

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI[®]

**Development of a Hybrid Electrokinetic System for the Simultaneous
Removal of Heavy Metals and PAHs from Clayey Soil**

By Mansour Hakimipour

A Thesis
In
The Department of Building,
Civil and Environmental Engineering

Presented in Partial Fulfillment of the Requirements
For the
Degree of Master of Applied Science at
Concordia University
Montreal, Quebec, Canada

March 2001

© Mansour Hakimipour, 2001



National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-59303-7

Canada

ABSTRACT

Development of a Hybrid Electrokinetic System for the Simultaneous Removal of Heavy Metals and PAHs from Clayey Soil

Mansour Hakimipour

Several industrial and municipal areas in North America are contaminated with heavy metals and petroleum products. This mixed contamination presents a particularly difficult task for remediation when dealing with clayey soil. The objective of this research was to develop a method to clean mixed contaminated clayey soils. A lab scale multifunctional hybrid electrokinetic method was investigated. Clayey soil, contaminated with lead (555 ppm), nickel (555 ppm) and phenanthrene (600 ppm), was subjected to simultaneous removal using an electrokinetic system. The electrokinetic surfactant supply system was applied to mobilize, transport and remove phenanthrene. A chelation agent (EDTA) was electrokinetically supplied to mobilize heavy metals. These supplied liquids were introduced in various sequences and at different periods in order to optimize the removal of both types of contaminants. The studies were performed on 8 lab scale electrokinetic cells connected to a DC power supply to achieve a voltage gradient of 0.3 V/cm. In order to avoid some negative impacts associated with electrokinetic processes, ion exchange textiles (IET) were incorporated into the system. Electrical parameters, pH, volume supplied and volume discharged were monitored continuously during each experiment. At the end of the tests, the soil and catholyte were subjected to physico-chemical analysis. Results showed that the optimal average simultaneous removal was 85 % for lead, 84 % for nickel, and 74 % for phenanthrene. The highest local removals achieved for lead, nickel and phenanthrene were 96 %, 95 %, and 84 % respectively. For the optimal removal conditions the consumption of energy was 28.4 kWh/m³. However, the

hybrid method can achieve a two-fold decrease in energy consumption. The results of this study can be applied as an in-situ hybrid electrokinetic technology for the remediation of clayey sites contaminated with petroleum products and heavy metals, (e.g. Manufacture Gas Plant Sites).

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisor, Dr. Maria Elektorowicz, for her help, encouragement, invaluable advice and support in the course of my research.

Also I would like to acknowledge the National Science and Engineering Research Council (NSERC) for their financial support. The author would like to thank l'Institut Textile de France, for their donation of textile samples that were used in this research.

Finally, I wish to express my deepest appreciation to my parents who dedicated their whole life for my education. And thanks to my wife Afsoon, for her support and understanding, and finally to my daughter Tara who are my reason to carry on.

TABLE OF CONTENTS

	Page
List of Tables	x
List of Figures	xi
CHAPTER 1: INTRODUCTION	1
1.1. Statement of the Problem	1
1.2. Objectives	3
CHAPTER 2: LITERATURE REVIEW	4
2.1. Principal Soil Components	4
2.1.1. Inorganic Components of Soil	4
2.1.2. Organic Components of Soil	7
2.2. Mix Contaminant Transport	8
2.2.1. The Effects on Inorganic Contaminants	9
2.2.2. The Effects on Organic Pollutants	13
2.2.3. Conclusions	14
2.3. Soil Remediation Methods	14
2.3.1. Major Remediation Technologies for Organic Removal from Soil	14
2.3.2. Major Remediation Technologies for Inorganic Removal from Soil	17
2.3.3. Conclusions	18
2.4. Electrokinetic Soil Remediation	18
2.4.1. Classical Electrokinetic Processes	20
2.4.1.1. Effects of Electroosmosis on Electrokinetic Remediation	20
2.4.1.2. Effects of Electrophoresis on Electrokinetic Remediation	22

2.4.1.3. Effect of Electrolytic Migration on Electrokinetics.	23
2.4.2. Conclusions Related to Classical Electrokinetics	23
2.4.2.1. Problem Related to High pH Development	24
2.4.2.2. Problems Related to Mobilizing Heavy Metals during Electrokinetics	24
2.4.2.3. Problems Related to Mobilizing Organics during Electrokinetics	25
2.4.3. Conclusions	25
2.5. Use of Surfactants for Organic Contaminant Desorption in Soil	25
2.6. Use of Chelation Agents (EDTA) for inorganic Contaminant Desorption in Soil	28
2.7. Ion Exchange Materials and Resins	29
CHAPTER 3: EXPERIMENTAL METHODOLOGY	32
3.1. Soil Characterization and Preparation	32
3.2. Experimental Setup and Cell Configuration	35
3.3. Liquid Supply System	37
3.4. Characteristics and Preparation of the Ion Exchange Textiles	39
3.5. Apparatus, Reagents and Equipment	39
3.5.1. Cell Construction and Experimental Setup	40
3.5.2. Measurements and Analyses	40
3.6. Analysis and Measurements During the Experiments	41
3.6.1. pH Measurement of Cathode Liquid	41
3.6.2. Volume Measurements of Injected and Extracted Liquid.	41
3.6.3. Measurements of Electrical Parameters.	41
3.7. Sampling, Analyses and Measurements after the Experiments.	43

3.7.1. Soil Sampling.	43
3.7.1.1. Moisture Content	44
3.7.1.2. pH Measurements	44
3.7.1.3. Measurements of Metal Content	45
3.7.1.4. Measurements of Phenanthrene Content	46
3.7.2. Analysis of Ion Exchange Textiles	48
CHAPTER 4: RESULTS AND DISCUSSION	50
4.1. Experiments T1.	50
4.1.1. Electrical Parameters	50
4.1.2. Results Pertaining to Cathode Liquids	53
4.1.3. Volume of Supplied liquids	55
4.1.4. Soil Samples	57
4.1.4.1. pH of the Soil	57
4.1.4.2. Metal Concentration in the Soil	58
4.1.4.3. Phenanthrene Concentration in the Soil	60
4.1.5. Analysis Ion Exchange Textiles	61
4.2. Experiments T2.	61
4.2.1. Electrical Parameters	62
4.2.2. Results Pertaining to Cathode Liquids	68
4.2.3. Volume of Liquids Supplied	71
4.2.4. Soil Samples	74
4.2.4.1. pH of the Soil	74
4.2.4.2. Metal Concentration in the Soil	76

4.2.4.3. Phenanthrene Concentration in the Soil	78
4.2.5. Analysis Ion Exchange Textiles	79
4.3. Experiments T3.	79
4.3.1. Electrical Parameters	80
4.3.2. Results Pertaining to Cathode Liquids	86
4.3.3. Volume of Liquids Supplied	86
4.3.4. Soil Samples	89
4.3.4.1. pH of the Soil	89
4.3.4.2. Metal Concentration in the Soil	90
4.3.4.3. Phenanthrene Concentration in the Soil	92
4.3.5. Analysis Ion Exchange Textiles	93
4.4. Results and Discussion for All Experiments	93
4.4.1. Contaminant Removal.	93
4.4.2. Power Consumption	94
4.4.3. Energy Consumption	96
CHAPTER 5: CONCLUSIONS.	98
REFERENCES	101
APPENDIX: Photographs of All Experiments	

LIST OF TABLES

	Page
Table 2.1 Structure of typical clay minerals	6
Table 2.2 Properties of clay minerals	6
Table 2.3 Lead and nickel concentration in typical waste	12
Table 2.4 Effect of pH on probable solution speciation of lead.	12
Table 2.5 Properties and comparison of organic ion exchange resins	31
Table 3.1 Characteristics of clayey soil used for experimentation	34
Table 3.2 Data from UV/Vis spectrometer	47
Table 3.3 UV Results for various phenanthrene concentrations (wavelength: 294.8 nm)	48
Table 4.1 Specific concentration of Pb, Ni and phenanthrene in IET (Experiment T1)	61
Table 4.2 Supplied periods of EDTA and surfactant (Test T2).	61
Table 4.3 Specific concentration of Pb, Ni and phenanthrene in textiles (Test T2) .	79
Table 4.4 Supplied periods of EDTA and surfactant (Test T3).	80
Table 4.5 Specific concentration of Pb, Ni and phenanthrene in textiles (Test T3) .	93

LIST OF FIGURES

	Page
Figure 2.1 Natural soil constituents (focus on solid phase).	4
Figure 2.2 Classification of organic matter by acid solubility	7
Figure 2.3 Typical electrokinetic process	19
Figure 3.1 Methodology used for the experimentation.	33
Figure 3.2 Configuration of all electrokinetic cells	36
Figure 3.3 Probe-electrodes placed on a plexiglas holder	37
Figure 3.4 Surfactant supply system in an electrokinetic cell	38
Figure 3.5 EDTA supply system in an electrokinetic cell	39
Figure 3.6 Scheme of electrical setup 1	42
Figure 3.7 Scheme of soil sampling	43
Figure 3.8 Soil sample dividing	44
Figure 3.9 Spectra of the phenanthrene-DCM system	47
Figure 3.10 Ion exchange textile dividing	48
Figure 4.1 Resistance distribution versus distance from the cathode (T1C1)	51
Figure 4.2 Resistance distribution versus distance from the cathode (T1C2)	52
Figure 4.3 Total resistance of soil for cells T1C1 and T1C2	53
Figure 4.4 pH of the extracted daily cathode liquids (T1C1 and T1C2).	54
Figure 4.5 Volume of extracted daily cathode liquids (T1C1 and T1C2)	55
Figure 4.6 Cumulative volume of water supplied to cell T1C1.	56
Figure 4.7 Cumulative volumes of surfactant and EDTA supplied in cell T1C2	56

Figure 4.8 pH distribution for cells T1C1 and T1C2 after experiment	57
Figure 4.9 Pb distribution in cells T1C1 and T1C2 after experiment	59
Figure 4.10 Ni distribution in cells T1C1 and T1C2 after experiment	59
Figure 4.11 Percentage of phenanthrene removal in soil samples (T1C1 and T1C2)	60
Figure 4.12 Resistance distribution versus distance from the cathode (T2C3) . .	63
Figure 4.13 Resistance distribution versus distance from the cathode (T2C4) . .	64
Figure 4.14 Resistance distribution versus distance from the cathode (T2C5) . .	65
Figure 4.15 Resistance distribution versus distance from the cathode (T2C6) . .	66
Figure 4.16 Total resistance of soil for cells T2C3, T2C4, T2C5 and T2C6 . .	67
Figure 4.17 pH of the extracted daily cathode liquids (T2C3 and T2C4)	69
Figure 4.18 pH of the extracted daily cathode liquids (T2C5 and T2C6)	69
Figure 4.19 Volume of extracted daily cathode liquids (T2C3 and T2C4)	70
Figure 4.20 Volume of extracted daily cathode liquids (T2C5 and T2C6)	70
Figure 4.21 Cumulative volume of surfactant and EDTA supplied in cell T2C3 . .	72
Figure 4.22 Cumulative volume of surfactant and EDTA supplied in cell T2C4 . .	72
Figure 4.23 Cumulative volume of surfactant and EDTA supplied in cell T2C45 . .	73
Figure 4.24 Cumulative volume of surfactant and EDTA supplied in cell T2C6 . .	73
Figure 4.25 pH distribution for cells T2C3 and T2C4 after experiments. . . .	75
Figure 4.26 pH distribution for cells T2C5 and T2C6 after experiments. . . .	75
Figure 4.27 Pb distribution in cells T2C3, T2C4, T2C5 and T2C6 after experiments.	77
Figure 4.28 Ni distribution in cells T2C3, T2C4, T2C5 and T2C6 after experiments.	77
Figure 4.29 Concentration of phenanthrene in cells T2C3, T2C4, T2C5 and T2C6 .	78
Figure 4.30 Resistance distribution versus distance from the cathode (T3C7) . .	81

Figure 4.31 Resistance distribution versus distance from the cathode (T3C8) . . .	83
Figure 4.32 Total resistance of soil for cells T3C7 and T3C8	85
Figure 4.33 pH of the extracted daily cathode liquids (T3C7 and T3C8) . . .	87
Figure 4.34 Volume of extracted daily cathode liquids (T3C7 and T3C8) . . .	87
Figure 4.35 Cumulative volume of surfactant and EDTA supplied in cell T3C7 .	88
Figure 4.36 Cumulative volume of surfactant and EDTA supplied in cell T3C8 .	88
Figure 4.37 pH distribution for cells T3C7 and T3C8 after experiment. . . .	89
Figure 4.38 Pb distribution in cells T3C7 and T3C8 after experiments	91
Figure 4.39 Ni distribution in cells T3C7 and T3C8 after experiments	91
Figure 4.40 Concentration of phenanthrene in cells T3C7 and T3C8	92
Figure 4.41 Percentage of the average removal of lead, nickel and phenanthrene in electrokinetic cells	94
Figure 4.42 Power consumption for all electrokinetic cells with 22 days test period.	95
Figure 4.43 Power consumption for electrokinetic cells T3C7 and T3C8	96
Figure 4.44 The total energy consumption in electrokinetic cells	97

CHAPTER 1 INTRODUCTION

1.1. Statement of the Problem

Contaminant removal is an important problem in sites throughout the world. Several industrial and municipal areas in North America are contaminated with heavy metals and petroleum products. Typical sites contaminated by hydrocarbons in Canada are manufacturing plants, petroleum refineries, fuel and chemical storage facilities, gasoline service stations, and vehicle depots. Several of these sites also contain heavy metals. Therefore, the mixture of contaminants that includes organic compounds and inorganic substances present a particular challenge for site remediation technology. The mixed contamination of clayey soil presents a particularly difficult task for remediation. In Quebec, 69% of the contamination is of organic form (Environment Quebec, 1994). Petroleum products comprise the major portion, followed by PAHs, chlorinated, phenolic, and monocyclic aromatic hydrocarbons (Environment Quebec, 1994). PAHs can be found in diesel fuel and in the exhaust of gasoline and diesel engines. They can be very difficult to remediate because of their ability to sorb to soil particles and their resistance to biodegradation.

