conclusions on the heavy metals removal by UESR can be drawn as:

- 1) For experiments conducted with constant currents, the removal efficiencies of heavy metals were inversely proportional to the specimen cross sectional area whereas were proportional to the current density. The removal efficiencies increased sharply (200%-500%) when the current density increased from 0.097 to 0.191 mA/cm². The increments for all heavy metals gradually reduced when current density further increased from 0.191 to 0.39 mA/cm² due to the excess amount of hydroxyl ions generated at the cathode.
- 2) For experiments conducted with constant voltages, the removal efficiencies of heavy metals showed no correlation with the specimen cross sectional area but were proportional to the voltage gradient.
- 3) The cathode chamber influents, either distilled water or 10⁻² N HNO₃, affected the heavy metals removal from the contaminated kaolin, but the effects varied with specific heavy metals. In some cases, the use of 10⁻² N HNO₃ enhanced the removal of Cu(II) and Cd(II), but hindered the removal of Pb (II) and As (III) at the same time.

- 4) The cathode chamber influents, either distilled water or 10^{-2} N HNO_3 , affected the distribution of heavy metals in kaolin specimens and cathode chamber effluent after UESR treatment. Experiments using 10^{-2} N HNO_3 had most of the removed heavy metals in cathode chamber effluent, while experiments using distilled water had most of the removed heavy metals deposited/precipitated on the cathode electrode as well as on the kaolin in the vicinity of cathode electrode due to the alkaline condition at cathode.
- 5) The remained contents of heavy metals in the inner zone were higher than that of the respective outer zone for experiments using with distilled water as cathode chamber influent. Nevertheless, the distribution of heavy metals was rather uniform between inner and outer zones for experiments using 10^{-2} N HNO_3 as cathode chamber influent. These distribution patterns were found to match the pH profile in the treated specimens.
- 6) The removal efficiencies for all the metals investigated were positively related to the treatment duration. The removal efficiencies of Cu(II), Cd(II), and Ni(II) had a different pattern of increase from that of As(III), Cr(III), Zn(II), and Pb(II) when treatment duration extended from 4 days to 6 days, and further extended to 9 days. Substantial increment to the removal efficiencies of the first group of heavy metals occurred during the second extension (6 to 9 days), while it occurred during the first extension (4 to 6 days) for the first group of heavy metals.
- 7) As(III) and Cr(III) were found to be the least mobile metals while Ni(II) and Cd(II) were found to be the most mobile metals. In most cases, the mobility of heavy metals followed the order $\text{Ni(II)} > \text{Cd(II)} > \text{Zn(II)} \approx \text{Cu(II)} > \text{Pb(II)} > \text{As(III)} > \text{Cr(III)}$. The results of Cd, Pb, and Cr were in good agreement with their reported effective mobility ($\text{Cd} > \text{Pb} > \text{Cr}$) (Acar and Alshawabkeh 1993).
- 8) The removal efficiencies of heavy metals were affected by the ionic strength of soil pore solution. Higher removal efficiencies of heavy metals were obtained from experiments using Kaolin II than those using Kaolin I because kaolin II had lower background ionic strength, or conductivity.
- 9) The removal efficiencies of heavy metals were affected in different ways when organic compounds were presented as co-contaminants and cathode

chamber influent was distilled water. The removal of Cu was enhanced with the presence of organic compounds, while the removal of Pb was hindered. However, there was no obvious effect by the introduction of organic contaminants on heavy metal removal efficiencies when experiments were carried out using 10^{-2} N HNO_3 as cathode chamber influent.

5.2 Conclusions on Organic Contaminants Removal in UESR

The conclusions on the removal of p-xylene and phenanthrene, which were presented as co-contaminants in the heavy metal contaminated kaolins are as follows

- 1) Higher removal efficiencies (82.8-92.8%) were observed for p-xylene after 6 days' treatment with constant current 15 mA, while the removal efficiencies were much lower (38.5-55.2%) for phenanthrene after the same treatment. Furthermore, 47.3-52.0% of phenanthrene was removed from contaminated kaolin when experiments were conducted with constant voltage 20 V for 30 days.
- 2) The removal efficiencies of p-xylene were higher than those of phenanthrene probably because p-xylene has much higher solubility than phenanthrene in water. Similar findings were reported by Bruell and Segal (1992) that organic substances with high water solubility were easily removed from clayey soils by electrokinetics treatment.
- 3) The size of the contaminated kaolin specimen affected the removal efficiencies of organic contaminants. For specimens treated with constant current 15 mA, those specimens with a smaller cross sectional area had higher phenanthrene removal efficiencies because of higher current density. Meanwhile, the removal efficiency of phenanthrene was higher for the specimen with larger height.
- 4) Cathode chamber influent, either distilled water or 10^{-2} N HNO_3 , affected the removal of both p-xylene and phenanthrene. The removal efficiencies of both organic contaminants were higher in experiments using distilled water than those using 10^{-2} N HNO_3 . This could be due to the smaller electroosmotic

- pore water flow resulted by the lower pH profile in the specimen when cathode chamber influent was 10^{-2} N HNO_3 .
- 5) The amount of contaminants observed in cathode chamber effluent was affected by both the cathode chamber influent and the solubility of the organic contaminants. The concentrations of p-xylene in cathode chamber effluent were higher when distilled water was supplied as the cathode chamber influent. The concentrations of phenanthrene in cathode chamber effluent were only around 1 mg/L since phenanthrene has water solubility approximately 1 mg/L.
 - 6) The removal efficiencies of both p-xylene and phenanthrene were affected by the ionic strength of soil pore solution. Higher removal efficiencies of the organic contaminants were observed from experiments using Kaolin II than those using Kaolin I because the pore solution of Kaolin I had higher ionic strength which diminished the zeta potential of the kaolin mineral and the electroosmotic flux.
 - 7) The concentrations of both p-xylene and phenanthrene remained in the inner zone were lower than their concentrations in the respective outer zone. The organic contaminants in the inner zone seemed to be removed faster than in the outer zone probably because the electric fields were not uniform and the field strength was larger in the inner zone.
 - 8) It was clear that dielectrophoresis transported part of the kaolin pore water and organic contaminants, especially phenanthrene, in the specimens treated by UESR.

5.3 Conclusions on Energy Consumption

The energy consumption for the experiments conducted ranged from 7.9 to 499.8 kWh/m³. The lowest energy cost was observed for T2S2 (Ø140 mm; 18 days; 10^{-2} N HNO_3 as cathode chamber influent) to be 1.29 S\$/m³, while the highest energy cost was observed for T1S1 (Ø70 mm; 6 days; distilled water as cathode chamber influent) to be 81.71 S\$/m³. The results showed that the use of 10^{-2} N HNO_3 significantly reduced the cost of energy. The energy consumptions were usually higher for experiments conducted with higher current density, longer duration, and

larger voltage gradient. The energy expenditures of the experiments in this study were comparable to the reported values, 18 to 700 kWh/m³, in the previous studies (Acar et al. 1990; Hamed et al. 1991; Acar et al. 1992; Segal and Bruell 1992; Hicks and Tondorf 1994; Acar et al. 1994; Yeung et al. 1996; Puppala et al. 1997; Alshawabkeh et al. 1999; Chung and Kang 1999; and Reddy et al. 2001). The normal energy consumption for total removal of metals from contaminated soils was believed to be 500 kWh/m³ (Acar and Alshawabakeh 1996).

5.4 Recommendation for Future Study

The work presented in this thesis expanded the varieties of electrokinetic remediation and introduced the UESR system for electrokinetic soil remediation. A few issues recommended for further studies are summarized below.

- Heavy metals like arsenic and chromium can form both cationic and ionic groups in subsurface. It caused the uncertain direction of migration and caused retardation to the removal of these metals. Further work is needed to investigate the transformation and migration of these metals in electrokinetic remediation.
- Electrodes material and design affect the overall electric fields, energy efficiency, and the cost of installation. Rod-shaped electrodes were easier to install but they may give rise to appreciable energy loss on electrodes. Further studies shall be carried out to improve the electrode design by comparing electrodes of different shapes and materials.
- The application of different cathode chamber influents had profound impact on the pH, pore water flow, and distribution of electric fields in the soil under UESR treatment. As a result, the removal efficiencies of contaminants and the distribution of contaminants among various fractions of the contaminated soil and cathode effluent were affected. Further investigation can be conducted to study the effect of using other cathode chamber influents such as other diluted acids, organic acids, as well as organic surfactants.

- Comprehensive studies shall be performed to examine the interactions between heavy metals, organic compounds, and the surface of clay minerals in subsurface during electrokinetic treatment.
- It was also recommended that further research be carried out with focus on the application of dielectrophoresis in soil remediation. Since most of the organic contaminants have much lower dielectric constants than the surrounding media, dielectrophoresis can provide a viable option to existing soil remedial technologies.

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APPENDIX A

KAOLIN PARTICLE SIZE DISTRIBUTION

Particle Size of Kaolin I and Kaolin II

APPENDIX B

FINAL PH OF TREATED KAOLIN

Table B-1 Final pH of Treated Soils

	T1D1			T1D2			T1D3		
	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average
0 cm									
2 cm	7.3	5.75	6.2	5.3	6.6	6.2	5.3	4.0	4.4
4 cm	5.7	3.8	4.4	3.1	2.8	2.9	2.7	2.7	2.7
6 cm	3.1	3.1	3.1	2.6	2.6	2.6	2.5	2.6	2.5
8 cm	2.8	2.75	2.8	2.4	2.6	2.5	2.3	2.2	2.3
10 cm	2.6	2.7	2.7	2.1	2.3	2.2	2.2	2.2	2.2

	T1F1			T7M2			T7M3		
	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average
0 cm									
2 cm	1.9	2	2.0	3.3	3.2	3.2	2.4	2.3	2.3
4 cm	1.9	2.1	2.0	2.7	2.8	2.8	2.1	2.1	2.1
6 cm	1.9	1.9	1.9	2.6	2.9	2.8	1.9	2	2.0
8 cm	1.9	1.8	1.8	2.6	2.1	2.3	1.8	1.9	1.9
10 cm	1.7	1.7	1.7	2.6	2.6	2.6	1.4	1.8	1.7

	T1S4				T1S1	T7M5	T7M4		
	Inner zone	Outer zone	Average		pH	pH	Inner zone	Outer zone	Average
0 cm									
2 cm	2.7	2.3	2.4		5.3	3.1	3.2	3.3	3.3
4 cm	2.6	2.3	2.4		3.4	2.8	2.6	2.5	2.5
6 cm	2.2	2.3	2.3		2.5	2.5	2.3	2.2	2.2
8 cm	2.3	2.1	2.2		2.2	2.5	1.8	1.8	1.8
10 cm	2.3	2.1	2.2		2.1	2.2	1.7	1.8	1.8

	T8V1			T8V2			T8V3		
	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average
0 cm									
2 cm	3.0	2.8	2.9	2.7	2.8	2.8	3.2	3.3	3.2
4 cm	2.7	2.7	2.7	2.7	2.7	2.7	3.0	3.2	3.1
6 cm	2.6	2.6	2.6	2.6	2.5	2.5	2.9	3.1	3.0
8 cm	2.2	2.4	2.4	2.5	2.4	2.4	2.8	3.1	3.0
10 cm	2.2	2.4	2.3	2.1	2.3	2.2	2.9	2.9	2.9

Note: Average pH values were determined based on the mass of inner zone and out part.