Among the many available in-situ remediation technologies, no one method can be directly applied for mixed contamination. In field conditions, clayey soil represents a major challenge due to its specific characteristics, such as high specific surface area, low permeability, and high cation exchange capacity (CEC). These provoke numerous physico-chemical phenomena leading to retardation, transport of contaminants and modified liquids through the clay. These phenomena influence the efficiency of soil remediation. Electrokinetic phenomena, when applied to clays contaminated with heavy

metals promises to be an effective in-situ remediation technique (Choudhury and Elektorowicz, 1997). The development of a new technology was required to satisfy in-situ remediation requirements in clayey soil with mixed contamination. Some successful removals have already been reported for polar organic compounds (Elektorowicz, *et al.* 1996a; Pamukcu *et al.* 1995). The electrokinetic technique electroosmosis, electrophoresis, and electromigration processes enhance the transport of various liquids within clayey soils (Elektorowicz and Hatim, 1999). Therefore, electrokinetics seems to be one of the most promising technologies for treating clayey soil with mixed contamination. In general, the principal advantages of electrokinetics are:

- a) It is a unique in-situ methodology that is effective in low permeability soils
- b) The flow direction can be controlled
- c) It is capable of removing a wide range of contaminants
- d) It has a low electric power consumption

There are some limitations that this technology presents. Reduction at the cathode produces OH^- ions, which readily increases the pH. This creates a precipitation barrier in this region and prevents the transport of heavy metals to desired locations. Oxidation at the anode creates precipitation of a mobilization liquid. The use of ion exchange textiles has proven to be effective in the transport, and localization of heavy metal contamination in natural clay soil (Elektorowicz *et al.*, 1996b). Natural clay soil does not facilitate easy mobilization of contaminants, therefore, may not allow for effective electrokinetic transport. This situation requires a special adaptation of electrokinetic techniques. The use of conditioning liquids injected at the cathode and/or anode has increased the mobilization of metals, thereby, enhancing electrolytic migration and contaminant removal. This hybrid approach attempts to alleviate the problems of classical

electrokinetic through the utilization of ion exchange textiles and a chelation agent (EDTA), in combination with electrokinetic transport. The remediation process often depends on desorption of a contaminant from the soil surface and its subsequent incorporation into the bulk aqueous phase. Organics are not easily transported from the solid phase to the aqueous phase. The use of conditioning liquids (e.g. surfactant) as agents for apparent solubility and mobility enhancement of organics has been a subject of intensive research (Elektorowicz and Hatim, 2000; Ju and Elektorowicz, 2000). As a result of the application of surfactants in electrokinetics, it is expected that the increased solubilization, desorption, and mobilization of organic contaminants can increase the efficiency of PAHs removal from the soil. If the contaminated site consists of a high fraction of clay materials, the uniform introduction of conditioning liquids presents a challenge. These facts require an improvement to existing electrokinetic technology. It is necessary to develop a hybrid method for cleaning clay soil contaminated with heavy metals and PAHs through the utilization of surfactants, ion exchange textiles and a chelation agent (EDTA) in combination with electrokinetic transport.

1.2. Objectives

The main objective of this thesis was to find a hybrid method to remediate mixed contaminated clayey soils. The secondary objective is the investigation of the impact of the hybrid components on the efficiency of mixed contaminant removal. The combination of EDTA (chelation agent), zwitterionic surfactant and cationic and anionic exchange textiles were investigated. This combination has never been applied to electrokinetic soil remediation methods. The efficiency was not evaluated nor were energy requirements estimated.

2.1. Principal Soil Components

Soil consists of components that can be subdivided based on their physical structure and their chemical behaviour related to contaminant fate. The subsurface can be subdivided into the solid phase (soil matrix), liquid phase (pore water) and the gaseous phase (i.e. air, VOCs). Using this criterion, the constituents of natural soil, excluding pore water and gases, can be subdivided as shown in Figure 2.1.

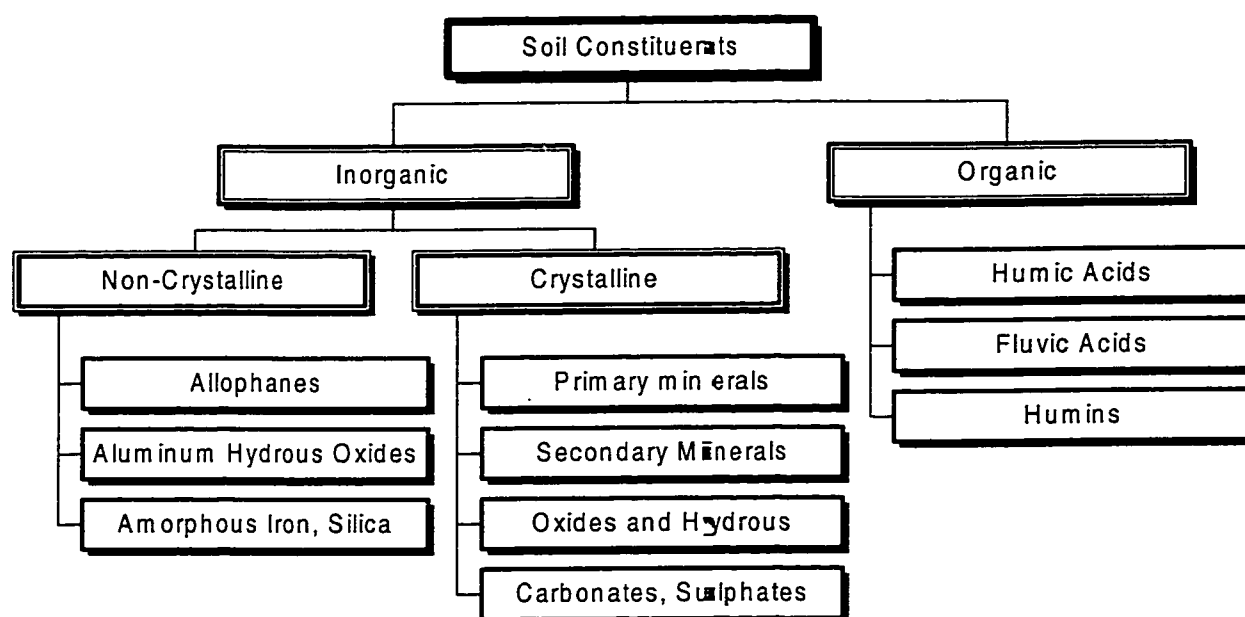


Figure 2.1 Natural soil constituents (focus on solid phase)

2.1.1. Inorganic Components of Soil

The inorganic components are subdivided into crystalline and non-crystalline types. Inorganic matter typically constitutes the majority of the soil's components. The inorganic portion of soil consists largely of aluminosilicates. Typically, feldspar minerals comprise 60% of an average inorganic rock (Hamblin, 1992).

Inorganic minerals are classified as primary minerals (derived from weathering of rock) and secondary minerals (transformed as fine particles). Primary minerals comprise a major portion of the sand and silt fraction. These minerals are significant to geo-environmental engineering, specifically contamination and attenuation processes, due to their low cation exchange capacities, low specific surface areas and high particle sizes. Typical examples of primary minerals are quartz, feldspar, amphiboles, and pyroxenes. Their importance to geo-environmental engineering and geotechnical engineering lies in their ability to be weathered and chemically transformed into secondary minerals (Choudhury, 1998).

Clay minerals are those derived from the previously mentioned primary counterparts. They typically consist of varying structures with silica tetrahedral and alumina octahedral as the basic structural groups. Most clay minerals are weakly crystalline, as a result of their smaller crystal sizes and an increased tendency for ionic substitution. Secondary minerals are characterized by a high specific surface area, a small particle size, and a high surface charge, which makes this group significant in influencing contaminant transport and attenuation. The principal layer silicates that comprise this group are kaolinite, chlorite, vermiculite, mica, and montmorillonite (Yong, *et al.*, 1992). Table 2.1 summarizes the basic properties of secondary minerals found in natural soils.

In order to discuss clay minerals adequately, a comparison of properties provides an accurate and relative scale. Table 2.2 displays a summary of the environmentally pertinent properties of the secondary minerals. Natural clay soil contains a mixture of the clay minerals shown in Table 2.2.

Table 2.1 Structure of typical clay minerals (after Yong, *et al.*, 1992)

Minerals	Structural Composition	Population of Octahedral Sheet	Isomorphous substitution
Kaolinite Dickite Halloysite	Silica: Alumina 1:1 (7.2 Å thick)	Diocahedral 2/3 of positions filled with Al	—
Chlorite	Silica: Alumina 2:2 (14.0 Å thick)	Diocahedral, Triocahedral or mixed	Al for Si Al for Mg
Illite Glaucanite	Silica: Alumina 2:1 (10 Å thick)	Octahedral	Al for Si
Vermiculite	Silica: Alumina 2:1 (10 Å thick)	Diocahedral	Al for Si
Montmorillonite Beldellite Nontronite	Silica: Alumina 2:1 (10 Å thick)	Triocahedral	Al for Si Mg for Al Fe for Al

Table 2.2 Properties of clay minerals (Ruggiero 1999)

Mineral	CEC [cmol/kg]	Specific Surface Area [m ² /g]	Swelling Potential	Plasticity
Kaolinite	2-15	7-30	Very Low	Very Low
Chlorite	10-40	25-150	Low	Low
Illite	20-40	90-130	Moderate	Moderate
Montmorillonite	80-150	600-800	Very High	Very High
Vermiculite	150-200	600-800	Moderate	High

Amorphous inorganic do not possess a definite structure and generally encompass allophanes, imoglites, amorphous silica, amorphous iron and aluminum hydrous oxides. They possess high specific surface areas (300-700 m²/g).

2.1.2. Organic Components of Soil

Soil organic matter consists of nonhumic and humic substances. The nonhumic substances include polysaccharides, proteins, fats and low molecular weight organic acids. Humic substances represent most of the organic matter in soil. On the basis of their different solubility in acid or base, humic substances are differentiated into fluvic acids, humic acids, and humins (Ruggiero, 1999). Classification of organic material based on acid solubility is shown in Figure 2.2. Soil organic matter plays a significant role in the fate of organic and inorganic soil contaminant because their pH dependent charge, which can affect the state and existence of contaminant in the subsoil. It comprises 0.5-5.0 % (by weight) of most mineral surface soils, with the exception of peat, which can attain 100% organic matter (Yong, *et al.*, 1992). Organic matter originates from the transformation and decay of vegetation and animal remains.

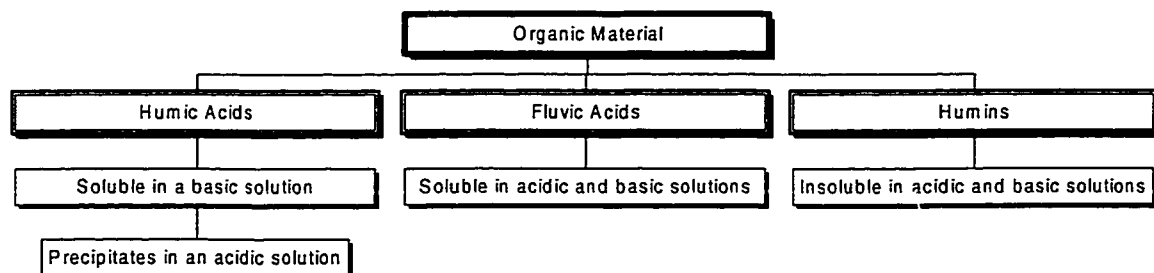


Figure 2.2 Classification of organic matter by acid solubility (after Yong, *et al.*, 1992)

Soil organic matter also provides sites for absorption of non-polar organic contaminants, such as PAHs. The sorption to organic colloids depends on their hydrophobicity and is related to their octanol-water partition coefficients (Ruggiero, 1999).