APPENDIX B

FINAL PH OF TREATED KAOLIN

Table B-2 Final pH of Treated Soils (continued)

	T2S1			T2S2
	Inner zone	Outer zone	Average	pH
0 cm				
2 cm	3.6	3.6	3.6	3.8
4 cm	3.3	3.4	3.4	3.4
6 cm	3.3	3.4	3.4	3.2
8 cm	3.2	3.2	3.2	3.2
10 cm	3.3	3.1	3.2	3.2
12 cm	3.3	3.3	3.3	3.1
14 cm	3.3	3.1	3.2	3.0
16 cm	3.0	3.0	3.0	3.0
18 cm	3.2	3.0	3.1	2.9
20 cm	3.0	2.9	2.9	2.8
22 cm	3.0	2.8	2.9	2.9
24 cm	2.9	2.9	2.9	2.8
26 cm	2.9	2.9	2.9	2.9
28 cm	2.6	2.8	2.7	2.9
30 cm	2.7	2.7	2.7	2.9

	T7M6
	pH
0 cm	
2 cm	3.5
4 cm	3.2
6 cm	3.0
8 cm	2.6
10 cm	2.6
12 cm	2.5
14 cm	2.3
16 cm	2.3

	T8S1			T8S2			T8S3		
	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average
0 cm									
2 cm	3.0	3.2	3.1	3.0	3.3	3.2	3.2	3.2	3.2
4 cm	3.2	3.1	3.1	2.9	3.0	3.0	3.1	2.8	2.9
6 cm	3.1	3.1	3.1	3.1	3.0	3.0	2.9	3.0	2.9
8 cm	3.0	2.9	2.9	2.9	2.8	2.8	2.8	2.8	2.8
10 cm	2.8	2.9	2.9	3.0	2.8	2.9	2.8	2.8	2.8
12 cm	2.9	2.9	2.9	2.8	2.6	2.6	2.9	3.0	3.0
14 cm	2.8	2.9	2.9	2.9	2.9	2.9	3.0	2.9	2.9
16 cm	3.0	3.1	3.0	2.9	3.1	3.0	2.7	3.1	3.0
18 cm	2.9	3.2	3.1	3.0	3.1	3.1	3.0	2.9	2.9
20 cm	3.1	3.1	3.1	3.0	3.0	3.0	3.2	3.0	3.0

Note: Average pH values were determined based on the mass of inner zone and out part.

APPENDIX C

WATER CONTENTS OF KAOLIN

Table C-1 Initial and Final Water Content of Treated Soils (%)

	T1D1			T1D2			T1D3		
	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average
Initial			63			74.0			65.5
2 cm	72.0	67.2	68.8	70.4	76.0	74.2	68.1	67.3	67.6
4 cm	66.3	63.8	64.6	74.1	76.5	75.7	64.8	64.8	64.8
6 cm	63.4	64.0	63.8	69.8	70.7	70.4	64.7	65.1	64.9
8 cm	64.5	64.0	64.2	75.5	77.4	76.7	64.9	63.8	64.1
10 cm	62.6	63.8	63.4	74.0	70.0	71.3	65.5	64.6	64.9

	T1F1			T7M2			T7M3		
	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average
Initial			62			50			61
2 cm	60.5	60.7	60.6	53.8	53.8	53.8	60.9	59.9	60.2
4 cm	61.4	60.0	60.5	55.0	56.2	55.8	61.8	59.8	60.4
6 cm	61.2	59.8	60.2	54.0	55.5	55.0	63.0	61.1	61.7
8 cm	61.3	60.9	61.0	53.0	55.3	54.5	62.7	61.5	61.9
10 cm	61.4	60.3	60.7	53.5	54.9	54.5	62.1	61.3	61.6

	T7M4			T7M5	T1S1
	Inner zone	Outer zone	Average		
Initial			61	61	63.0
2 cm	59.3	57.5	58.1	54.4	65.9
4 cm	60.0	59.2	59.5	52.0	63.6
6 cm	61.9	59.9	60.6	54.0	62.1
8 cm	62.3	61.1	61.5	53.3	61.8
10 cm	62.0	61.1	61.4	56.8	63.7

	T1S4		
	Inner zone	Outer zone	Average
			59.0
	62.8	61.4	61.9
	59.1	60.1	59.8
	59.0	59.4	59.2
	58.9	59.6	59.4
	60.1	60.6	60.4

	T8V1			T8V2			T8V3		
	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average
Initial			61			61			61
2 cm	56.9	57.7	57.4	58.9	59.0	59.0	56.2	57.4	57.0
4 cm	58.4	58.2	58.3	60.4	59.9	60.0	57.4	57.2	57.2
6 cm	59.5	58.9	59.1	60.3	58.6	59.2	58.1	58.0	58.0
8 cm	59.9	58.5	58.9	60.0	58.2	58.8	58.3	58.1	58.2
10 cm	59.0	59.2	59.1	59.9	58.4	58.9	57.6	57.6	57.6

Note: Average water content values were determined based on the mass of inner zone and out part.

APPENDIX C

WATER CONTENTS OF KAOLIN

Table C-2 Initial and Final Water Content of Treated Soils (%) (continued)

	T2S1			T2S2
	Inner zone	Outer zone	Average	
Initial			53	60
2 cm	54.7	53.7	54.1	67.4
4 cm	53.2	51.5	52.1	63.0
6 cm	53.0	51.9	52.3	62.4
8 cm	52.4	51.7	51.9	62.8
10 cm	52.8	51.9	52.2	62.0
12 cm	53.1	47.2	49.2	61.9
14 cm	54.1	52.5	53.0	61.0
16 cm	54.0	52.8	53.2	61.3
18 cm	53.9	52.2	52.8	60.0
20 cm	53.8	52.2	52.7	60.2
22 cm	53.0	51.5	52.0	59.7
24 cm	52.1	51.0	51.3	60.6
26 cm	51.4	51.2	51.2	60.0
28 cm	51.2	48.9	49.7	61.3
30 cm	49.9	48.2	48.8	59.3

	T7M6
	61
2 cm	58.4
4 cm	58.4
6 cm	58.1
8 cm	58.1
10 cm	57.7
12 cm	58.6
14 cm	58.1
16 cm	57.4

	T8S1			T8S2			T8S3		
	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average	Inner zone	Outer zone	Average
Initial			60			53			49
2 cm	58.3	58.9	58.7	53.7	52.8	53.1	50.8	54.4	53.2
4 cm	58.2	59.8	59.2	52.6	52.0	52.2	53.6	49.9	51.1
6 cm	58.7	58.2	58.3	52.5	51.4	51.8	52.2	50.8	51.2
8 cm	58.6	56.9	57.5	52.4	51.7	52.0	51.3	51.1	51.1
10 cm	57.2	55.2	55.8	52.4	50.7	51.3	49.4	50.3	50.0
12 cm	56.1	54.4	54.9	53.1	51.6	52.1	47.9	47.9	47.9
14 cm	55.5	52.7	53.6	53.8	51.9	52.5	46.7	46.9	46.9
16 cm	55.2	53.3	54.0	52.6	50.7	51.4	45.1	45.6	45.4
18 cm	54.5	53.4	53.8	51.6	50.3	50.8	44.7	46.0	45.5
20 cm	54.0	53.0	53.3	52.0	50.0	50.6	45.2	45.9	45.7

Note: Average water content values were determined based on the mass of inner zone and out part.

Table D-1 Treatment Conditions and Removal Rates of Heavy metals

	T1D1	T1D2	T1S1	T1D3	T1S4	T2S2	T2S1	T7M2	T7M3
Cell Diameter (mm)	100	100	70	100	140	70	140	100	100
Cell Height (mm)	100	100	100	100	100	300	300	100	100
Current (mA)	15	15	15	15	15	15	15	15	15
Duration (Days)	9	6	6	4	6	18	18	6	6
Cathode chamber influent	Distilled water					0.01 M HNO ₃			
pH	3.0	2.8	3.0	2.8	2.5	3.0	3.1	3.0	2.6
Moisture Content, %	63	72	63	66	59	60	53	50	61
As Removal, %	27.0	26.0	43.1	1.8	11.1	3.0	13.9	23.2	
Cr Removal, %	49.7	45.6	52.3	16.0	8.6	13.0	1.9		
Ni Removal, %	68.3	50.0	56.6	43.9	11.8	37.7	27.2	57.2	
Cu Removal, %	51.2	33.8	45.9	27.7	11.1	38.3	24.1	56.2	51.8
Zn Removal, %	49.6	51.6	59.3	14.4	10.2	37.3	25.5	53.2	
Pb Removal, %	52.5	42.1	48.4	6.4	7.4	20.1	18.2	35.7	38.4
Cd Removal, %	67.2	42.8	50.5	31.3	12.1	34.3	24.7	56.4	

	T7M4	T7M5	T7M6	T8V1	T8V2	T8V3	T8S1	T8S2	T8S3
Cell Diameter (mm)	100	70	70	100	100	140	140	140	140
Cell Height (mm)	100	100	160	100	100	100	200	200	200
Current/ Voltage	15 mA	15 mA	15 mA	3.5 V	3.5 V	3.5 V	20 V	20V	20V
Duration (days)	6	6	6	18	6	18	30	30	30
Cathode chamber influent	0.01 M HNO ₃								
pH	2.6	3.6	3.6	2.6	2.6	3.0	4.4	4.9	4.9
Moisture Content, %	61	61	61	61	61	61	60	53	49
As Removal, %				12.9	15.4	17.7			
Cr Removal, %				12.6	27.2	5.5			
Ni Removal, %				65.3	32.8	64.3			
Cu Removal, %	44.0	71.5	62.1	62.5	32.2	63.3			
Zn Removal, %				61.0	30.6	60.4			
Pb Removal, %	25.4	43.5	35.2	44.9	25.9	43.9	68.6	62.2	78.1
Cd Removal, %				61.3	32.0	62.8			

APPENDIX E

CATHODE EFFLUENT pH

Table E-1 Cathode Effluent pH

	T1D1
Time (hrs)	Cathode pH
0	3.7
5	4.8
19	10.4
31	9.1
43	7.1
48	6.7
52	6.6
72	5.1
78	7
91	6.7
97	6.2
126	9.5
137	8.8
149	9.2
162	9.6
172	9.4
184	8.1
196	8
208	7.2
216	7.2

	T1D2
Time (hrs)	Cathode pH
0	4
2	4.4
5	4
20	4.7
24	7.1
28	7.1
42	6.4
47	5.4
52	4.5
97	5.5
100	5.9
106	5.7
118	5.3
130	4.6
146	4.6

	T1S1
Time (hrs)	Cathode pH
0	4
2	4.3
5	4.9
20	5.3
24	5.9
28	5.3
42	5
47	4.9
52	6
97	4.5
100	4.7
106	4.8
118	4.8
130	4.7
146	4.8

	T7M2
Time (hrs)	Cathode pH
0	2.1
24	2.6
36	2.7
48	2.1
60	2.2
72	2
84	2.4
108	2.1
120	2
132	2.1
144	2.1

	T1S4
Time (hrs)	Cathode pH
0	1.5
12	2.1
24	1.8
36	2.5
60	2.6
72	2.6
84	2.8
96	2.9
108	2.7
120	2.6
132	2.5
144	3

	T1F1
Time (hrs)	Cathode pH
0	1.7
8	1.9
20	2
32	1.9
44	1.9
56	1.8
68	2
80	2
92	2.2
104	2.2
116	2.3
128	2
144	2.1

	T7M3	T7M4
Time (hrs)	Cathode pH	Cathode pH
0	2.6	3.5
12	4.4	8.95
24	2.1	8.8
36	2.1	8.8
48	2.2	8.8
72	2.2	9.1
84	2.1	8.8
96	2.7	8.8
108	2.6	9
120	2.1	8.9
132	1.9	8.4
144	1.9	8.4

	T7M5	T7M6
Time (hrs)	Cathode pH	Cathode pH
0	2.7	2.9
12	2.5	2.4
24	2.5	2.5
36	2.4	2.3
48	2.3	2.3
60	2.3	2.2
72	2.3	2.3
84	2.2	2.2
96	2.2	2.2
108	2.2	2.2
120	2.2	2.2
132	2.2	2.2
144	2.2	2.2

	T1D3-1
Time (hrs)	Cathode pH
0	3.3
12	4.2
22.5	4
34.5	4.4
59	4
71	6.4
83	5.9
96	6.9

	T1D3-2
Time (hrs)	Cathode pH
0	3.4
12	3.5
22.5	4.1
34.5	6
59	5.7
71	6.9
83	8.8
96	7.4

Table E-2 Cathode Effluent pH (continued)

	T2S1
Time (hr)	pH
0	2.14
7	1.7
19	1.8
31	2
44	2.2
56	2.3
68	1.8
80	1.8
92	1.8
104	2.3
116	2.3
152	2.2
164	2.2
176	1.8
188	1.8
200	1.8
212	1.8
224	1.8
236	1.8
260	2.3
272	2.6
284	2.2
296	3
308	2.2
320	2.2
332	2.7
344	2.7
356	2.3
368	2.2
380	2.2

	T2S2
Time (hr)	pH
0	1.6
11	2.2
22	2.3
32	1.8
47.5	1.8
56	1.9
70	2.1
79.5	2.2
93.5	2.2
106	2.2
118	2
130	2.6
142	2.3
156	2.5
189	2.4
199	2
213	2.1
225	1.6
238	1.6
250	1.6
263	1.8
274	2.9
286	2.8
298	2.5
310	2.4
322	2.6
334	2.4
340	2.5
355	2
367	2.6
379	2.5
391	2.4
403	2.4
415	2.4
427	2.4
432	2.4

	T8V1	T8V3	T8V3
Time (hrs)	pH	pH	pH
0	2.1	2.2	2.2
6	2.15	2.2	2.2
8	2.11	2.15	2.15
16	2.15	2.21	2.21
28	2.17	2.26	2.26
40	2.22	2.28	2.28
52	2.17	2.23	2.23
64	2.19	2.22	2.22
76	2.21	2.24	2.24
88	2.15	2.18	2.18
100	2.33	2.3	2.3
124	2.17	2.21	2.21
136	2.28	2.18	2.18
144	2.24	2.2	2.2
156	2.13	2.21	2.21
168	2.15	2.17	2.17
180	2.15	2.15	2.15
192	2.15	2.2	2.2
204	2.11	2.14	2.14
216	2.15	2.16	2.16
228	2.08	2.12	2.12
240	2.19	2.21	2.21
252	2.1	2.13	2.13
264	2.2	2.19	2.19
276	2.24	2.33	2.33
288	2.14	2.24	2.24
300	2.32	2.34	2.34
312	2.24	2.32	2.32
324	2.18	2.25	2.25
336	2.14	2.27	2.27
348	2.16	2.26	2.26
360	2.16	2.3	2.3
372	2.18	2.27	2.27
384	2.14	2.26	2.26
396	2.2	2.24	2.24
408	2.18	2.24	2.24
420	2.18	2.24	2.24
432	2.26	2.33	2.33

Table E-3 Cathode Effluent pH (continued)

	T8S1		T8S2	T8S3
Time (hrs)	pH	Time (hrs)	pH	pH
6	10.74	6	2.25	9.56
18	11.23	18	2.39	11.07
30	3.07	30	2.55	10.63
42	2.56	42	2.65	11.12
54	2.72	54	3.31	5.91
66	2.5	66	2.74	3.51
78	2.48	78	2.74	3.91
80	2.54	90	3.53	4.26
92	2.42	102	3.65	2.43
104	2.39	114	3.73	2.39
116	2.27	126	2.72	2.38
128	2.2	138		2.34
140	2.1	150	2.3	2.27
152	2.52	162	2.45	2.91
164	2.45	186	2.49	3.08
176	2.12	210	2.72	2.71
188	2.53	234	2.24	3.87
200	2.97	246	2.21	3.82
212	2.8	258	2.19	2.65
224	2.84	270	2.15	2.51
236	3.01	282	2.14	2.4
248	2.35	294	2.15	2.34
260	2.35	306	2.24	2.44
272	2.41	318	2.18	
296	2.52	330	2.19	2.33
320	2.41	354	2.18	2.13
344	2.16	366	2.83	6.6
356	2.22	378	2.13	2.65
368	2.17	390	2.62	3.84
380	2.17	402	2.43	2.6
392	2.13	426	2.33	2.31
404	2.13	438	2.3	2.24
416	2.27	462	2.27	2.22
428	2.22	474	2.22	2.18
440	2.25	486	2.19	2.15
464	2.23	498	2.17	2.11
476	4.16	522	2.19	2.13
488	1.74	534	2.14	2.16
500	4.16	546	2.17	2.17
512	2.72	558	2.14	2.16
536	2.44	570	2.15	2.14
548	2.46	582	2.17	2.17
572	2.36	594	2.13	2.13
584	2.33	606	2.1	2.13

	T8S1		T8S2	T8S3
Time (hrs)	pH	Time (hrs)	pH	pH
596	2.28	618	2.13	2.13
608	2.22	642	2.16	2.14
632	2.25	654	2.18	2.15
644	2.23	666	2.17	2.15
656	2.29	678	2.1	2.11
668	2.27	702	1.97	1.95
680	2.23	726	2.19	2.2
692	2.25	740	2.21	2.26
710	2.24			

APPENDIX F HEAVY METALS IN CATHODE EFFLUENT

Table F-1 Heavy Metal Amounts and Concentrations in Cathode Effluent

		T1F1			T1S4			T2S1
	Total in effluent (mg)	Average Concentration (ppm)		Total in effluent (mg)	Average concentration (ppm)		Total in effluent (mg)	Average concentration (ppm)
As	55.2	4.7		16.5	1.6		74.15	2.60
Cr	0.1	0.0		0.0	0.0		0.27	0.01
Ni	60.9	5.2		29.7	2.9		299.25	10.48
Cu	57.9	4.9		28.3	2.8		205.06	7.18
Zn	64.4	5.5		32.1	3.2		329.75	11.55
Pb	43.5	3.7		23.7	2.3		195.36	6.84
Cd	54.6	4.6		30.1	3.0		314.00	10.99

		T7M3			T7M4			T7M5
	Total in effluent (mg)	Average concentration (ppm)		Total in effluent (mg)	Average concentration (ppm)		Total in effluent (mg)	Average concentration (ppm)
Cu	205.6	20.4		50.7	5.03		133.4	13.23
Pb	129.1	12.8		30.8	3.06		69.5	6.90

		T8V2			T8V1			T8V3
	Total in effluent (mg)	Average concentration (ppm)		Total in effluent (mg)	Average concentration (ppm)		Total in effluent (mg)	Average concentration (ppm)
As	16.00	2.15		23.16	0.93		29.43	2.17
Cr								
Ni	47.59	5.51		96.76	3.44		75.05	5.99
Cu	52.11	6.06		100.50	3.57		79.68	5.78
Zn	54.00	6.31		111.29	3.96		84.65	6.68
Pb	43.70	5.21		87.45	3.12		67.86	5.26
Cd	48.96	5.84		97.05	3.51		78.78	6.01

		T2S2			T7M2			T7M6
	Total in effluent (mg)	Average concentration (ppm)		Total in effluent (mg)	Average Concentration (ppm)		Total in effluent (mg)	Average concentration (ppm)
As	58.19	1.924		22.9	2.27			
Cr	0.28	0.009						
Ni	253.34	8.378		69.0	6.84			
Cu	174.12	5.758		74.4	7.38		169.4	16.81
Zn	278.26	9.202		76.7	7.61			
Pb	158.27	5.234		55.0	5.46		91.6	9.08
Cd	259.38	8.577		67.1	6.66			

		T8S1			T8S2			T8S3
	Total in effluent (mg)	Average concentration (ppm)		Total in effluent (mg)	Average Concentration (ppm)		Total in effluent (mg)	Average concentration (ppm)
Pb	321.89	4.28		217.59	2.74		263.64	2.52

APPENDIX F

HEAVY METALS IN CATHODE EFFLUENT

Table F-2 P-xylene Concentration in T7M3 and T7M4 Cathode Effluent

	T7M3			T7M4	
Time (hours)	P-xylene concentration in effluent (mg/l)	Mass (mg)		P-xylene concentration in effluent (mg/l)	Mass (mg)
0	3.79	3.18		3.89	3.27
12	3.7	3.11		9.7	8.15
24	9.02	7.58		3.68	3.09
36	6.02	5.06		9.36	7.86
48	3.89	3.27		9.61	8.07
60	4	3.36		10.58	8.89
84	5.9	4.96		8.8	7.39
96	3.96	3.33		10.75	9.03
108	6.04	5.07		3.68	3.09
120	6.13	5.15		9.49	7.97
132	6.43	5.40		8.51	7.15
144	5.34	4.49		9.63	8.09
	Total mass (mg)	53.94		Total mass (mg)	82.05
	Average concentration (mg/l)	5.35		Average concentration (mg/l)	8.14