2.2. Mixed Contaminant Transport

A major factor complicating the cleanup of many hazardous waste sites is the remediation of organic compounds and heavy metals, so called mixed contamination. Previous and current research on remediation technologies has focused on either organic compounds or metals. An in-situ method that could simultaneously remove organic compounds and heavy metals from soils would improve the ability to remediate hazardous waste sites. For a mixed contaminant system, the presence of each contaminant does not appear to significantly influence the complexation/solubilization of the other contaminants (Brusseau and Wang, 1997).

Secondary minerals and organic material present in soil have the largest influence on contaminant fate and to a lesser extent, remediation engineering due to their ability to exchange cationic contaminants (i.e. heavy metals) and adsorb organic substances. A contaminant present in the subsurface is transported to other locations in the soil, by pore water (liquid phase) through advection, dispersion, diffusion and suction in the vadose zone. In clay soils, molecular diffusion is a transport mechanism due to the low permeability of clay. While the contaminant is transported through the media, retardation occurs which aids in immobilizing these contaminants onto the solid phase.

Organic and inorganic chemicals being transported through the subsurface are influenced by this complex medium, particularly by the constituents of the phase in

which they are present. As a result they undergo two main processes: 1) Transformation and 2) Transport. In soil, abiotic transformation rates are strongly influenced by a wide variety of environmental factors that control the types and rates of the chemical reactions. These environmental factors include: moisture content, pH, redox potential, temperature, adsorption and binding to surfaces. Transformation rates also related to: chemical structure, molecular size, functional group, polarity and charge.

2.2.1. The Effects on Inorganic Contaminants

Theoretically, secondary mineral exchange cations according to a specified hierarchy which is based on the following properties of the cations in question:

1) Ionic charge (valence) 2) Atomic size 3) Concentration of cations in solution 4) pH of the soil 5) Type of the cations in solution (Choudhury, 1998).

Generally, as the valence of the ion and the atomic size increases, its ability to exchange increases (with some exceptions). Frequently, the shape of the cation in solution can dictate whether any cations exchange with the soil. For example, potassium has an atomic shape that fits exactly into the gaps of silica sheets. Based on the factors mentioned above, following exchange hierarchy results (Choudhury, 1998):

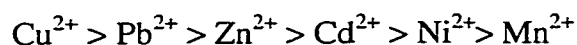


The presence of organic matter coupled with secondary minerals has significant effects on contaminant fate and electrokinetic processes. Humic material also has an inherently high CEC (cation exchange capacity), which can also immobilize inorganic contamination.

Sorption is defined as the retardation of a substance that typically occurs between phases (i.e. solid/liquid phase). This retardation can be at the surface (adsorption),

through the surface (absorption) or through chemical bonding based on the valence of the substance in question (ion exchange). The amount of metal adsorbed to the soil is dependent on the properties of the metal in question and the particular physico-chemical properties of the soil.

From these properties, the decreasing sequence of ion exchange can be expressed in the following manner (Choudhury, 1998):



Generally, the capacity of soils for sorption of most metal ions increases with increasing pH, but the natural mobility of the cations is decreased. For example, the mobility of PbOH^+ increases with increasing pH. This phenomenon has serious ramifications on any remediation technique. Increasing pore water metal concentration by decreasing the pH decreases the mobility of the cations (Merian, 1991).

Humus and in particular humic acid can interact with metal ions, metal oxides, and hydroxides present in soil forming complexes of different solubility and chemical and biological stabilities related strongly to pH. With rising pH and humic acid concentration, there is an increase in sorption of metals efficiency on humic acid. However this efficiency decreases with increasing metal concentration (Kendorff and Schnitzer, 1980). The behaviour of metals depends on a variety of characteristics related to the metal itself and its spatial location. Particular focus will be placed on lead and nickel, as these heavy metals comprise the target contaminants for this thesis, and due to their different behaviour in the environment.

Metals in the environment may undergo complexation, precipitation, dissolution, and change in their oxidation states. They can react with the inorganic and organic in the

water phase and/or at the surface of the solid phase (i.e. sediment). The fate of metals in the subsurface, which includes their physical transport, chemical transformation and retardation is of particular importance to the understanding of contamination effect and any eventual remediation technique that is to be employed. It is generally understood that the degree of mobility and activity of metals is influenced by pH, redox potential, cation exchange capacity of the solid phase, competition with other metal ions, complex metal and soil composition, and concentration in the soil solution (Merian, 1991).

Nickel in the Environment

Nickel, particularly when in its +2 oxidation state is present in aqueous media in a variety of water-soluble forms. These include nickel compounds of acetate, bromide, chloride, fluoride, iodide, nitrate, sulfamate and sulfate salts. Their high solubility increases their mobility in the water thereby spreading contamination quickly. Nickel exists in aqueous solutions primarily as the green hexaquaonickel ion, $\text{Ni}(\text{H}_2\text{O})_6^{+2}$ which is poorly absorbed by most living organisms (Merian, 1991).

Table 2.3 shows the concentration of nickel, lead and other heavy metals found in typical waste. The retention of nickel is primarily due the presence of organic matter, precipitation (with hydroxide ions) and due to the tendency of nickel for hydrolysis. As with all metals, the solubility of nickel compounds increases with decreasing pH.

Lead in the Environment

In most inorganic compounds, lead has an oxidation state of +2. The salts of Pb (II), lead oxides and lead sulfide are not readily soluble in water, with the exception of lead acetate, lead chlorate and to a lesser degree, lead chloride. Inorganic Pb (IV) compounds are unstable and strong oxidizing agents. In addition, lead also partitions itself between different soil components depending on the CEC and structure. This is typically observed in natural clay soils.

Table 2.3 Lead and nickel concentration in typical waste (Legret and Raimbault, 1991)

Heavy Metal	Type of Waste				
	Unaltered Sites (mg/kg.ms)	Spiked Waste sites (mg/kg.ms)	Interstitial Water (mg/L)	Metal Stockpiles (mg)	Waste (mg/kg.ms)
Pb	127	6 721	14.9	43 350	273
Ni	24	1 360	2.7	8 770	55.3

The degree to which metals are hydrolyzed is a major factor determining the amount of lead retained at any given pH. If it assumed that hydrolysis characteristics are unaffected by soil colloids, the speciation of lead in solution can be predicted (Choudhury, 1998). These values are shown in Table 2.4.

Table 2.4 Effect of pH on probable solution speciation of lead (Merian, 1991)

Species	pH=4	pH=5	pH=6	pH=7	pH=8
Pb ²⁺	100	100	98	83	33
Pb(OH) ⁺	-	-	2	17	66
Pb(OH) ₂ ⁰	-	-	-	-	1

2.2.2. The Effects on Organic Pollutant

The fate of organic pollutants in the soil and subsoil are affected by the presence of soil constituents, where processes such as adsorption, partitioning, solubilization, hydrolytic degradation, volatilization, and photo-decomposition will affect to a greater or lesser degree, their fate (Senesi and Miano, 1995). The presence of organic matter in the subsurface can drastically influence the fate of contaminants in the environment. Humic substances have shown to have a considerable impact on adsorption phenomena in soils and are effective at absorbing low molecular-weight organic compounds. Adsorption of organic compounds to the soil is via specific mechanisms with different strengths. These mechanisms include: 1) ionic bonding, 2) hydrogen and covalent bonding, 3) electron donor or acceptor mechanisms, 4) cation bridge, 5) Van der Waals forces, 6) water bridging (Petruzzeli and Helfferich, 1993).

Hydrocarbons are characterized by high molecular weight, low solubility and hydrophobicity, which contributes to their strong sorption to soil matrices. The remediation process often depends on desorption of the contaminant from the soil surface and its subsequent solubilization into the bulk aqueous phase.

Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) are compounds with multiple benzene rings. These compounds can be found in diesel fuel originating from the exhaust of gasoline and diesel engines, chemical manufacturing plants and disposal areas, disposal wells and leach fields, landfills and leaking storage tanks. The most critical PAHs in the environment are flurene, phenanthrene, pyrene. The fate of PAHs is derived by chemical oxidation, hydrolysis, volatilization, and adsorption to soil particles and leaching.

2.2.3. Conclusions

Soil components that mainly influence the fate of contaminants and remediation processes are secondary minerals and organic matter. Therefore, knowledge of the interaction of the main soil components with contaminants can create an understanding of the various processes, which control the fate of these contaminants. The fate of contaminants in the environment is dramatically influenced by the presence of clay colloids, associated organic matter and amorphous inorganic materials. In field conditions, clay material represents a major challenge. Design of a remediation system for contaminated clayey soils must be preceded by exhaustive analysis of the clay fraction, its petrographical structure, organic matter content, and inorganic amorphous material associated with the clay fraction (Elektorowicz *et al.*, 1999).

2.3. Soil Remediation Methods

Site remediation technologies can be generally classified into two major groups, 1) Organic compound removal, and 2) Inorganic compound removal.

2.3.1. Major Remediation Technologies for Organic Removal from Soil

1- Thermal Treatment: Thermal treatment processes employ indirect or direct heat exchanges to desorb, vaporize, or separate organic compounds. It is proven for treating non-hazardous wastes and can be used for treating petroleum-contaminated soils. It can be used for volatile organic compounds, semivolatiles, and PCBs contaminated soils. This technology has a low to medium efficiency and is very expensive. Clay soil can be difficult to treat because of the tendency to stick to process equipment and to aggregate into large clumps that can inhibit heat transfer in the thermal desorber (US EPA, 1998).

2- Soil flushing: In-situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Soil flushing has been used most often at sites contaminated with organics. Soil flushing methods remove contaminants by dissolving and/or by mobilizing them so they can be extracted. The application of soil flushing to soils with low permeability, such as clay, is limited (US EPA, 1997).

3- Incineration: Incineration is a remedial technology that destroys organic compounds in the soil. This technology reduces the volume and toxicity of organic compounds. This treatment technology may not be effective for soil containing metals and soil having a low organic content may be costly to incinerate. This technology will not be applicable to soil requiring in-situ treatment (US EPA, 1997).

4- Soil Vapour Extraction (SVE): This technology involves the use of vacuum pumps or blowers to produce air flow through the contaminated soil (vadose zone). This causes the movement of vapours containing volatile organic compounds (VOCs) towards extraction wells. Extracted vapors are treated, as necessary, and discharged to the atmosphere or reinjected to the subsurface. The movement of contaminants in the soil gas through the soil media can be described by two processes: advection and diffusion. The SVE is not useful at sites with low-permeability soil (clay) and can not be applied in saturated zone (US EPA, 1997).

5- Chemical Extraction: Solvent extraction has been used to treat PAHs (Weisman *et al.*, 1994). Excavated soil is treated through heap leaching and liquid/solid contactors (Ram *et al.*, 1993).

6- Composting: This technology has been used to degrade organic compounds to humic material for use as a soil conditioner. The soil is piled and mixed with an organic

bulking agent, such as straw or wood chips. The success rate is predicated on aeration, pH, moisture, and nutrient level control (Wilson and Jones, 1993).

7- Solidification/Stabilization: This approach involves the mixing of specialized additives or reagents with soil to reduce physically or chemically the solubility or mobility of contaminants in the environment. The binding agent used in this method is carbon-grade fly ash. The solidification and stabilization are closely related due to the fact that both use chemical, physical, and thermal processes to detoxify the soil. This technology does not destroy inorganic compound, but may alter or change organic compound (US EPA, 1997).

8- Phytoremediation: It can enhance the rate and extent of degradation of PAHs in contaminated soil (Santharam *et al.*, 1994). It uses the root system of plants to accumulate contaminants or to enhance biodegradation (Johns and Nyer, 1996).

9- Bioremediation: This technology uses biodegradation of organic contaminants through stimulation of indigenous microbial populations by providing certain amendments, such as adding oxygen or limiting nutrients, or adding exotic microbial species. It uses naturally occurring or externally applied microorganisms to degrade and transform hazardous organic into compounds of reduced toxicity and/or availability. In-situ bioremediation applications requiring circulation of fluids should be avoided in case of tight clay where oxygen transfer limitations exist. This technology requires time to be effective (US EPA, 1997).

10- Bioventing: This method combines the beneficial effects of both, bioremediation and SVE. Hot vapour will remove the volatile portion of hydrocarbons

and by the same time will stimulate the biodegradation of the heavier hydrocarbons such as diesel fuel, jet fuel, and fuel oils (Brown *et al.*, 1993).

2.3.2. Major Remediation Technologies for Inorganic Removal from Soil

1- Soil Washing: Soil washing is an ex-situ, generally water-based process that relies on traditional chemical and physical extraction and separation processes for removing organic and inorganic compounds from soil. This aqueous-based technology uses mechanical processes and/or solubility characteristics of contaminants to separate them from the excavated soil. The process frees and concentrates contaminants in a residual portion of the soil. Soils with high silt and clay content may be problematic due to the difficulty of removing the contaminant from very fine particles. Complex mixtures of contaminants make it difficult to formulate a suitable washing fluid that will remove all the contaminant types. In addition remediating mixed contaminated sites can be cost prohibitive (US EPA, 1997).

2- Vitrification: Vitrification is a soil-melting technology. It uses an electric current passed between electrodes, to heat the soil to high temperatures (1600-2000°C). The soil and contained material are converted to a stable glass. This technology can be applied for soils contaminated with organic and inorganic compounds, but has a very high cost (US EPA, 1997).

3- Electrokinetic Remediation Technology: Electrokinetic remediation involves the application of low-density direct current between electrodes placed in the soil in order to mobilize contaminants in the form of charged species. Electrokinetics can be used to extract radionuclides, metals, and organics from saturated and unsaturated soils (US EPA, 1997). As an in-situ treatment method, it offers the removal of organic and inorganic

contaminants at a relatively low cost compared with other technologies. The applicability of this method in clayey soil is considered a breakthrough in the process of soil decontamination. Chapter 2.4 deals with about electrokinetic soil remediation.

2.3.3. Conclusions

The above-mentioned review of conventional treatment technologies revealed certain disadvantages and deficiencies, which can be summarized as follows:

1. They are generally costly and/or ineffective.
2. The techniques that are highly effective do not allow for the reuse of the soil.
3. Ex-situ techniques have proven to be expensive. The cost of excavating soil from the site constitutes over 50% of the total remediation costs.
4. Natural clay soil presents a medium that makes remediation extremely difficult. Due to its low hydraulic conductivity, high specific surface area, high cation exchange capacity, the above mentioned methods are rendered ineffective or will take years for decontamination to occur below specified limits.
5. Most of these techniques are applied specifically for organic or inorganic contaminants, and they cannot be applied for mix-contaminated soil.

Therefore there is a need to explore and develop a new technology, which can overcome the deficiencies and the disadvantages of the conventional methods and in particular can be adopted to clayey soils with mixed organic and inorganic contaminants where conventional methods have failed.

2.4. Electrokinetic Soil Remediation

Electrokinetics is an emerging engineering technique for the remediation of contaminated soil. The application of a direct current to soil, by insertion of electrodes,

leads to the generation of hydrogen ions at the anode and hydroxyl ions at the cathode (Maini *et al.*, 2000). When an electrical field is applied to a system having charged particles, three general transport phenomena are observed: electrolytic migration, electrophoresis, electroosmosis. Electrolytic migration is the movement of ions within the pore water. Electrophoresis is the movement of charged colloids, while electroosmosis is the movement of the pore water within the subsurface. Electroosmosis could be seen as the dragging of pore water by traveling ions. Within a clay soil system, typically of low permeability, electrolytic migration and electroosmosis are the dominant mechanisms.

A system consisting of anode or cathode, a DC power supply will incite electrokinetic processes such as electroosmosis, electrolytic migration and electrophoresis in clayey soil. With an applied DC current, oxidation-reduction reactions occur at the anode and the cathode respectively in order to maintain electroneutrality (Choudhury, 1998). Figure 2.3 displays a typical electrokinetic process.

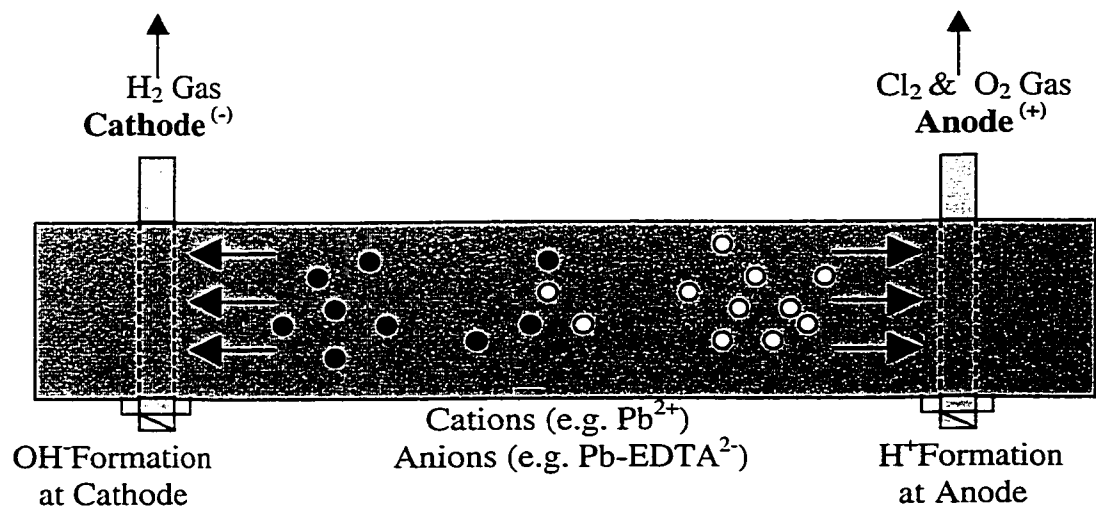


Figure 2.3 Typical electrokinetic process

Due to oxidation-reduction processes, the pH decreases at the anode area, and increases at the cathode area (Elektorowicz *et al.*, 1995; Elektorowicz and Hatem, 1999). Choudhury and Elektorowicz (1997) reported that the use of EDTA coupled with electrokinetic could improve the solubility of lead and nickel in clayey soil.

2.4.1. Classical Electrokinetic Processes

Electroosmosis, electrophoresis and electrolytic migration are the three major phenomena occurring in soil during the removal of contaminant under an electric field. The following three sections describe the detailed principles of these phenomena.

2.4.1.1. Effects of Electroosmosis on Electrokinetic Remediation

Electroosmosis (EO) is the transport of pore fluid under an electric gradient (US EPA, 1997). The most widely accepted theory for electroosmotic flow, is that net water flow results when the transfer of momentum between migrating ions of one sign exceeds that of the ion of the opposite sign. As cations flow to the cathode and anions flow toward the anode, it has been hypothesized that water surrounding the ions is dragged along via frictional forces (Eykholt and Daniel, 1994).

The driving force caused by electroosmotic flow is indicated by the coefficient of electroosmotic permeability (k_e), which is defined as the volume rate of water flowing through a unit cross-sectional area due to unit electric gradient under constant conditions and for a short duration of testing. The electroosmotic flow rate estimated in the laboratory developed by Casagrande and is expressed by equation 2.1.

$$q_e = k_e i_e A = k_e I \quad (2.1)$$

Where: q_e = Electroosmosis flow rate [cm^3/s]
 k_e = coefficient of EO permeability [$\text{cm}^2/\text{V.s}$]

i_e = potential gradient [V/cm]
 A = cross-sectional area [cm²]
 k_i = coefficient of water transport efficiency [cm³/A.s]
 I = applied current [A]

The value of k_e has been found to be a function of zeta potential, viscosity of the pore fluid, porosity, and electrical permeability of the soil medium. Hunter (1982) displays that zeta potential decreases linearly with a decrease in the logarithm of ionic concentration and/or the pH of the soil medium. It is hypothesized that the drop in pH of the soil due to electrokinetic processing will cause a decrease in the coefficient of electroosmotic permeability associated with the drop in zeta potential.

Soluble species in the pore water may also be carried to the cathode following electroosmotic flow. Since clay can attract a cluster of excess cations close to the surface, under an electric field, the excess cations close to the surface move towards the cathode along with the movement of water molecules, thereby following electroosmotic flow in the same direction (Acar *et al.*, 1993). They also indicated that, this coupling effect might result in a high-conductivity region at the anode and a low conductivity region at the cathode, when applying a constant current.

When an electric field is applied to wet soil, the soil pH undergoes transient and spatial variation due to dissociation of water, which in turn affect soil surface properties such as cation exchange capacity, ion (cation and anion) adsorption capacity, and magnitude and sign of the electrokinetic potential. It is suggested that the effect of the soil pH on the electroosmotic flow was an important factor in removing organic contaminants from soil (Kim *et al.*, 2000).

2.4.1.2. Effects of Electrophoresis on Electrokinetic Remediation

Electrophoresis involves the movement of charged particles under the influence of an electric field (Mitchell, 1976). This definition includes all electrically charged particles like colloids, clay particles in pore solution, organic particles and droplets. within the pore solution, these particles transfer the electrical charges and affect the electrical conductivity and the electroosmotic movement. The electric force on the charged particle is equal to the hydrodynamic fractional force on the particle by the liquid.

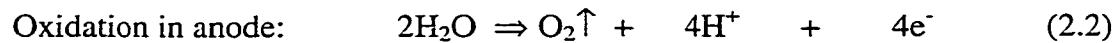
Electrophoresis becomes an important mechanism in electrokinetic soil remediation when surfactant is introduced into the fluid to form micelles (charged particles) (Pamukcu and Wittle, 1992; Acar and Alshawabkeh, 1996). In addition, electrophoresis of clay colloids may play an important role in decontamination if the colloids migrate with adsorbed chemicals. Electrophoresis movement can contribute to the transport of contaminants in the form of colloidal electrolytes or ionic micelles. Ionic micelles often carry a high charge and exhibit high conductance in dilution. As the concentration of surfactants increases, a build-up of charge occurs due to further aggregation, and the conductance consequently increases (Pamukcu *et al.*, 1995).

In this research, the target organic contaminant is phenanthrene, which is a nonpolar insoluble organic compound. It is strongly sorbed to the clay particle and/or soil organic matter. Consequently, it cannot be effectively transported with electroosmotic flow. However, due to the introduction of surfactants, phenanthrene forms ionic micelles, subjected to electrokinetic phenomena including electrophoretic flow, which can enhance its mobility and subsequent removal.

2.4.1.3. Effect of Electrolytic Migration on Electrokinetics

When a DC electric current is applied to a soil system, cations and anions move toward the respective electrodes. The effective ion mobility is a measure of how fast ions will migrate toward the oppositely charged electrode. The average mobility of ions lies around $5 \times 10^{-8} \text{ m}^2/\text{V.s}$, which is ten times greater than that of the electroosmotic mobility (Lageman, 1989).

Electrolysis reactions at the electrodes need to be considered together with the mass flux of species that occurs in the electric field. Due to the application of DC current, oxidation occurs at anode while reduction at the cathode. The reactions are shown in equations 2.2 and 2.3.



The hydrogen and hydroxyl ions migrate into the soil under the action of the electric field and produce acidic conditions near the anode and alkaline condition near cathode (Joseph *et al.*, 1997). The hydrogen and hydroxyl ions generated at the electrodes by the electrolysis reactions may transport to the opposite electrode. In unenhanced electrokinetic remediation, the protons along with hydroxyl groups, can be transported across the soil mass, and generate water (Acar and Alshawabkeh, 1993).

2.4.2. Conclusions Related to Classical Electrokinetics

Moderately high removal efficiencies have been documented and costs are lower than comparable soil remediation techniques. However, there are numerous problems

with this technique that must be overcome in order to increase the efficiency of metal removal.

2.4.2.1. Problem Related to High pH Development

A high pH development in the cathode region creates a precipitation barrier, which has adverse effects on electrokinetic remediation. In order to maintain electroneutrality, OH^- ions are constantly produced at the cathode. These ions begin migrating towards the anode at a rate that is a function of their ionic mobility.

Elektorowicz, (1995), dealt with the technical requirements related to electrokinetic removal of contaminants from soil. One of the major requirements was lowering the pH in the cathode region and allows mobilization and accessibility of heavy metals to electrokinetic transport. A system consisting of washing zones close to cathode and anode was used.

2.4.2.2. Problems Related to Mobilizing Heavy Metals during Electrokinetics

In order for electrokinetic processes to be successful, heavy metals must remain in ionic form (in the liquid phase) so that they can be transported to desired locations. The low water solubility of lead and nickel, the high pH development in the cathode region and the CEC of the soil, prevents the mobilization of heavy metals. The problem becomes more difficult in the case of natural clay soil, where high CEC values and high initial pH values are observed. Choudhury and Elektorowicz, (1997) used EDTA for recovery of lead and nickel from soils during electrokinetic processes.