APPENDIX G

VOLTAGE AND CURRENT

Table G-1 Voltage and Current

T1D1		T1D2		T1S1		T1F1	
Time (hrs)	Voltage (V)	Time (hrs)	Voltage (V)	Time (hrs)	Voltage (V)	Time (hrs)	Voltage (V)
0	4	0	3.4	0	4	0	2.2
5	4	2	4	2	4.7	8	2.6
19	4	5	8	5	61	20	2.8
31	21	20	52	20	82	32	3
43	21	24	68	24	100	44	3.2
48	25	28	85	28	105	56	3.4
52	30	42	93	42	50	68	3.4
72	55	47	75	47	55	80	3.5
78	72	52	61	52	51	92	4.1
91	79	97	95	97	80	104	5.1
97	66	100	125	100	90	116	6
126	85	106	100	106	110	128	4.6
137	94	118	120	118	120	144	5
149	112	130	120	130	115		
162	131	146	140	146	125		
172	132						
184	163						
196	156						
208	141						
216	143						

T1S4		T7M3		T7M4
Time (hrs)	Voltage (V)	Time (hrs)	Voltage (V)	Voltage (V)
0	2.7	2	4.1	4.7
12	2.8	19	6.5	101.4
24	2.8	31	4.2	118.2
36	2.3	43	4.2	156
60	2.4	55	4.3	137.5
72	2.6	79	4.7	111.2
84	3	91	5.1	112.6
96	3.2	103	7.3	103.4
108	3.9	115	7.8	106.3
120	5	127	5.4	96.7
132	6.2	139	5.4	95.4
144	6.9	144	4.8	90

T7M5		T7M6
Time (hrs)	Voltage (V)	Voltage (V)
0	6.6	7.8
12	7.6	8.6
24	11	12
36	7.5	11.2
48	6.8	10.6
60	5.4	8.4
72	5.3	8.5
84	4.4	7.4
96	4.4	7.3
108	4.2	6.7
120	4.2	6.6
132	4.1	6.1
144	4.3	5.7

Table G-2 Voltage and Current (continued)

T2S1		T2S2		T8V1		T8V2	T8V3
Time (hr)	Voltage (V)	Time (hr)	Voltage (V)	Time (hrs)	Current (mA)	Current (mA)	Current (mA)
0	3.3	0	3.2	0	12	16	32
7	2.8	11	3.8	6	11	16	23
19	2.8	22	4.9	8	11	16	26
31	2.9	32	5.3	16	9	16	19
44	2.9	48	5.7	28	8	15	20
56	2.6	56	6.9	40	10	14	18
68	2.6	70	9.2	52	10	13	16
80	2.5	80	10.7	64	9	13	16
92	2.5	94	12.5	76	10	14	16
104	2.5	106	11.2	88	10	15	16
116	2.5	118	11.5	100	8	12	12
152	2.4	131	12.5	124	9	11	11
164	2.3	142	13.3	136	10	12	10
176	2.3	156	12.8	144	10	11	11
188	2.3	189	13.2	156	9		13
200	2.3	199	12.4	168	9		14
212	2.6	213	12.1	180	8		13
224	2.7	226	13.4	192	11		14
236	2.7	238	11.6	204	11		16
260	2.9	250	20.4	216	11		14
272	3.6	263	38	228	10		15
284	3.6	274	63.6	240	9		12
296	4	286	82	252	9		12
308	3.6	298	23.7	264	7		12
320	3.6	310	17.5	276	15		17
332	4.1	322	13.5	288	14		17
344	4.2	334	14.3	300	14		16
356	4.2	340	13.4	312	14		15
368	3.8	355	12.5	324	14		16
380	4	367	13.8	336	12		17
452	18	379	19.5	348	11		17
		391	21.4	360	11		17
		403	22.7	372	11		16
		415	18.8	384	10		16
		427	14.8	396	10		15
		432	14	408	10		14
				420	9		13
				432	7		12

Table G-3 Voltage and Current (continued)

	T8S1		T8S2	T8S3		T8S1		T8S2	T8S3
Time (hrs)	Current (mA)	Time (hrs)	Current (mA)	Current (mA)	Time (hrs)	Current (mA)	Time (hrs)	Current (mA)	Current (mA)
6	32	6	40	123	572	77	594	27	19
18	36	18	52	118	584	63	606	26	19
30	45	30	64	130	596	60	618	24	19
42	47	42	55	101	608	55	642	24	16
54	57	54	68	91	632	49	654	22	17
66	54	66	68	99	644	46	666	22	15
78	52	78	72	92	656	45	678	22	15
80	51	90	92	80	668	44	702	22	16
92	66	102	93	80	680	42	726	20	14
104	62	114	112	74	692	41	740	18	13
116	67	126	91	75	710	40			
128	56	138	91	66					
140	59	150	59	52					
152	77	162	70	43					
164	68	186	98	63					
176	68	210	131	70					
188	88	234	85	105					
200	103	246	67	110					
212	104	258	53	85					
224	101	270	48	86					
236	105	282	45	59					
248	102	294	43	53					
260	81	306	34	43					
272	59	318	31	38					
296	55	330	28	34					
320	48	354	26	34					
344	38	366	151	211					
356	32	378	159	205					
368	30	390	117	143					
380	28	402	87	94					
392	26	426	64	52					
404	25	438	58	46					
416	25	462	51	41					
428	23	474	41	32					
440	21	486	39	33					
464	19	498	38	29					
476	173	522	33	26					
488	186	534	32	25					
500	147	546	31	23					
512	105	558	31	23					
536	85	570	30	21					
548	84	582	28	21					

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-1 Distribution of Heavy Metals after Treatment (T1D1)

		Inner zone							Outer zone						
Concentration		As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Top	223.9	488.0	248.6	908.3	811.2	973.6	912.6							
	2cm	116.9	364.0	235.5	886.5	758.4	871.0	890.2	95.1	245.9	44.6	229.6	158.0	226.8	134.8
	4cm	102.5	216.8	71.4	362.9	405.2	344.9	228.2	146.7	70.4	7.6	53.2	122.3	196.1	21.4
	6cm	70.6	82.0	27.9	114.7	112.1	259.1	96.2	104.9	94.3	20.6	93.0	74.0	208.0	73.6
	8cm	101.1	68.6	27.7	117.6	117.7	239.0	94.7	241.9	121.6	8.5	114.0	147.5	244.8	42.8
	10cm	93.3	69.0	21.5	107.4	109.4	214.5	81.5	100.6	67.1	12.1	69.8	68.6	142.2	47.6
	Initial heavy metal concentration	163.8	232.6	85.6	286.2	279.8	472.4	287.4							
Mass		mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg
	Top	6.2	8.8	3.2	10.8	10.6	17.9	10.9							
	2cm	2.1	6.7	4.3	16.3	13.9	16.0	16.3	11.3	29.2	5.3	27.3	18.8	26.9	16.0
	4cm	5.8	12.2	4.0	20.4	22.8	19.4	12.8	17.4	8.4	0.9	6.3	14.5	23.3	2.5
	6cm	4.0	4.6	1.6	6.5	6.3	14.6	5.4	12.5	11.2	2.4	11.0	8.8	24.7	8.7
	8cm	5.7	3.9	1.6	6.6	6.6	13.4	5.3	28.7	14.4	1.0	13.5	17.5	29.1	5.1
	10cm	5.2	3.9	1.2	6.0	6.2	12.1	4.6	11.9	8.0	1.4	8.3	8.1	16.9	5.7
	Subtotal Inner/Outer (mg)	22.8	31.2	12.7	55.8	55.8	75.5	44.5	81.8	71.2	11.1	66.4	67.7	120.9	38.0
Total metal remain in soil (mg)		104.7	102.4	23.8	122.2	123.5	196.3	82.5							
Initial spiked metal (mg)		143.3	203.5	74.9	250.43	244.8	413.3	251.5							
Deposited metal (mg)		37.5	109.3	45.0	96.0	98.0	215.0	144.7							
Percentage remain (%)		73.0	50.3	31.7	48.8	50.4	47.5	32.8							
Percentage removal (%)		27.0	49.7	68.3	51.2	49.6	52.5	67.2							

Note: The amount of heavy metals in effluent was not measured.

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-2 Distribution of Heavy Metals after Treatment (T1D2)

		Inner							Outer							
		As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd	
Concentration		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
	Top	138.6	787.6	461.7	1613.9	1346.3	1414.0	1543.0								
	2cm	207.0	497.0	157.2	699.5	478.8	623.3	623.8	165.7	286.1	81.3	364.2	238.7	330.0	355.9	
	4cm	255.8	135.0	23.8	157.1	229.3	322.3	94.1	124.0	111.9	28.8	146.5	115.7	239.1	100.6	
	6cm	106.0	85.0	72.4	258.2	299.7	434.3	240.1	115.6	190.4	56.7	227.4	149.6	301.1	212.8	
	8cm	105.2	183.3	57.7	228.0	135.0	272.4	222.7	95.5	174.0	52.7	210.1	119.7	244.6	204.2	
	10cm	110.8	86.7	64.2	227.7	235.4	426.4	223.2	91.5	60.8	38.2	136.4	138.0	255.7	138.5	
Initial concentration		165.2	289.1	107.2	338.0	363.0	514.0	358.6								
Mass		mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	
	Top	5.5	31.5	18.5	64.6	53.9	56.6	61.7								
	2cm	7.5	18.0	5.7	25.4	17.4	22.6	22.6	16.4	28.3	8.0	36.0	23.6	32.6	35.1	
	4cm	14.4	7.6	1.3	8.8	12.9	18.1	5.3	14.7	13.3	3.4	17.4	13.7	28.4	11.9	
	6cm	6.0	4.8	4.1	14.5	16.9	24.4	13.5	13.7	22.6	6.7	27.0	17.8	35.8	25.3	
	8cm	5.9	10.3	3.2	12.8	7.6	15.3	12.5	11.3	20.7	6.3	24.9	14.2	29.0	24.3	
	10cm	6.2	4.9	3.6	12.8	13.2	24.0	12.6	10.9	7.2	4.5	16.2	16.4	30.4	16.4	
Subtotal of Inner/Outer (mg)		40.0	45.6	18.0	74.4	67.9	104.5	66.5	67.0	92.0	29.0	121.5	85.7	156.1	113.1	
Total heavy metal left in soil (mg)		107.0	137.6	46.9	195.9	153.6	260.6	179.5								
Initial spiked total (mg)		144.5	253.0	93.8	295.8	317.6	449.8	313.8								
Deposited metal (mg)		40.2	104.9	23.5	56.6	101.3	184.7	66.0								
Percentage remain (%)		74.0	54.4	50.0	66.2	48.4	57.9	57.2								
Percentage removal (%)		26.0	45.6	50.0	33.8	51.6	42.1	42.8								

Note: The amount of heavy metals in effluent was not measured.