A chelation agent is a substance whose molecules can form several coordinate bonds to a single metal ion (Joseph *et al.*, 1997). Despite some research with chelating agents, definitive conclusions related to their effectiveness during electrokinetics are

limited. Clay soil represents a difficult case for heavy metal mobilization, due to its inherently high pH and CEC. The use of chelating agents has been shown to be effective in mobilizing heavy metals in soil (Choudhury and Elektorowicz, 1997).

2.4.2.3. Problems Related to Mobilizing Organics During Electrokinetics

Soils contaminated by organics can be classified by whether the organic compounds are soluble or insoluble in water. Insoluble organics, such as heavy molecular weight hydrocarbons, are essentially not ionized (hydrophobic). The removal of hydrophobic compounds can be achieved by electroosmotic purging using surfactants to solubilize the compounds and mobilize them by an advancing surfactant front (Elektorowicz and Hatim, 1999).

2.4.3. Conclusions

Many industrial sites especially gas manufacturing plants contain mixed organic and inorganic compounds, each of which may interact differently with the soil. Therefore, the remediation of such sites has to proceed in stages, that will mobilize both organic and inorganic contaminants (Elektorowicz *et al.*, 1995). A hybrid electrokinetic technology is required to create optimum mobilization, transport, and removal of mix contaminants from clay soil.

2.5. Use of Surfactants for Organic Contaminant Desorption in Soil

PAHs are not easily transported from the solid to the aqueous phase, especially in soil containing fine fractions. Consequently, they are unaffected by conventional treatment methods. Therefore, the use of surfactants as agents for the apparent solubility and mobility enhancement has been a subject of intensive research (Elektorowicz and Hatim, 1999).

Recently, surfactants are used in technologies such as soil-washing, soil-flushing, pump-and-treat for increasing the solubilization of sorbed hydrophobic contaminants (Abdul *et al.*, 1992). The removal of petroleum hydrocarbons can be a few times higher when surfactants are added to the washing system (Ellis *et al.*, 1985). Edwards *et al.*, (1991) utilized four commercial nonionic surfactants to enhance the solubility of naphthalene, phenanthrene, and pyrene. Surfactant addition to PAH-contaminated soil has been demonstrated to be effective in the dissolution and desorption of PAHs from soil systems, resulting in higher mass transfer rates (Miller, 1995). Therefore, addition of surfactants into the soil can enhance the solubility and bioavailability of PAHs. Surfactants have the capability to enhance the removal of PAHs by means of two mechanisms: solubilization and mobilization.

The use of surfactants with electrokinetics in soil remediation is a new concept. The combination of both technologies (surfactant and electrokinetic) has been thought to take advantage of electrophoretic flow in addition to electroosmotic flow. Hatim (1999) showed that, among different concentrations of surfactant, the 0.0025 M surfactant concentration had a better phenanthrene removal efficiency in electrokinetic soil remediation.

Properties of surfactants are derived from their nature as amphiphilic chemicals, which have dual characteristics: hydrophilic and hydrophobic. These characteristics are derived from polar and non-polar regions, which allow the molecules to concentrate at interfacial surface: air-water, oil-water, and solid-liquid interfaces (Cain, 1994). One of the most characteristic properties of surfactants is their capacity to aggregate in solution. The aggregation process depends on the amphiphilic species and the condition of the

system in which they are dissolved. A dynamic cluster is formed when the bulk solution concentration of a given surfactant is greater than a specific threshold value defined as the critical micelle concentration (CMC). The molecular aggregates that form concentrations above the CMC are known as micelles. The average number of surfactant molecules in each micelle is called the aggregation number. The CMC is a function of surfactant structure and the temperature of the surfactant solution (Moroi, 1992). The CMC is different for every surfactant and is typically between 0.1 and 10 mM/L.

Surfactants are classified according to the nature of hydrophiles and hydrophobes. This results in the existence of anionic, cationic, zwitterionic (or amphoteric) and nonionic surfactants.

- 1- Anionic surfactants, with the hydrophilic group carrying a negative charge, are the largest class of surfactants in use (e.g. carboxyl (RCOO^-M^+), sulfonate (RSO_3^-M^+), or sulfate ($\text{ROSO}_3^-\text{M}^+$)).
- 2- Cationic surfactants, with the hydrophile bearing a positive charge, are very important roles as antiseptic agents (e.g. quaternary ammonium halides ($\text{R}_4\text{N}^+\text{VI}^-$)).
- 3- Zwitterionic (amphoteric) surfactants contain hydrophobic groups consisting of both negative and positive charges (sulfobetaines $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$).
- 4- Nonionic surfactants contain hydrophilic groups without charge (e.g. polyoxyethylenes ($-\text{OCH}_2\text{CH}_2\text{O}-$) or polyol groups).

A careful selection of surfactant and their concentrations is required to prevent soil colloid dispersion. Choosing a surfactant usually follows certain criteria, which are summarized as follows:

- 1- Aqueous solubility: Due to the fact that the surfactant is prepared in solution of water, its solubility in water is one of the fundamental aspects in any remedial action.
- 2- CMC: It indicates the amount of the surfactant to be used. The lower the CMC, the less surfactant is needed. Nonionic surfactant has a lower CMC, followed by anionics, and cationics (Myers, 1992).
- 3- Potential for electrokinetic transport: Under an electric gradient cationic micelles will be moving in the same direction as the electroosmotic flow. Anionic micelles will migrate in an opposite direction to the electroosmotic flow. Nonionic micelles will only flow by electroosmosis (Taha, 1996).

2.6. Use of Chelation Agents (EDTA) for inorganic Contaminant Desorption in Soil

Ethylenediaminetetraacetic acid (EDTA) is a highly branched and high molecular weight acidic compound. EDTA has a specific gravity of 0.86, a molecular weight of 292.25 g/mol, is slightly soluble in water and tends to exist as white, odorless crystals (Choudhury, 1998).

Due to EDTA ability of form strong water-soluble chelates with most metals, it has been extensively used to extract heavy metals from contaminated soil with 90% efficiency, through solubility and mobility enhancement (Yeung and Menon, 1996). When the electroosmotic flow is from anode to cathode, injecting a strong anionic complexing agent such as EDTA into the contaminated soil from the cathode can enhance electrokinetic extraction of heavy metals from the contaminated soil by the formation of soluble heavy metal ions-EDTA complexes (Yeung and Menon, 1996; Choudhury and Elektorowicz, 1997).

Under normal conditions, ionic migration is considerably greater than the flux due to electroosmosis. Therefore anionic complexing agents and metal complexes may still migrate toward the anode even when electroosmotic flux is toward the cathode (Yeung and Menon, 1996). In natural clay soil, the use of EDTA has the potential to keep more heavy metals in the solution phase, thereby allowing electrokinetic methods to transport an increasingly higher amount of metals. It should be noted that if electrokinetic methods were used with EDTA, electrolytic migration would tend toward the anode, due to formation of negative metal-EDTA complexes (Choudhury, 1998).

Based on the stability constants for heavy metals and hydrometallic complexes, the utilization of EDTA presents a suitable method for solubility enhancement of metal ions in natural clay soil. The log of the stability constants for the Pb-EDTA and Ni-EDTA are 18.0 and 18.6 respectively (Yeung and Menon, 1996). In addition, the six possible exchange sites on the EDTA ion enhances the degree of complexation. The use of EDTA coupled with electrokinetic method enhances the removal of precipitated metals from soil (Joseph *et al.*, 1997).

Important considerations in selecting a chelating agent for soil remediation work include (Joseph *et al.*, 1997):

- the chelates should be highly stable over a wide pH range;
- neither the chelating agents nor their chelates should adsorb on the soil;
- the chelating agent should have low toxicity;
- the chelating agent should be cost effective.

2.7. Ion Exchange Materials and Resins

Ion exchangers are solid and suitably insolubilized high molecular weight polyelectrolytes, which can exchange their mobile ions for ions of equal charge from the

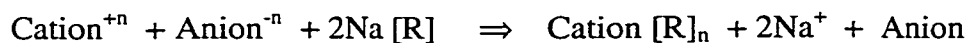
surrounding medium. Ion exchange materials are classified in two groups: inorganic ion exchange materials and organic ion exchange resins.

Clay minerals (e.g. kaolinite, illite, montmorillonite, chlorite and vermiculite) possess a natural ability to exchange cations, which makes them instrumental in the ion exchange process. Organic ion exchange resins are produced through a specific type of polymerization reaction known as addition or vinyl polymerization (Harland, 1994). Organic ion exchange resins are classified according to their composition, function (anion or cation exchanger) and the solution used for the activation of the polymer (Harland, 1994). The following classification occurs:

- Styrenic cation exchange resins (strong and weak acid);
- Acrylic cation exchange resins (strong and weak acid);
- Styrenic anion exchange resins (strong and weak base);
- Acrylic anion exchange resins (strong and weak base).

Ion Exchange Theory

In equal concentrations, multivalent cations with large atomic radii and atomic charges are adsorbed more strongly than sodium. As the water comes into contact with the medium (Choudhury, 1998), the following reaction occurs instantaneously, where [R] is the exchange media:



The exchange of cations continues until all of the exchange sites on the medium have been filled. At this point, metals become evident in the effluent and the medium must be regenerated.

Organic ion exchange resins have high pH flexibility (most resins are efficient in all pH ranges) and inorganic ion exchange materials have high pH sensitivity (the exchange of metals onto the surface is highly dependent on pH) (Harland, 1994). Properties and comparison of organic ion exchange resins is shown in Table 2.5.

Table 2.5 Properties and comparison of organic ion exchange resins (Harland, 1994)

Property	Strong Acid	Weak Acid	Strong Base	Weak Base
pH range of Applicability	0-14	4-14	0-14	0-9

The textiles activated under the electron bundle initiated the reaction of grafting in presence of monomers. Cation exchange substances (carboxylic function) and anion exchange substances (tertiary amine) were the first applied in solid medium (soil) as CET and AET respectively in laboratory of Concordia University. Studies were conducted on the use of different types of exchangers that described above. Ion exchange textiles were applied for removal of lead and nickel from natural clay soils (Elektorowicz, 1995; Elektorowicz, *et al.*, 1996a; Choudhury and Elektorowicz, 1997). The previous studies on the removal efficiency indicate the potential application of ion exchange textiles for soil remediation. The principal drawback related to its use in conjunction with electrokinetic methodology is that heavy metals do not remain in the pore water phase, due to the low water solubility of lead and nickel compounds and high cation exchange capacity of the soil. Present studies on coupling the electrokinetic methods with other processes (Hatim, 1999 and Choudhury, 1998) encourage the application of these processes to remove inorganic and organic contaminants.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

The description of the experimental setup and the analytical methods used in all experiments for obtaining data was required removal of mix contaminants to verify the accuracy and precision of all parameters measured. To accomplish the objectives outlined in this chapter, a series of experiments were performed using a methodology defined in Figure 3.1.

The experiments were divided into three test series (T1, T2 and T3), which allowed for the determination of several phenomena. Particular objectives were to investigate:

- T1: Response of mixed contaminated sites to the use of surfactant, EDTA and ion exchange textiles.
- T2: Sequential desorption through the application of surfactant and EDTA in various sequences.
- T3: Effect of injection time on contaminant removal and energy consumption.

3.1. Soil Characterization and Preparation

A non-contaminated clayey soil was used and its characterization results were described in previous works (Hatim G, 1999 and Choudhury A, 1998).

The soil was predominantly fine-grained (passing through the No. 200 sieve) material of clay nature. Table 3.1 summarises the results that comprise its characterization.

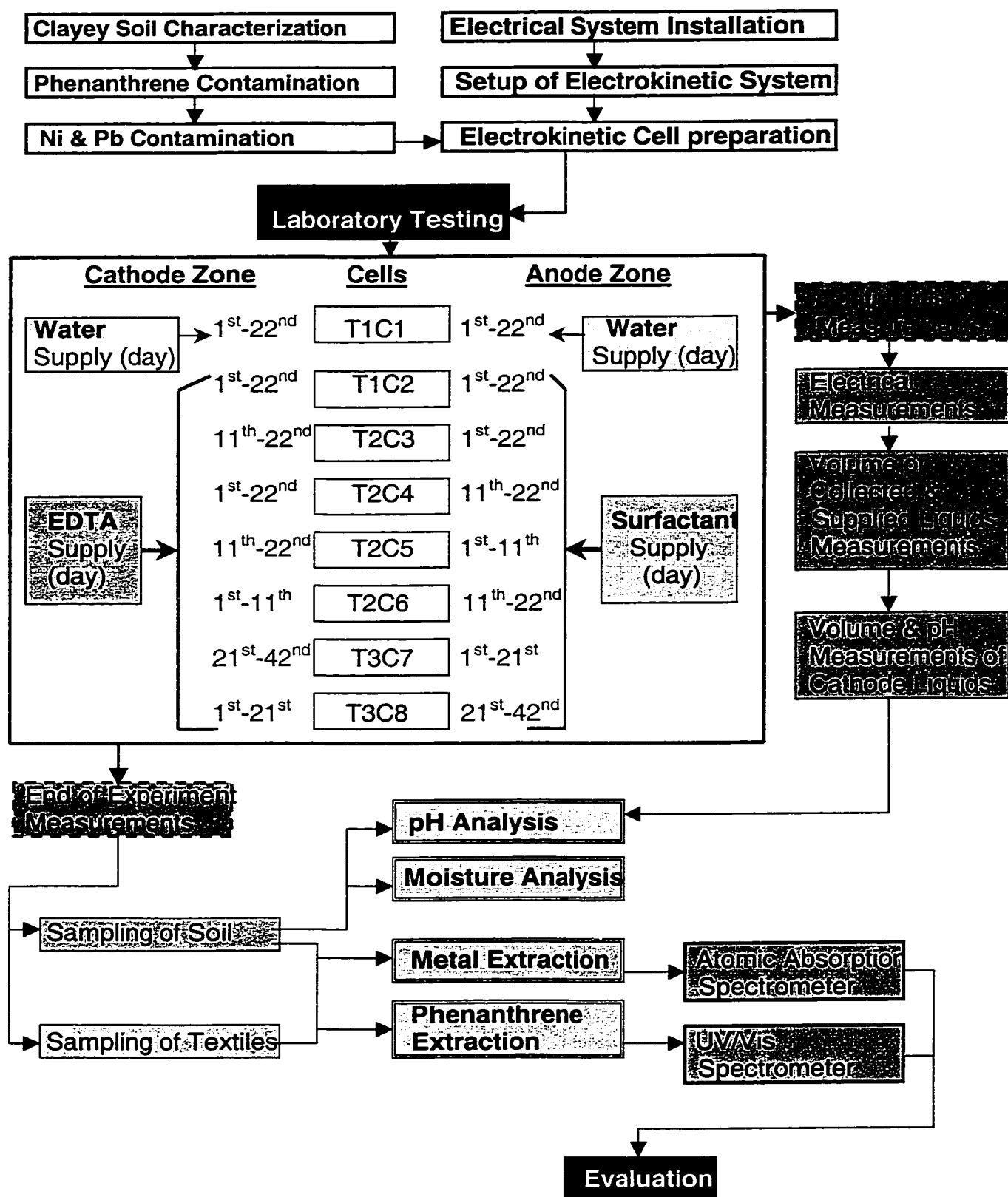


Figure3.1 Methodology used for the experimentation

Table 3.1 Characteristics of clayey soil used for experimentation

Soil Mineralogy	Metal Content	Other Parameters
<ul style="list-style-type: none"> Quartz 4.6 % Feldspar 21 % Dolomite 3.2 % Amphibole 6 % Illite 49.8 % Chlorite 14.1 % Kaolinite 1.3 % 	<ul style="list-style-type: none"> Fe: 273 mg/kg K: 176 mg/kg Ca: 250 mg/kg Ni: 31 mg/kg Pb: 9 mg/kg 	<ul style="list-style-type: none"> Carbonate Content 4.5 % Organic Matter 1.3 % CEC 21 meq/100g Specific Gravity 2.75 Sulfate 0.6 ppm as SO_4^{2-} pH: 7.60

The complete preparation of the soil for its implementation into the electrokinetic cells took place in the following way:

1. The soil was shredded and air-dried for 4 days.
2. The soil was powdered and then sieved using No. 200 mesh.
3. Phenanthrene was used as a model for PAHs contamination in soil. Phenanthrene (98% purity), an isomer composed of three benzene rings, was purchased from Fisher Scientific. Amount of 3.6 g of phenanthrene was dissolved in 600 ml of methanol to obtain the required concentration.
4. The phenanthrene solution was added to 6 kg of dried soil to obtain the soil contamination of 600 mg phenanthrene per 1 kg of dry soil.
5. The soil was again air dried for 48 hours and then powdered to obtain smaller size material.
6. The solution containing lead chloride and nickel chloride (1000 ppm each) was added to a known mass of dried soil contaminated with phenanthrene to obtain to the concentration of 555 mg nickel chloride and lead chloride per 1 kg of dry soil.
7. The soil was then placed into electrokinetic cells in five layers. Tamping was performed on each layer in order to minimize air pockets. To minimize moisture

losses during the test, polyethylene film was used to cover the cell's top surface.

This construction of cells allowed for gas emission during the tests.

It should be noted that both characterization and preparation of the soil for all experiments represented a standard method in order to maintain consistency and allow for an accurate comparison between experiments.

3.2. Experimental Setup and Cell Configuration

Cells were made from rigid polyethylene. In all experiments, the cells had the same dimensions (length = 23.0 cm, width = 5.3 cm, depth = 4.5 cm).

Based on previous experiments (Elektorowicz *et al*, 1995) perforated tubes were used (diameter = 1.0 cm) as cathode and anode, fixed to the cell at an edge-to-edge distance of 16.0 cm. The cathode and anode were made of stainless steel.

The cathode extended through the cell, in order to permit the attachment of a 20 ml sampling vial at the bottom. This facilitated the collection of liquid samples on a daily basis. The cation exchange textile (CET) was placed judiciously in order to alleviate the problem of high pH formation at the cathode. Based on experiments performed previously by (Elektorowicz *et. al.*, 1996b), high pH develops within 3.0-3.5 cm of the cathode for an anode-cathode distance of 16.0 cm. In addition, pH values lower than that of the original soil occur within 3.0-3.5 cm of the anode. Therefore, the ion exchange textiles were placed 3.5 cm from the edge of the electrodes. It was assumed that the placement of the anion exchange textile (AET) would alleviate the problem of anionic precipitation near the anode and will allow for the localization of anions (i.e. metal-EDTA complexes). Figure 3.2 shows the configuration of all electrokinetic cells.

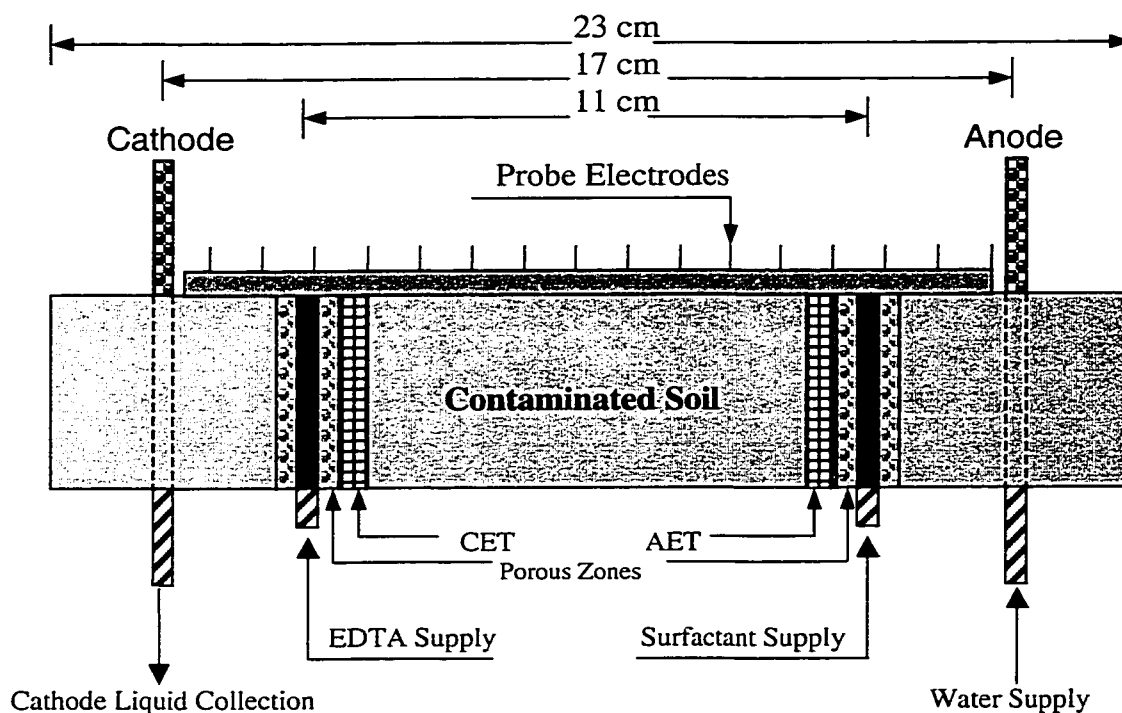


Figure 3.2 Configuration of all electrokinetic cells

Electrical parameters along the distance between the anode and the cathode, were monitored during the tests using special silver probe-electrodes, 0.10 cm in diameter and spaced 1.0 cm apart. The probe-electrodes were inserted into the soil to a depth of 3 cm. However a portion was maintained 1 cm above the soil surface. Figure 3.3 illustrates probe-electrodes set on a Plexiglas base. It should be noted that electrical potential supplied to each cell was 4.8 Volts. The voltage distribution between the electrodes was monitored by direct measurements of the potential between electrodes and each probe-electrode. Potential measurements were obtained every 24 hours, at each probe electrode location for the entire duration of the experiments.

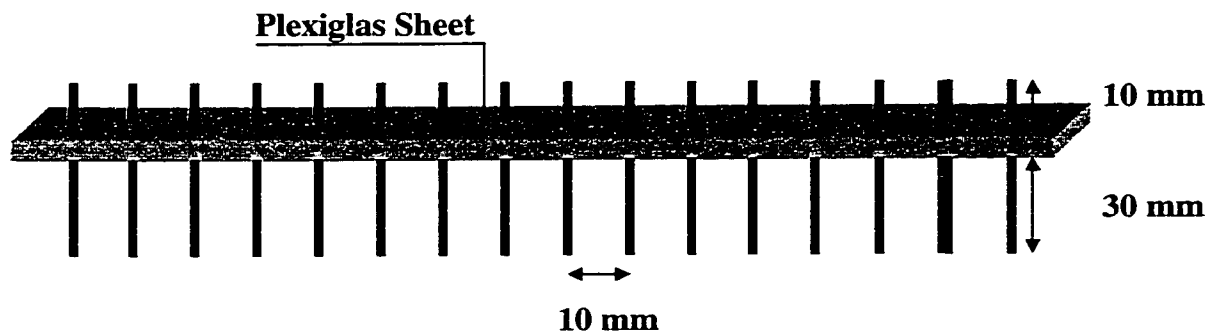


Figure 3.3 Probe-electrodes placed on a plexiglas holder

3.3. Liquid Supply System

In the design of the liquid supply system, the following requirements were considered:

1. No head pressure.
2. Continuous liquid supply.
3. Controlled liquid level.

Supplying surfactant, EDTA and water to the electrokinetic cells were done through the use of reservoirs connected to the cell through a hydraulic valve. This solution proved to be simple and at the same time fulfilled the above-mentioned requirements. Flexible and chemical resistant tubing were used in the system. The hydraulic valve allowed for the control of the liquid level in the soil so that no overflow would occur during the test. Water was supplied directly through the anode. Surfactant and EDTA were supplied using a perforated PVC tube, 0.9 cm in diameter. The delivered surfactant and EDTA entered the porous area (fine sand) prior to their transport through the cell. The perforated area ensured a homogeneous distribution of surfactant and EDTA on the entire soil cross section. For practical purposes and to support the sand, a rigid

PVC mesh was used as a confinement compartment for the sand. The porous sand zones were 1.5 cm in thickness and were located 2.0 cm from the anode and cathode (edge-to-edge). In all cells, the surfactant was supplied in the porous zone close to the anode. Figure 3.4 illustrates the surfactant supply system.