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-3 Distribution of Heavy Metals after Treatment (T1D3-1)

	Inner zone				Outer zone			
	As	Cr	Ni	Cu	Zn	Pb	Cd	
Concentration	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Top	85.5	381.2	167.3	585.6	512.6	589.5	561.3	
2 cm	346.5	325.7	158.3	650.3	661.1	1146.8	529.8	160.3
4 cm	157.0	160.6	42.0	140.4	173.1	265.6	120.3	143.1
6 cm	171.6	211.8	58.1	205.2	223.8	369.0	197.7	230.4
8 cm	58.9	127.2	8.6	161.7	154.1	266.7	158.5	168.7
10 cm	90.6	99.4	0.0	98.6	98.9	225.8	107.4	195.2
Initial metal	165.2	205.5	101.8	362.1	402.1	537.8	352.5	
Mass	mg	mg	mg	mg	mg	mg	mg	mg
Top	6.8	30.5	13.4	46.8	41.0	47.2	44.9	
2cm	12.6	11.8	5.7	23.6	24.0	41.6	19.2	14.2
4cm	8.8	9.0	2.4	7.9	9.7	14.9	6.8	17.0
6cm	9.6	11.9	3.3	11.5	12.6	20.8	11.1	27.4
8cm	3.3	7.2	0.5	9.1	8.7	15.0	8.9	20.0
10cm	5.1	5.6	0.0	5.5	5.6	12.7	6.0	23.2
T1D3-1 total metal left (mg)	110.2	166.6	60.6	219.3	218.3	378.9	218.7	
Total Initial metal (mg)	119.3	125.7	34.1	162.1	183.3	340.8	153.9	
Deposited metal (mg)	0.0	25.7	16.0	21.0	8.8	20.8	11.8	
Percentage remain (%)	108.3	75.4	56.3	73.9	84.0	89.9	70.3	
Percentage removal (%)	-8.3	24.6	43.7	26.1	16.0	10.1	29.7	

Note: The amount of heavy metals in effluent was not measured.
The average of T1D3-1 and T1D3-2 (Table H-4) was reported as T1D3.

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-4 Distribution of Heavy Metals after Treatment (T1D3-2)

		Inner zone								Outer zone							
Concentration	Top 2 cm 4 cm 6 cm 8 cm 10 cm Initial metal	As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd		
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
		98.3	318.9	216.2	723.5	768.2	726.9	756.9									
		77.2	371.7	78.7	414.1	437.1	615.7	340.5	65.8	136.2	24.5	128.8	185.5	514.3	117.5		
		141.7	132.4	3.6	110.0	152.2	309.6	112.4	124.8	155.5	30.6	145.6	252.2	459.2	171.0		
		213.3	185.4	44.1	223.3	263.8	929.1	180.9	143.9	225.6	19.7	160.2	161.7	339.7	148.3		
		132.0	142.5	53.8	195.0	236.7	384.1	192.3	126.9	185.8	54.2	223.1	290.6	362.0	200.9		
		89.5	138.3	42.4	147.3	155.2	304.6	93.3	76.5	234.4	70.5	235.0	245.3	456.8	249.2		
Mass	Top 2cm 4cm 6cm 8cm 10cm	Initial metal	165.2	205.5	101.8	362.1	402.1	537.8	352.5								
		mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	
		7.9	25.5	17.3	57.9	61.5	58.1	60.6									
		2.8	13.5	2.9	15.0	15.8	22.3	12.3	5.8	12.1	2.2	11.4	16.5	45.6	10.4		
		8.0	7.4	0.2	6.2	8.6	17.4	6.3	14.8	18.5	3.6	17.3	29.9	54.5	20.3		
		12.0	10.4	2.5	12.6	14.8	52.3	10.2	17.1	26.8	2.3	19.0	19.2	40.3	17.6		
		7.4	8.0	3.0	11.0	13.3	21.6	10.8	15.1	22.1	6.4	26.5	34.5	43.0	23.9		
		5.0	7.8	2.4	8.3	8.7	17.1	5.2	9.1	27.8	8.4	27.9	29.1	54.3	29.6		
Total Initial metal (mg)		110.2	166.6	60.6	219.3	218.3	378.9	218.7									
T1D3-2 total metal left (mg)		97.1	154.4	33.9	155.2	190.5	368.5	146.7									
Deposited metal (mg)		8.0	0.0	16.0	24.0	0.0	0.0	26.4									
Percentage remain (%)		88.2	92.6	55.9	70.7	87.3	97.3	67.1									
Percentage removal (%)		11.8	7.4	44.1	29.3	12.7	2.7	32.9									

Note: The amount of heavy metals in effluent was not measured.
The average of T1D3-1 (Table H-3) and T1D3-2 was reported as T1D3.

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-5 Distribution of Heavy Metals after Treatment (T1S1)

	T1S1						
	As	Cr	Ni	Cu	Zn	Pb	Cd
Concentration	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
2cm	179.2	763.0	369.6	1329.6	1143.9	1178.7	1482
4cm	94.4	43.8	4.3	42.3	82.8	196.4	7.7
6cm	111.4	155.2	36.2	159.7	89.2	265.8	138.6
8cm	78.8	190.1	57.6	205.2	136.5	287.6	211.9
10cm	139.1	100.0	36.8	155.3	128.6	265.7	137.3
Before treatment	165.2	289.1	107.2	338.0	363.0	514.0	358.6
Initial metal (mg)	44.8	78.3	29.1	91.6	98.4	139.3	97.2
Heavy metal left (mg)	27.4	42.8	15.0	58.2	47.5	80.7	57.5
Percentage remain (%)	59.9	53.4	50.4	62.1	47.2	56.6	57.8
Percentage removal (%)	40.1	46.6	49.6	37.9	52.8	43.4	42.2

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-6 Distribution of Heavy Metals after Treatment (T1S4)

		Inner zone							Outer zone						
		As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd
Concentration		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Top		489.0	234.9	1000.4	1129.8	1061.0	1054.8	934.2							
2 cm		196.6	244.8	145.8	144.1	127.2	222.6	138.7	221.8	274.7	217.5	228.6	205.5	288.9	212.6
4 cm		253.1	247.3	274.5	264.2	268.9	356.8	264.0	219.2	243.9	222.0	228.9	248.4	289.8	214.9
6 cm		269.2	190.3	315.4	326.2	348.6	360.3	303.5	241.1	246.4	275.1	288.4	311.0	331.4	270.7
8 cm		275.5	236.8	302.5	326.4	331.7	374.3	292.6	290.4	256.4	333.8	361.9	357.6	389.5	324.1
10 cm		270.2	336.0	240.8	281.8	273.0	299.1	238.2	263.9	333.9	265.5	313.4	293.7	323.9	261.6
Initial		277.3	285.6	293.1	311.5	308.4	346.7	286.3							
Mass		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Top		14.7	7.0	30.0	33.9	31.8	31.6	28.0							
2 cm		14.7	18.4	10.9	10.8	9.5	16.7	10.4	41.6	51.5	40.8	42.9	38.5	54.2	39.9
4 cm		23.7	23.2	25.7	24.8	25.2	33.4	24.8	41.1	45.7	41.6	42.9	46.6	54.3	40.3
6 cm		25.2	17.8	29.6	30.6	32.7	33.8	28.5	45.2	46.2	51.6	54.1	58.3	62.1	50.8
8 cm		25.8	22.2	28.4	30.6	31.1	35.1	27.4	54.4	48.1	62.6	67.9	67.0	73.0	60.8
10 cm		25.3	31.5	22.6	26.4	25.6	28.0	22.3	49.5	62.6	49.8	58.8	55.1	60.7	49.0
Subtotal inner/outer (mg)		114.9	113.1	117.2	123.2	124.1	147.1	113.4	231.8	254.1	246.3	266.5	265.5	304.4	240.7
Heavy metals in top matter (mg)		14.7	7.0	30.0	33.9	31.8	31.6	28.0							
Heavy metals in effluent (mg)		16.5	0.0	29.7	28.3	32.1	23.7	30.1							
Heavy metals deposited on cathode (mg)		10.8	0.0	8.8	18.7	9.1	19.1	9.2							
Total recovered heavy metal (mg)		388.6	374.3	432.0	470.6	462.7	525.9	421.4							
Initial spiked total metal (mg)		389.9	401.6	412.1	438.1	433.7	487.6	402.6							
Mass balance (%)		99.7	93.2	104.8	107.4	106.7	107.8	104.7							
Percentage remain (%)		88.9	91.4	88.2	88.9	89.8	92.6	87.9							
Percentage removal (%)		11.1	8.6	11.8	11.1	10.2	7.4	12.1							

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-7 Distribution of Heavy Metals after Treatment (T2S1)

	Inner zone							Outer zone						
	As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd
Concentration	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Top	491.4	211.5	1336.3	2018.6	1479.6	953.5	1185.0							
2cm	148.3	263.9	68.9	104.9	82.7	175.9	67.7	148.6	264.6	76.9	105.8	92.2	173.8	75.4
4cm	215.7	289.7	153.5	193.0	180.7	284.3	158.0	209.8	262.1	146.7	181.4	171.4	261.9	152.3
6cm	329.8	277.7	218.2	244.8	259.0	318.8	221.7	324.5	269.2	226.2	258.5	261.4	324.4	235.9
8cm	340.0	256.9	245.8	278.2	277.7	337.5	251.9	319.1	271.5	231.7	265.8	261.4	334.0	241.5
10cm	392.9	250.3	278.2	298.4	310.9	369.2	287.3	334.6	267.2	250.1	283.4	282.7	338.5	263.5
12cm	415.1	270.3	311.0	351.6	356.8	371.6	329.9	323.1	266.0	258.3	282.1	291.4	336.2	268.3
14cm	381.5	230.7	290.0	317.7	324.9	360.0	304.4	397.6	254.8	294.4	319.4	322.0	369.7	309.6
16cm	409.6	277.2	292.8	315.1	333.0	372.7	316.9	391.7	233.2	297.1	319.3	325.7	367.3	306.4
18cm	393.9	224.3	276.0	301.0	308.9	365.5	290.7	400.7	289.5	284.6	304.5	321.8	377.1	302.7
20cm	414.6	241.2	284.4	306.0	322.8	366.9	300.6	410.2	228.5	276.7	292.1	299.5	373.9	291.8
22cm	425.1	227.5	281.5	289.9	314.0	369.9	295.4	412.7	233.6	265.1	280.0	296.9	363.3	282.3
24cm	447.8	234.7	257.4	278.5	292.4	361.4	284.4	416.6	230.7	248.3	268.9	284.9	357.4	267.2
26cm	435.7	239.9	230.1	245.3	259.0	354.1	253.6	396.9	271.8	250.7	268.5	293.2	355.3	275.5
28cm	358.3	202.1	220.8	241.0	243.2	336.2	240.5	367.0	196.6	196.1	209.1	222.9	312.3	222.1
30cm	368.2	188.6	190.7	202.1	216.1	272.9	218.7	368.3	209.2	215.4	229.3	242.6	346.3	239.4
Initial metal	405.8	247.5	321.2	338.4	354.5	401.7	329.6							

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-8 Distribution of Heavy Metals after Treatment (T2S1) (continued)