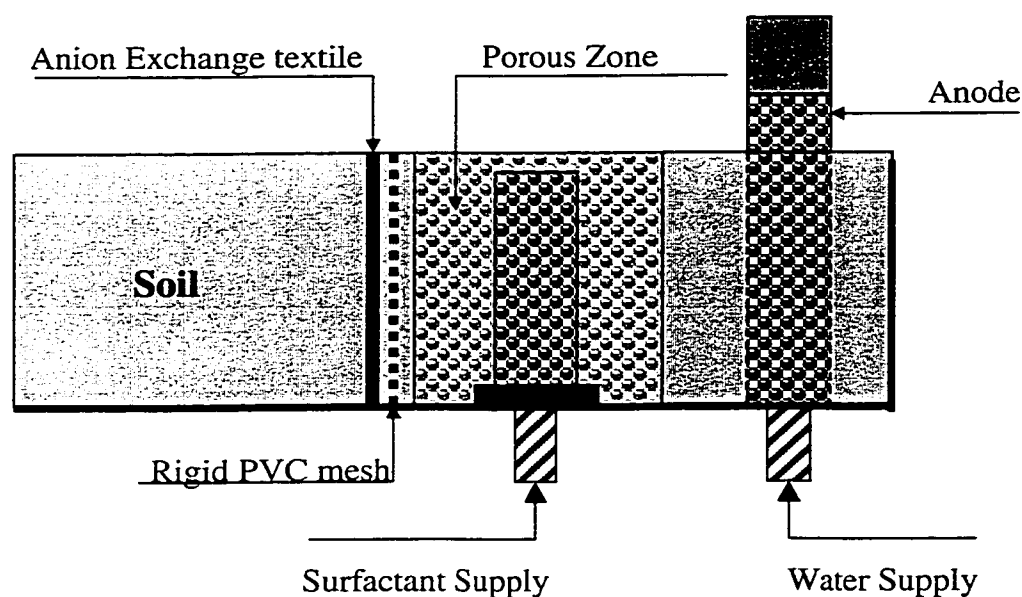


Figure 3.4 Surfactant supply system in an electrokinetic cell

The EDTA was supplied in the porous zone close to cathode using a configuration similar to the one used to supply surfactant. Figure 3.5 illustrates the EDTA supply system in the electrokinetic cells.

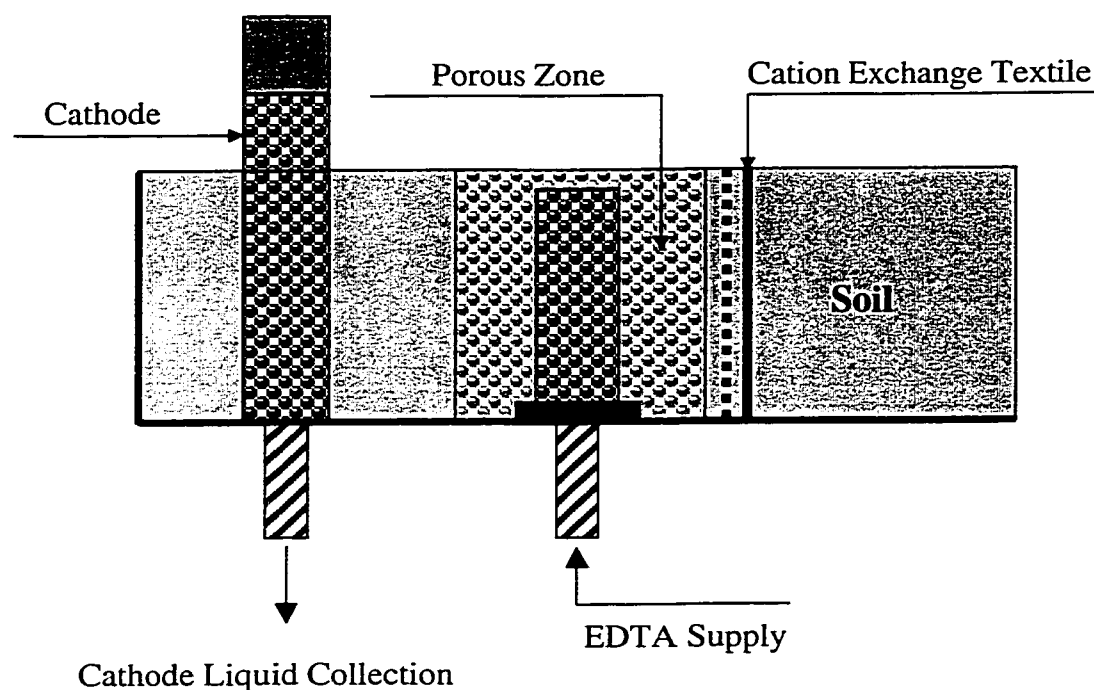


Figure 3.5 EDTA supply system in an electrokinetic cell

3.4. Characteristics and Preparation of Ion Exchange Textiles

Both anion and cation exchange textiles were used in all experiments. Both textiles types were obtained from l'Institut Textile de France. Each textile was cut into a size that matched the cross-section of the cell, which was (width = 5.3 cm, depth = 4.5 cm). The textiles were placed exactly next to porous zones.

Cationic textile was carboxylic ($\text{R-COO}^- \text{Na}^+$) with an exchange capacity of 3.8 meq/g. The anionic textile was pleximon ($\text{R-N}^+(\text{CH}_3)_3\text{OH}^-$) with an exchange capacity of 0.6 meq/g.

3.5. Apparatus, Reagents and Equipment

The following section deals with a summary of the significant apparatus and equipment used in the experiments and analyses.

3.5.1. Cell Construction and Experimental Setup

- Apparatus and Equipment
 - 16 Stainless steel electrodes ($D = 1.0\text{ cm}$)
 - 128 Silver probe electrodes ($D = 0.10\text{ cm}$)
 - 500 of 50 ml Plastic sampling bottle (collecting of cathode liquids)
 - 16 Reservoirs for surfactant, EDTA and water
 - 1 DC power supply (TES 6230 and XANTREX XKW 40-25)
 - Digital multimeter (Mastercraft)
 - Flexible plastic tubing
 - 16 PVC perforated tubes for liquid supplying system
- Reagents
 - 1000 ppm solution of PbCl_2 and NiCl_2 (prepared from stock of PbCl_2 and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)
 - Phenanthrene solution with methanol (3.6 g of phenanthrene per 600 ml methanol)
 - 0.1 M EDTA (prepared from *Disodium Ethylenediamine Tetraacetate* $\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$ (M.W. = 372.24 g/mol)).
 - 0.0025 M Surfactant (prepared from *Alkyl Dimethylbetaine* (CMC = 0.00099 M)).

3.5.2. Measurements and Analyses

- Mechanical shaker (AROS 160)
- pH meter (Accumet 1003 from Fisher Scientific)
- UV/Vis spectrometer (Perkin Elmer, Lambda 700)
- Atomic Absorption spectrometer (Perkin Elmer, Analyst 100)

3.6. Analysis and Measurements During the Experiments

3.6.1. pH Measurements of Cathode Liquid

The pH values of the cathode liquid (collected daily) were measured during the tests using the pH meter model Accumet 1003.

3.6.2. Volume Measurements of Injected and Extracted Liquid

The volume of extracted cathode liquids was measured daily. The volume of EDTA, surfactant and water supplied through the use of graduated reservoirs. Each cell had separate reservoirs. The supply system was modular; thereby allowing for its disconnection and reuse in either experiment.

3.6.3. Measurements of Electrical Parameters

Electrical potential along the distance between the cathode and the anode was monitored during the test. Readings were carried out using a digital multimeter. Each reading represented a potential gradient between the cathode and the subsequent probe-electrode. Total current in each cell was also monitored. Figure 3.7 shows the scheme of electrical setup.

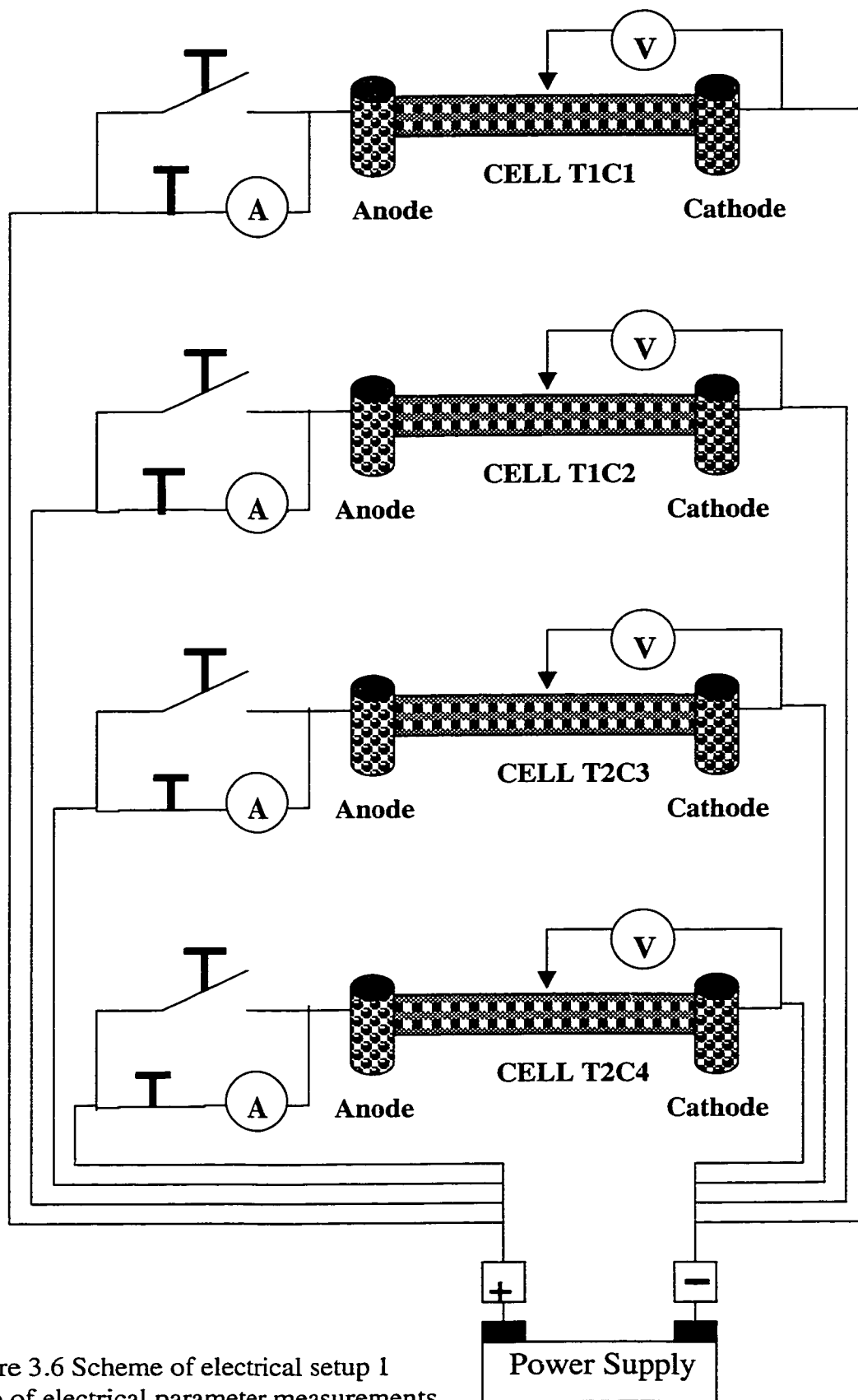


Figure 3.6 Scheme of electrical setup 1
State of electrical parameter measurements

3.7. Sampling, Analyses and Measurements after the Experiments

3.7.1. Soil Sampling

After the tests, the soil was sampled in approximately equal thickness and at known distances. Eighteen soil samples were obtained from each cell. The large number of samples was necessary in order to obtain an accurate representation of the pH and the metal and phenanthrene content in soil which, permitted the verification of the degree of mobility and removal of contaminants from the soil. Figure 3.8 shows scheme of the soil sampling in each electrokinetic cell.

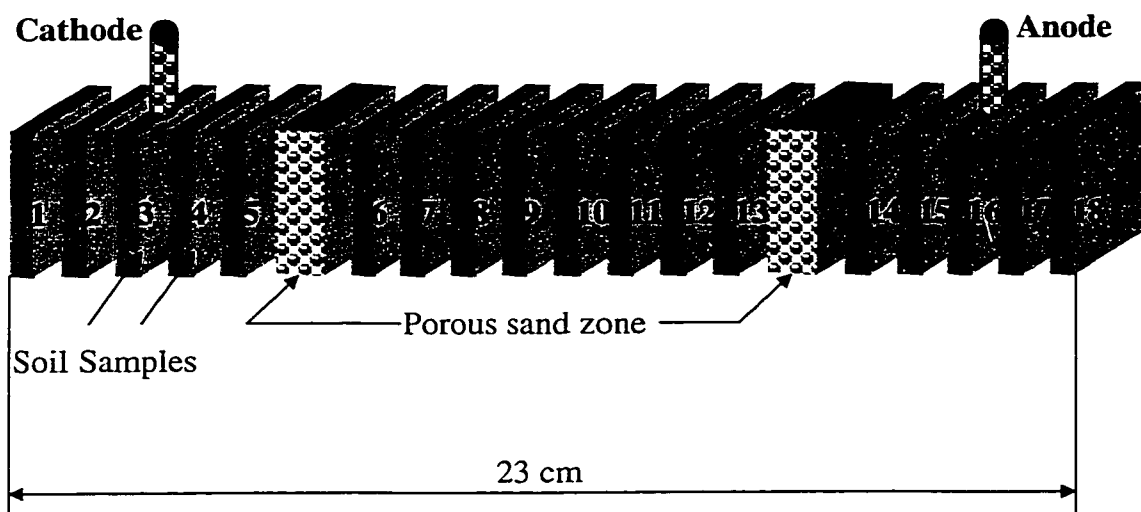


Figure 3.7 Scheme of soil sampling

Each soil sample was divided in to 3 portions (Figure 3.8). Portion A for pH analysis, portion B for phenanthrene content analysis and portion C for moisture and metal analysis. Amounts of portions A, B and C were approximately 20%, 40% and 40% of an entire soil sample respectively. Finally entire numbers of samples reached 700. They were subjected to more than 2000 analyses.