		Inner zone						Outer zone							
		As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd
Mass		mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg
	Top	46.3	19.9	125.9	190.2	139.4	89.9	111.7							
	2cm	9.6	17.1	4.5	6.8	5.3	11.4	4.4	24.2	43.0	12.5	17.2	15.0	28.3	12.3
	4cm	21.1	28.4	15.0	18.9	17.7	27.8	15.5	41.5	51.9	29.0	35.9	33.9	51.9	30.2
	6cm	32.3	27.2	21.4	24.0	25.4	31.2	21.7	64.1	53.2	44.7	51.1	51.6	64.1	46.6
	8cm	33.5	25.3	24.2	27.4	27.3	33.2	24.8	63.1	53.7	45.8	52.6	51.7	66.0	47.8
	10cm	38.6	24.6	27.3	29.3	30.5	36.3	28.2	66.1	52.8	49.4	55.9	55.8	66.8	52.0
	12cm	40.7	26.5	30.5	34.4	35.0	36.4	32.3	65.8	54.2	52.6	57.5	59.4	68.5	54.7
	14cm	37.1	22.5	28.2	30.9	31.6	35.0	29.6	78.2	50.1	57.9	62.8	63.3	72.7	60.9
	16cm	39.9	27.0	28.5	30.7	32.4	36.3	30.9	76.9	45.8	58.3	62.7	63.9	72.1	60.1
	18cm	38.4	21.9	26.9	29.3	30.1	35.6	28.3	79.0	57.1	56.1	60.0	63.4	74.3	59.7
	20cm	40.4	23.5	27.7	29.8	31.5	35.8	29.3	80.9	45.0	54.5	57.6	59.0	73.7	57.5
	22cm	41.7	22.3	27.6	28.4	30.8	36.3	29.0	81.7	46.2	52.5	55.4	58.8	71.9	55.9
	24cm	44.2	23.2	25.4	27.5	28.8	35.7	28.1	82.8	45.8	49.3	53.4	56.6	71.0	53.1
	26cm	43.2	23.8	22.8	24.3	25.7	35.1	25.1	78.8	53.9	49.8	53.3	58.2	70.5	54.7
	28cm	35.5	20.0	21.9	23.9	24.1	33.3	23.9	73.9	39.6	39.5	42.1	44.9	62.9	44.7
	30cm	36.8	18.9	19.1	20.2	21.6	27.3	21.9	74.6	42.4	43.6	46.4	49.1	70.1	48.5
	Subtotal inner/outer	533.0	352.0	351.0	385.9	397.9	486.8	372.9	1031.5	734.7	695.6	763.9	784.8	984.9	738.6
	Total heavy metal left in soil	1564.5	1086.7	1046.6	1149.9	1182.7	1471.7	1111.5							
	Heavy metal in top matter	46.3	19.9	125.9	190.2	139.4	89.9	111.7							
	Heavy metal deposited on cathode	11.3	0.0	15.9	75.9	21.5	26.3	10.9							
	Heavy metal in effluent	74.1	0.3	299.2	205.1	329.8	195.4	314.0							
	Total recovered heavy metal	1696.2	1106.9	1487.7	1621.1	1673.4	1783.2	1548.0							
	Total initial spiked	1816.8	1108.3	1438.3	1515.3	1587.3	1798.6	1475.6							
	Mass balance (%)	93.4	99.9	103.4	107.0	105.4	99.1	104.9							
	Percentage remain (%)	86.1	98.1	72.8	75.9	74.5	81.8	75.3							
	Percentage removal (%)	13.9	1.9	27.2	24.1	25.5	18.2	24.7							

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-9 Distribution of Heavy Metals after Treatment (T2S2)

Concentration	As mg/kg	Cr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Pb mg/kg	Cd mg/kg		As mg	Cr mg	Ni mg	Cu mg	Zn mg	Pb mg	Cd mg
Top	537.5	934.4	886.5	1088.4	1053.2	694.1	895.1	Mass	25.2	43.8	41.5	51.0	49.3	32.5	41.9
2 cm	549.5	917.3	1181.7	1453.8	1408.0	857.9	1196.8	Top	26.3	43.8	56.5	69.5	67.3	41.0	57.2
4 cm	693.8	978.7	374.5	428.0	457.1	753.6	395.5	2 cm	34.0	48.0	18.4	21.0	22.4	37.0	19.4
6 cm	633.6	795.1	505.4	562.2	593.6	747.0	531.6	4 cm	31.2	39.2	24.9	27.7	29.2	36.8	26.2
8 cm	631.8	771.7	549.9	620.5	640.5	763.5	598.9	6 cm	31.0	37.9	27.0	30.5	31.5	37.5	29.4
10 cm	611.6	903.1	513.6	574.7	612.6	732.1	577.7	8 cm	30.2	44.6	25.4	28.4	30.2	36.1	28.5
12 cm	624.1	1004.4	506.0	560.9	603.5	706.0	595.3	10 cm	30.8	49.6	25.0	27.7	29.8	34.9	29.4
14 cm	640.2	1124.6	481.2	549.7	582.9	722.4	575.6	12 cm	31.8	55.9	23.9	27.3	29.0	35.9	28.6
16 cm	633.0	1218.5	466.4	524.5	552.3	719.8	573.9	14 cm	31.4	60.4	23.1	26.0	27.4	35.7	28.5
18 cm	577.1	1026.0	398.2	443.1	490.9	656.3	508.2	16 cm	28.9	51.3	19.9	22.2	24.5	32.8	25.4
20 cm	544.2	1034.0	397.7	453.4	481.1	648.1	503.4	18 cm	27.2	51.6	19.9	22.6	24.0	32.4	25.1
22 cm	505.3	1008.3	399.6	460.2	480.0	634.6	497.7	20 cm	25.3	50.5	20.0	23.0	24.0	31.8	24.9
24 cm	565.8	817.2	438.8	505.2	527.0	688.7	549.9	22 cm	28.2	40.7	21.9	25.2	26.3	34.3	27.4
26 cm	586.6	774.1	465.7	544.8	555.0	711.9	571.0	24 cm	29.3	38.7	23.3	27.2	27.8	35.6	28.6
28 cm	481.0	737.4	386.0	450.0	455.7	476.5	466.6	26 cm	23.8	36.6	19.1	22.3	22.6	23.6	23.1
30 cm	602.6	1384.5	501.9	581.1	591.3	711.7	587.0	28 cm	30.3	69.5	25.2	29.2	29.7	35.7	29.5
Initial	539.7	982.0	643.9	739.0	763.9	760.5	720.7	30 cm							
Total heavy metal left in soil															
Heavy metal in top matter															
Total initially spiked															
Percentage remain (%)															
Percentage removal (%)															

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-10 Distribution of Heavy Metals after Treatment (T7M2)

	Inner Ring							Outer Ring						
	As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd
Concentration	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Top	102.4		325.7	384.3	360.7	309.6	315.6							
2 cm	94.2		44.6	59.1	70.3	130.0	45.3	94.4		47.9	63.1	63.8	127.5	47.7
4 cm	128.0		73.3	89.3	81.5	153.8	74.3	108.6		60.2	74.5	75.6	133.7	61.4
6 cm	149.9		93.3	114.6	112.2	178.0	98.6	143.6		83.3	103.6	114.6	163.8	85.9
8 cm	133.2		64.9	79.7	77.8	150.3	71.2	149.2		77.5	95.1	101.6	158.5	83.7
10 cm	128.0		24.6	36.0	37.3	99.8	31.7	114.8		30.2	42.4	44.6	107.5	37.2
Initial	153.5		133.5	164.8	159.2	205.6	138.9							
Mass	mg		mg	mg	mg	mg	mg	mg		mg	mg	mg	mg	mg
Top	5.2		16.6	19.5	18.3	15.7	16.0							
2 cm	2.4		1.2	1.5	1.8	3.4	1.2	11.7		5.9	7.8	7.9	15.8	5.9
4 cm	7.4		4.3	5.2	4.7	8.9	4.3	13.2		7.3	9.1	9.2	16.3	7.5
6 cm	8.8		5.5	6.7	6.6	10.4	5.8	17.5		10.2	12.7	14.0	20.0	10.5
8 cm	7.8		3.8	4.7	4.6	8.8	4.2	18.3		9.5	11.6	12.4	19.4	10.2
10 cm	7.5		1.4	2.1	2.2	5.8	1.9	14.1		3.7	5.2	5.5	13.2	4.6
Subtotal of treated soil	34.0		16.1	20.2	19.9	37.4	17.3	74.8		36.6	46.4	49.0	84.6	38.7
Total left in soil	108.7		52.7	66.6	68.9	122.0	56.0							
Metal in top matter	5.2		16.6	19.5	18.3	15.7	16.0							
Total metal in effluent	22.9		69.0	74.4	76.7	55.0	67.1							
Total recovered	136.8		138.3	160.5	163.9	192.8	139.1							
Initial spiked metal	141.7		123.3	152.1	147.0	189.8	128.3							
Mass balance (%)	96.6		112.2	105.5	111.5	101.5	108.5							
Percentage remain (%)	76.8		42.8	43.8	46.8	64.3	43.6							
Percentage removal (%)	23.2		57.2	56.2	53.2	35.7	56.4							

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-11 Distribution of Heavy Metals after Treatment (T7M3 and T7M4)

		T7M3				T7M4			
		Inner zone		Outer zone		Inner zone		Outer zone	
		Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
Concentration		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Concentration	0 cm	1173.5	876.0			3946.8	2338.6		
	2 cm	239.1	469.8			659.6	667.2		726.2
	4 cm	397.4	599.8	266.2	466.0	207.7	672.6	577.0	686.4
	6 cm	454.0	606.7	442.5	622.2	399.7	590.7	518.7	694.1
	8 cm	428.5	619.9	467.8	630.6	431.2	628.6	477.5	682.4
	10 cm	329.4	518.6	420.6	580.4	348.4	558.9	514.3	730.3
Initial		740.3	820.3			740.3	820.3		
Mass		mg	mg	mg	mg	mg	mg	mg	mg
Mass	Top	139.7	104.3			343.0	203.2		
	2 cm	5.9	11.7	20.0	35.0	24.8	25.1	51.3	64.6
	4 cm	22.1	33.4	53.7	74.0	11.7	37.8	45.4	81.9
	6 cm	25.1	33.5	52.2	68.0	22.2	32.8	61.6	82.5
	8 cm	23.7	34.3	55.0	74.2	23.9	34.9	56.3	80.5
	10 cm	18.3	28.8	49.5	68.4	19.4	31.1	60.7	86.1
Total metal left in soil		325.5	461.1			377.3	557.2		
Metal in top matter		139.7	104.3			343.0	203.2		
Metal in effluent		205.6	129.1			50.7	30.8		
Metal deposited on cathode		9.47	7.72			6.69	6.52		
Total recovered metal		680.3	702.2			777.8	797.8		
Total initial spiked		675.8	748.8			673.9	746.8		
Mass balance		100.7%	93.8%			115.4%	106.8%		
Percentage remain		48.2%	61.6%			56.0%	74.6%		
Percentage removal		51.8%	38.4%			44.0%	25.4%		

		T7M3				T7M4			
		Inner zone		Outer zone		Inner zone		Outer zone	
		Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
Concentration		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Concentration	0 cm	1173.5	876.0			3946.8	2338.6		
	2 cm	239.1	469.8			659.6	667.2		726.2
	4 cm	397.4	599.8	266.2	466.0	207.7	672.6	577.0	686.4
	6 cm	454.0	606.7	442.5	622.2	399.7	590.7	518.7	694.1
	8 cm	428.5	619.9	467.8	630.6	431.2	628.6	477.5	682.4
	10 cm	329.4	518.6	420.6	580.4	348.4	558.9	514.3	730.3
Initial		740.3	820.3			740.3	820.3		
Mass		mg	mg	mg	mg	mg	mg	mg	mg
Mass	Top	139.7	104.3			343.0	203.2		
	2 cm	5.9	11.7	20.0	35.0	24.8	25.1	51.3	64.6
	4 cm	22.1	33.4	53.7	74.0	11.7	37.8	45.4	81.9
	6 cm	25.1	33.5	52.2	68.0	22.2	32.8	61.6	82.5
	8 cm	23.7	34.3	55.0	74.2	23.9	34.9	56.3	80.5
	10 cm	18.3	28.8	49.5	68.4	19.4	31.1	60.7	86.1
Total metal left in soil		325.5	461.1			377.3	557.2		
Metal in top matter		139.7	104.3			343.0	203.2		
Metal in effluent		205.6	129.1			50.7	30.8		
Metal deposited on cathode		9.47	7.72			6.69	6.52		
Total recovered metal		680.3	702.2			777.8	797.8		
Total initial spiked		675.8	748.8			673.9	746.8		
Mass balance		100.7%	93.8%			115.4%	106.8%		
Percentage remain		48.2%	61.6%			56.0%	74.6%		
Percentage removal		51.8%	38.4%			44.0%	25.4%		

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-12 Distribution of Heavy Metals after Treatment (T7M5 and T7M6)

	T7M5				T7M6			
	Cu mg/kg	Pb mg/kg	Cu mg	Pb mg	Cu mg/kg	Pb mg/kg	Cu mg	Pb mg
Top	3283.8	1832.0	54.0	30.2	3061.9	2067.9	49.2	33.2
2 cm a	128.3	520.1	2.9	11.8	173.6	409.7	3.8	9.0
2 cm b	151.5	501.2	3.4	11.4	164.6	362.0	3.6	8.0
4 cm a	218.4	491.5	7.3	16.3	282.9	675.1	8.9	21.3
4 cm b	239.8	496.5	7.8	16.2	238.0	701.5	7.5	22.2
6 cm a	278.9	530.8	9.0	17.2	410.1	603.6	13.0	19.1
6 cm b	279.6	510.5	9.1	16.7	430.9	636.2	13.6	20.1
8 cm a	246.6	525.0	8.1	17.2	364.3	599.3	11.5	18.8
8 cm b	216.9	446.3	7.1	14.5	381.7	626.8	12.2	20.0
10 cm a	176.9	395.9	5.7	12.7	357.6	599.1	11.3	18.9
10 cm b	237.8	482.3	7.6	15.4	347.9	637.5	11.1	20.4
Initial	740.3	820.3			291.2	562.2	9.2	17.7
					313.9	571.8	9.9	18.1
Total metal left in soil			67.9	149.2				
Metal in top matter			54.0	30.2	227.0	488.6	7.2	15.6
Total deposited metal			19.1	9.8	211.7	436.8	6.6	13.7
Heavy metals in effluent			133.4	69.5	178.9	380.2	5.7	12.1
Total initial spiked			238.1	263.8	195.6	400.6	6.2	12.7
Total recovered metal			274.4	258.6	Total metal left in soil			
Mass balance			115.3%	98.0%	Metal in top matter			
Percentage remain			28.5%	56.5%	Total deposited metal			
Percentage removal			71.5%	43.5%	Heavy metals in effluent			
					Total initial spiked			
					Total recovered metal			
					Mass balance			
					Percentage remain			
					Percentage removal			

Note: T7M5 and T7M6 had same initial heavy metal.
Two samples from each layer, a and b, were taken.

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-13 Distribution of Heavy Metals after Treatment (T8V1)

		Inner zone						Outer zone						
	As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd
Concentration	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Top	132.7		102.0	166.6	121.4	212.8	120.1							
2 cm	141.8		41.0	61.2	60.5	123.9	57.9	120.6		34.6	48.1	49.7	115.3	43.2
4 cm	149.5		54.0	66.6	73.5	129.8	61.7	138.4		49.7	66.0	67.2	119.4	54.9
6 cm	149.2		69.9	88.2	89.8	136.5	79.0	149.9		73.5	90.0	93.8	140.1	83.0
8 cm	139.4		71.7	86.7	92.6	133.1	82.9	157.3		72.4	88.1	92.6	132.6	83.0
10 cm	155.0		65.2	84.0	85.5	128.9	77.6	167.4		75.3	96.4	95.0	141.8	86.3
Mass	mg		mg	mg	mg	mg	mg	mg		mg	mg	mg	mg	mg
Top	3.3		2.5	4.1	3.0	5.3	3.0							
2 cm	7.9		2.3	3.4	3.4	6.9	3.2	11.8		3.4	4.7	4.8	11.3	4.2
4 cm	8.8		3.2	3.9	4.3	7.7	3.6	14.2		5.1	6.8	6.9	12.3	5.6
6 cm	9.1		4.2	5.4	5.5	8.3	4.8	14.3		7.0	8.6	8.9	13.3	7.9
8 cm	8.2		4.2	5.1	5.4	7.8	4.9	15.5		7.1	8.7	9.1	13.1	8.2
10 cm	13.2		5.5	7.1	7.3	10.9	6.6	20.0		9.0	11.5	11.3	16.9	10.3
Total left in soil	126.2		53.6	69.3	70.1	113.8	62.4							
Precipitated on Cathode	1.6		6.9	9.8	7.1	9.6	6.3							
Total metal in effluent	23.2		96.8	100.5	111.3	87.4	97.1							
Initial spiked	144.9		154.3	184.8	179.8	206.6	161.0							
Total recovered	154.3		159.8	183.7	191.4	216.1	168.7							
mass recovery (%)	106.4		103.6	99.4	106.4	104.6	104.8							
Percentage remained (%)	87.1		34.7	37.5	39.0	55.1	38.7							
Percentage removal (%)	12.9		65.3	62.5	61.0	44.9	61.3							

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-14 Distribution of Heavy Metals after Treatment (T8V2)

	Inner zone						Outer zone							
	As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd
Concentration	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Top	171.4		418.4	476.3	462.0	458.6	377.6							
2 cm	102.5		67.6	86.6	86.2	139.4	71.7	104.4		79.7	98.9	99.5	145.6	84.1
4 cm	141.5		115.5	141.2	141.1	174.0	123.1	132.1		108.4	132.0	132.3	161.6	114.7
6 cm	154.7		121.2	144.4	144.6	178.6	131.3	153.2		127.0	151.5	151.6	182.5	135.5
8 cm	153.9		114.9	137.4	141.0	168.6	125.9	152.4		124.0	153.4	151.9	180.0	134.9
10 cm	169.6		101.7	125.9	125.7	161.1	115.5	158.6		122.2	149.2	147.8	179.7	133.1
Mass	mg		mg	mg	mg	mg	mg	mg		mg	mg	mg	mg	mg
Top	5.2		12.7	14.5	14.1	14.0	11.5							
2 cm	3.7		2.5	3.2	3.2	5.1	2.6	13.0		9.9	12.3	12.3	18.1	10.4
4 cm	7.0		5.7	7.0	7.0	8.7	6.1	16.8		13.8	16.8	16.8	20.6	14.6
6 cm	8.8		6.9	8.2	8.2	10.1	7.5	19.4		16.1	19.2	19.2	23.2	17.2
8 cm	8.2		6.1	7.3	7.5	9.0	6.7	14.4		11.7	14.5	14.4	17.0	12.8
10 cm	9.9		5.9	7.4	7.4	9.4	6.8	18.9		14.5	17.8	17.6	21.4	15.8
Total left in soil	125.4		106.0	128.1	127.7	156.4	112.0							
Precipitated on Cathode	0.55		1.2	1.8	1.3	1.9	1.4							
Total metal in effluent	16.00		47.6	52.1	54.0	43.7	49.0							
Total recovered	147.16		167.53	196.49	196.98	215.98	173.81							
Initial spiked	148.21		157.8	189.0	183.9	211.2	164.6							
Mass recovery (%)	99.3		106.2	104.0	107.1	102.3	105.6							
Percentage remain (%)	84.6		67.2	67.8	69.4	74.1	68.0							
Percentage removal (%)	15.4		32.8	32.2	30.6	25.9	32.0							

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-15 Distribution of Heavy Metals after Treatment (T8V3)

	Inner zone							Outer zone						
	As	Cr	Ni	Cu	Zn	Pb	Cd	As	Cr	Ni	Cu	Zn	Pb	Cd
Concentration	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Top	184.0		152.4	241.2	161.1	210.5	153.6							
2 cm	129.3		30.3	40.6	46.2	117.7	41.9	121.3		32.6	52.5	48.6	117.2	38.5
4 cm	135.2		54.1	75.5	68.7	135.3	57.1	114.8		53.1	70.3	71.9	128.2	55.1
6 cm	160.3		76.3	93.2	97.3	142.7	81.9	145.7		87.3	100.7	107.2	156.0	92.5
8 cm	169.9		81.2	94.0	103.1	140.3	88.4	147.1		86.3	99.1	106.0	153.0	90.4
10 cm	175.2		79.1	90.8	101.6	142.1	89.2	145.5		79.0	90.9	99.4	144.9	83.4
Mass	mg		mg	mg	mg	mg	mg	mg		mg	mg	mg	mg	mg
Top	5.2		4.3	6.9	4.6	6.0	4.4							
2 cm	14.3		3.4	4.5	5.1	13.0	4.6	25.3		6.8	11.0	10.2	24.5	8.0
4 cm	15.0		6.0	8.4	7.6	15.0	6.3	22.9		10.6	14.0	14.3	25.5	11.0
6 cm	19.4		9.2	11.3	11.8	17.2	9.9	25.2		15.1	17.4	18.5	27.0	16.0
8 cm	20.6		9.8	11.4	12.5	17.0	10.7	26.3		15.4	17.7	18.9	27.3	16.2
10 cm	20.2		9.1	10.5	11.7	16.4	10.3	24.3		13.2	15.2	16.6	24.2	13.9
Total left in soil	213.4		98.6	121.2	127.2	207.2	107.0							
Precipitated on Cathode	8		29.3	49.4	29.9	41.6	26.9							
Total metal in effluent	29.4		75.0	79.6	84.6	67.8	78.7							
Total recovered	256.0		207.2	257.1	246.3	322.6	217.0							
Initial spiked	259.1		275.9	330.5	321.5	369.3	287.8							
Mass recovery (%)	98.8		75.1	77.8	76.6	87.3	75.4							
Percentage remained (%)	82.3		35.7	36.7	39.6	56.1	37.2							
Percentage removal (%)	17.7		64.3	63.3	60.4	43.9	62.8							

APPENDIX H

DISTRIBUTION OF HEAVY METALS

Table H-16 Distribution of Heavy Metals after Treatment (T8S1, T8S2, and T8S3)

	T8S1				T8S2				T8S3			
	Inner/Outer zone		Inner/Outer zone		Inner/Outer zone		Inner/Outer zone		Inner/Outer zone		Inner/Outer zone	
	mg/kg	mg	mg/kg	mg	mg/kg	mg	mg/kg	mg	mg/kg	mg	mg/kg	mg
Top	1681.3	129.3			1148.7	131.7			143.39			12.42
2 cm	78.0	9.9	72.0	17.7	86.7	14.5	92.3	18.6	35.3	24.8	3.30	4.03
4 cm	65.6	9.5	65.7	14.5	69.0	8.5	75.1	13.7	11.0	21.2	0.97	3.17
6 cm	62.0	7.6	61.3	11.1	67.1	8.6	76.0	16.0	6.0	18.4	0.65	4.00
8 cm	54.3	6.3	61.5	12.6	64.7	7.2	72.6	14.3	1.5	15.8	0.13	2.62
10 cm	54.7	6.1	63.2	11.2	64.6	5.6	81.5	13.7	4.5	21.1	0.45	4.36
12 cm	54.7	6.4	69.7	15.9	71.6	7.1	87.4	14.6	9.6	25.6	0.98	5.37
14 cm	62.0	6.3	72.1	13.7	77.4	8.5	98.3	19.4	24.6	68.2	2.50	12.16
16 cm	72.1	5.3	92.3	14.4	88.7	9.6	103.8	17.1	49.5	79.8	5.42	14.80
18 cm	80.9	7.7	89.7	13.1	102.2	11.1	108.1	22.7	83.2	81.3	10.81	20.34
20 cm	86.4	7.1	102.3	14.0	125.7	12.8	133.4	25.1	98.4	115.5	15.66	24.93
Initial	219.6				225.7				200.5			
	Total left in soil	210.4			Total left in soil	268.8			Total left in soil			136.7
	Top matter	129.28			Top matter	131.7			Top matter			12.4
	Deposited on cathode	100.36			Deposited on cathode	103.6			Deposited on cathode			78.78
	Total in effluent	321.89			Total in effluent	217.59			Total in effluent			263.6
	Total recovered Pb	761.93			Total recovered Pb	721.7			Total recovered Pb			491.5
	Pb in bottom layer	22.5			Pb in bottom layer	9.4			Pb in bottom layer			N.A.
	Total initial spiked	671.11			Total initial spiked	710.2			Total initial spiked			623.8
	Mass balance	110.2%			Mass balance	100.3%			Mass balance			78.8%
	Percentage remain	31.4%			Percentage remain	37.8%			Percentage remain			21.9%
	Percentage removal	68.6%			Percentage removal	62.2%			Percentage removal			78.1%

APPENDIX I DISTRIBUTION OF ORGANIC CONTAMINANTS

Table I-1 Distribution of Organic Contaminants after Treatment (T7M4)

	T7M4			T7M4 Control					
	Inner zone			Outer zone			Inner zone		
	p-xylene mg/kg	phenanthrene mg/kg		p-xylene mg/kg	phenanthrene mg/kg		p-xylene mg/kg	phenanthrene mg/kg	
2 cm	70.1	527.7		87.6	541.8		715.8	967.5	983.0
4 cm	42.9	290.0		33.4	246.1		1359.5	893.1	929.7
6 cm	20.6	187.4		47.2	297.8		584.4	1042.2	726.1
8 cm	30.4	226.8		61.6	422.3		1178.1	987.7	592.3
10 cm	75.7	494.4		81.9	490.3		599.2	803.7	503.5
	mg	mg		mg	mg		mg	mg	mg
2 cm	4.2	31.7		12.3	75.8		42.9	58.1	137.6
4 cm	3.9	26.1		6.3	46.8		122.4	80.4	176.6
6 cm	1.9	16.9		9.0	56.6		52.6	93.8	138.0
8 cm	2.7	20.4		11.7	80.2		106.0	88.9	112.5
10 cm	6.8	44.5		15.6	93.2		53.9	72.3	95.7
Total	74.3	492.1					1038.3	1098.4	
	Percentage remain								
	P-xylene in effluent			7.2%			44.8%		
	Percentage removal			82.05			55.2%		
				92.8%					

APPENDIX I DISTRIBUTION OF ORGANIC CONTAMINANTS

Table I-2 Distribution of Organic Contaminants after Treatment (T7M3)

	T7M3				T7M3 Control					
	Inner zone		Outer zone		Inner zone			Outer zone		
	p-xylene mg/kg	phenanthrene mg/kg	p-xylene mg/kg	phenanthrene mg/kg	p-xylene mg/kg	phenanthrene mg/kg	p-xylene mg/kg	phenanthrene mg/kg	phenanthrene mg/kg	
Concentration										
2 cm	115.7	554.0	136.3	348.2	715.8	967.5	983.0	734.2		
4 cm	77.9	452.9	136.9	345.8	1359.5	893.1	929.7	762.2		
6 cm	94.5	585.4	130.4	603.9	584.4	1042.2	726.1	657.4		
8 cm	135.8	577.0	217.1	598.0	1178.1	987.7	592.3	907.1		
10 cm	128.6	531.0	105.8	546.4	599.2	803.7	503.5	842.5		
Mass	mg	mg	mg	mg	mg	mg	mg	mg		
2 cm	4.6	22.2	16.4	41.8	28.6	38.7	118.0	88.1		
4 cm	7.0	40.8	26.0	65.7	122.4	80.4	176.6	144.8		
6 cm	8.5	52.7	24.8	114.7	52.6	93.8	138.0	124.9		
8 cm	12.2	51.9	41.2	113.6	106.0	88.9	112.5	172.3		
10 cm	11.6	47.8	20.1	103.8	53.9	72.3	95.7	160.1		
Total	172.4	655.0			1004.3	1064.4				
	Percentage remain		17.2%	61.5%						
	P-xylene in effluent		53.94							
	Percentage removal		82.8%	38.5%						

APPENDIX I DISTRIBUTION OF ORGANIC CONTAMINANTS

Table I-3 Distribution of Organic Contaminants after Treatment (T7M5 and T7M6)

	T7M5 Control			T7M5			T7M6 Control			T7M6		
	phenanthrene			phenanthrene			phenanthrene			phenanthrene		
	mg/kg	mg		mg/kg	mg		mg/kg	mg		mg/kg	mg	
2 cm a	544.4	27.2		334.1	16.7	2 cm a	665.26	33.3		347.4	17.4	
2 cm b	426.6	21.3		432.9	21.6	2 cm b	633.16	31.7		417.5	20.9	
4 cm a	633.9	31.7		230.6	11.5	4 cm a	630.67	31.5		198.5	9.9	
4 cm b	406.5	20.3		463.3	23.2	4 cm b	781.75	39.1		414.0	20.7	
6 cm a	391.6	19.6		269.2	13.5	6 cm a	765.50	38.3		432.9	21.6	
6 cm b	461.3	23.1		265.3	13.3	6 cm b	761.44	38.1		415.5	20.8	
8 cm a	510.7	25.5		141.0	7.1	8 cm a	764.66	38.2		191.1	9.6	
8 cm b	560.1	28.0		136.7	6.8	8 cm b	715.11	35.8		240.9	12.0	
10 cm a	168.2	8.4		171.0	8.6	10 cm a	771.16	38.6		246.2	12.3	
10 cm b	425.8	21.3		275.1	13.8	10 cm b	771.16	38.6		236.9	11.8	
	Total	226.5		Total	136.0	12 cm a	754.62	37.7		135.7	6.8	
						12 cm b	754.62	37.7		150.6	7.5	
	Percentage remain			60.0%		14 cm a	492.86	24.6		98.8	4.9	
	Percentage removal			40.0%		14 cm b	492.86	24.6		93.0	4.7	
						16 cm a	852.11	42.6		67.0	3.3	
						16 cm b	852.11	42.6		103.2	5.2	
						Total	573.0	Total		189.5		
							Percentage remain			33.1%		
							Percentage removal			66.9%		

APPENDIX I DISTRIBUTION OF ORGANIC CONTAMINANTS

Table I-4 Distribution of Organic Contaminants after Treatment (T8S1, T8S2, and T8S3)

	T8S1						T8S2						T8S3					
	phenanthrene						phenanthrene						phenanthrene					
	Inner zone	Outer zone	Inner zone	Outer zone	Inner zone	Outer zone	Inner zone	Outer zone	Inner zone	Outer zone	Inner zone	Outer zone	Inner zone	Outer zone	Inner zone	Outer zone		
	mg/kg	mg/kg	mg	mg	mg/kg	mg/kg	mg	mg	mg/kg	mg/kg	mg	mg	mg/kg	mg/kg	mg	mg		
2 cm	269.7	253.9	34.2	62.3	317.7	342.0	53.3	68.9	255.7	259.7	23.9	42.2						
4 cm	272.5	287.5	39.3	63.5	329.5	344.7	40.4	62.8	272.0	283.3	23.9	42.3						
6 cm	264.8	266.0	32.5	48.3	275.6	359.7	35.4	75.6	331.3	327.0	35.9	70.9						
8 cm	190.6	213.4	22.1	43.7	170.1	227.6	18.9	45.0	98.0	242.0	8.9	40.2						
10 cm	109.7	160.1	12.3	28.4	100.4	117.4	8.8	19.8	119.1	90.9	12.0	18.7						
12 cm	125.4	246.4	14.7	56.3	80.5	90.6	8.0	15.1	121.4	113.6	12.4	23.8						
14 cm	182.5	237.9	18.5	45.2	68.3	92.0	7.5	18.2	133.4	83.4	13.5	14.9						
16 cm	169.1	250.0	12.3	39.1	72.1	117.0	7.8	19.3	131.3	121.0	14.4	22.4						
18 cm	225.2	201.6	21.4	29.4	118.9	317.9	12.9	66.8	104.4	276.2	13.6	69.1						
20 cm	144.1	163.8	11.9	22.4	159.7	269.8	16.3	50.7	96.9	225.2	15.4	48.6						
Initial	408.3				401.9				380.0									
	Total left in soil		658.0		Total left in soil		651.4		Total left in soil		567.7							
	Total initial spiked		1247.6		Total initial spiked		1264.6		Total initial spiked		1182.4							
	Percentage remain		52.7%		Percentage remain		51.5%		Percentage remain		48.0%							
	Percentage removal		47.3%		Percentage removal		48.5%		Percentage removal		52.0%							