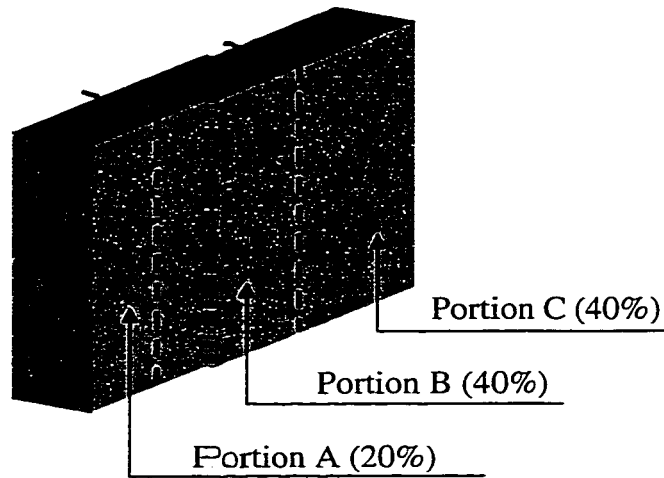


Figure 3.8 Soil sample dividing

3.7.1.1. Moisture Content

The ASTM standard method (No ASTM 2216-90 vol. 4.08) was used to determine the moisture content of the soil. Soil samples (portion C) were oven dried for 24 hours at a temperature of 105 °C. After drying, soil samples were placed into a desiccator for 15 minutes. The samples were then weighed and water content was calculated according to the equation:

$$W = (M_w - M_s) \times 1000/M_s$$

Where: M_w = mass of wet soil

M_s = mass of dry soil

3.7.1.2. pH Measurements

The pH measurements of soil samples were conducted according to the following procedure: 3.0 g of crushed air-dried soil from portion A from each sample was placed in a 50 ml centrifuge tube. Distilled water (100.0 mL) was added to the soil. The suspensions

were shaken for 1 hour. The pH of the supernatant was obtained once the reading become stable.

3.7.1.3. Measurements of Metal Content

The removal of metals from the cell was evaluated by measuring metal concentration in the soil samples. The measurements were conducted as follows:

- Extraction of heavy metals from soil samples:

After moisture analysis, soil samples (portion C) were crushed and 5 g of each sample was subjected to the metal extraction procedure. Crushed soil was placed in 50 mL centrifuge tubes. 25 mL of HCl (4M) was added to the soil. The suspensions obtained were shaken overnight and allowed to settle for 3 hours. The filtration process with suction was applied and the liquids collected from filtration were analysed using an Atomic Absorption Spectrometer (Perkin Elmer, Analyst 100).

- AA spectrometer analysis:

The liquids collected from the samples were directly subjected to AA analysis for lead and nickel. The concentration of lead and nickel was determined using flame AA analysis with the wavelength of 283.3 nm and 351.5 nm respectively. Four solutions of lead (12.5, 25.0, 50.0, 100.0 mg/L) in HCl (4M) defined the standard curve for lead. The standard curve for nickel was obtained based on the following four solutions (6.25, 12.50, 25.00, 50.00 mg/L) of nickel in HCL (4M).

3.7.1.4. Measurement of Phenanthrene Content

Soil samples, designate to be analysed for their phenanthrene concentration, were subjected to solvent extraction, and then extracts were analysed for their phenanthrene content using the UV/Vis spectrometer (Perkin Elmer, Lambada 700). A calibration curve was determined in separate batch tests. The measurements were conducted as follows:

- Extraction of phenanthrene from soil samples:

Soil samples (portion B) were air dried for 24 hours and crushed to a powder. Dichloromethane CH_2CL_2 (DCM) was chosen for solvent extraction of phenanthrene. Five grams of powdered soil from each sample was placed in a 50 mL centrifuge tube. Five grams of powdered Sodium Sulfate (Na_2SO_4) was added to each soil sample. Amount of 25 mL of DCM was added to each soil sample in order to extract the phenanthrene. The suspensions were shaken overnight and then centrifuged for 15 minutes in 4500 r/min. The supernatant obtained was subjected to UV/Vis analysis.

- UV/Vis analysis:

To find the range of phenanthrene absorbency and its wavelength, a 10 mg/L phenanthrene-DCM solution was scanned in the UV spectrometer. The data are presented in Figure 3.9 and Table 3.2 along with the chosen absorbency and the wavelength.

The defined wavelength under which the phenanthrene could be identified was used as a basis to prepare a standard curve. Four solutions of phenanthrene in DCM (1.25, 2.50, 5.00, 10.00 mg/L) defined the curve. The data shown in Table 3.3 were used to form a standard curve.

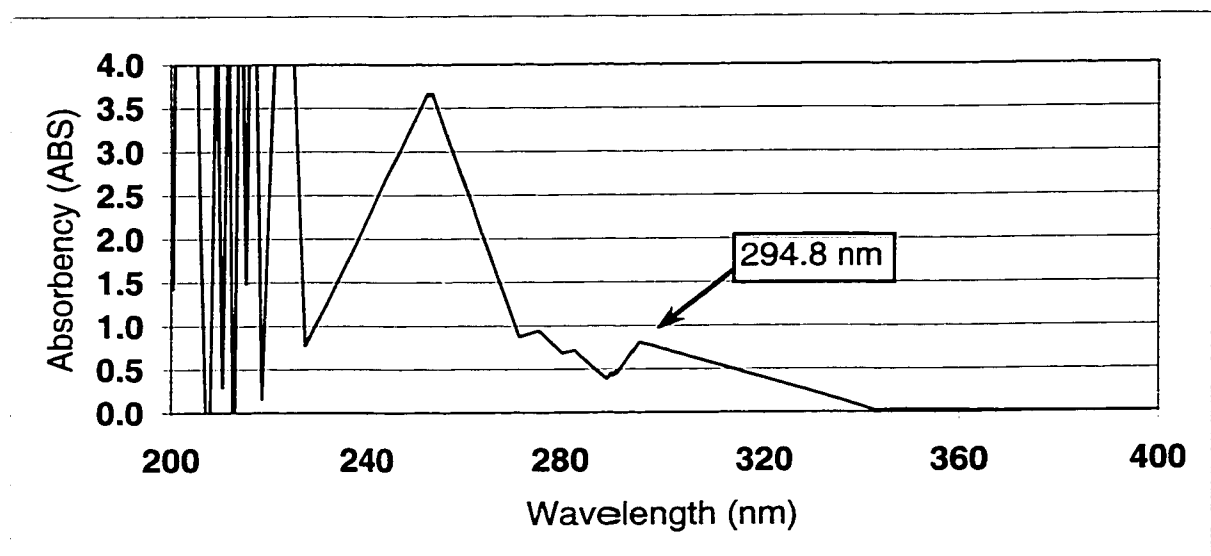


Figure 3.9 Spectra of the phenanthrene-DCM system

Table 3.2 Data from UV/Vis spectrometer

Wavelength (nm)	Absorbency (ABS)
346.8	0.026
343.2	0.015
294.8	0.811
289.2	0.387
282.8	0.718
280.4	0.685
275.6	0.945
271.6	0.873
252.8	3.665
227.2	0.777
222.8	6.816
218.4	0.161
216.4	6.960
215.2	1.489
214.0	6.523
212.8	-1.146
211.6	4.742
207.6	-1.213
206.0	2.013
204.4	6.902
200.4	1.431

Table 3.3 UV Results for various phenanthrene concentrations (wavelength: 294.8 nm)

Solution No.	Absorbency (ABS)	Concentration (mg/L)
1	0.08000	1.25
2	0.16500	2.50
3	0.35300	5.00
4	0.74600	10.00

3.7.2. Analysis of Ion Exchange Textiles

The sampling of ion exchange textile in each cell was necessary in order to determine the concentration of metals exchanged onto the textile as well as the possibility of transferring phenanthrene micelles. The concentration of metals on the textile indicated the heavy metal removal efficiency and the degree of localization. Another part of each textile was used to analyse the phenanthrene content. Figure 3.10 shows the division of each ion exchange textile.

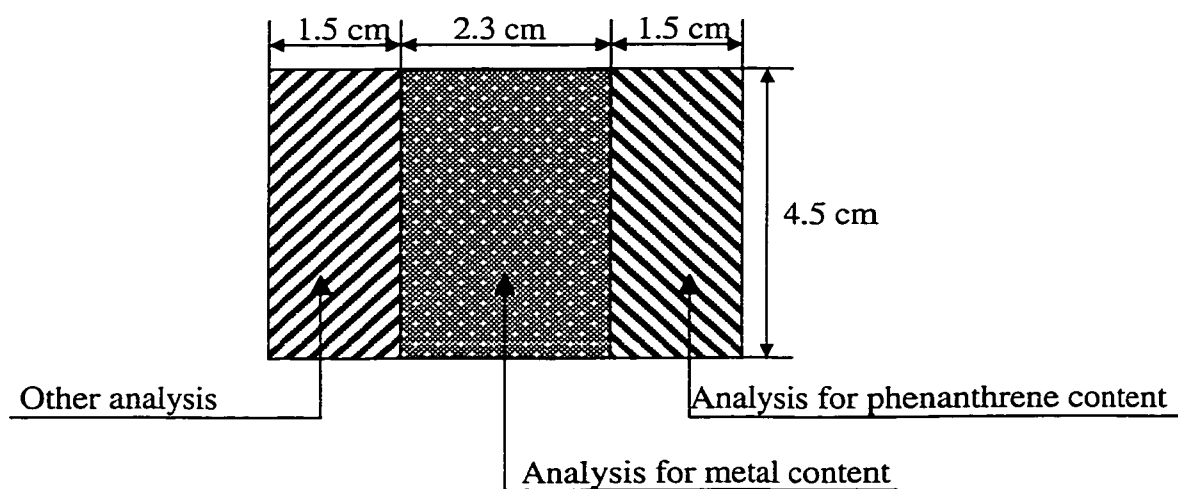


Figure 3.10 Ion exchange textile dividing

- Analysis of Textile for Metal Content:

The middle part of each textile (23 mm × 45 mm) were cut into 1 mm × 1 mm pieces and placed in a 50 mL centrifuge tube. The amount of 25 mL of HCL (4M) was added to each sample. The suspensions obtained were shaken overnight and allowed to settle for 3 hours. The filtration (for 30 min) was applied and liquids collected were analysed using an AA spectrometer.

- Analysis of Textile for Phenanthrene Content:

A side part of each textile (15 mm × 45 mm) were cut into 1 mm × 1 mm pieces and placed in 50 mL centrifuge tube. A volume of 25 mL of DCM was added to each sample. The suspensions obtained were shaken overnight and filtrated. The filtrate was analysed with a UV/Vis spectrometer.

CHAPTER 4 RESULTS AND DISCUSSION

4.1. Experiment T1: Response of mixed contaminated soil to the use of surfactant, EDTA and ion exchange textiles.

Experiment T1 consisted of two tests, where an investigation of introducing a surfactant and EDTA was performed. In test T1C1 (control cell), water was supplied for 22 days through porous zones close to electrodes. In test T1C2, surfactant and EDTA were supplied in the anode and cathode zones respectively.

4.1.1. Electrical Parameters

Measurements related to the potential at each probe and currents within each cell were performed daily. The resistance and its variation with the distance from the cathode was calculated from the equation below:

$$R = V/I$$

R = resistance (Ohms)

V = electrical potential (V)

I = current (A)

The resistance variation with distance from the cathode is displayed graphically in Figure 4.1 and Figure 4.2 for cell T1C1 and cell T1C2 respectively. They clearly show that the resistance tended to decrease from the anode to the cathode. The average resistance gradients that were observed in cell T1C1 and cell T1C2 were 28 Ohms/cm and 31 Ohms/cm respectively. As time progressed, the resistance in both cells increased accordingly, due to the electrokinetic phenomena thereby decreasing the conductivity of the soil in the anode region. The main reason for the increase of resistance is probably caused by the oxidation process, resulting in the accumulation of oxygen in soil pores. The impact of IET was also observed in both cells. Due to the presence of IET, the

resistance distribution can be divided onto three distinguish zones. Higher resistance gradients were observed between electrodes and IETs.

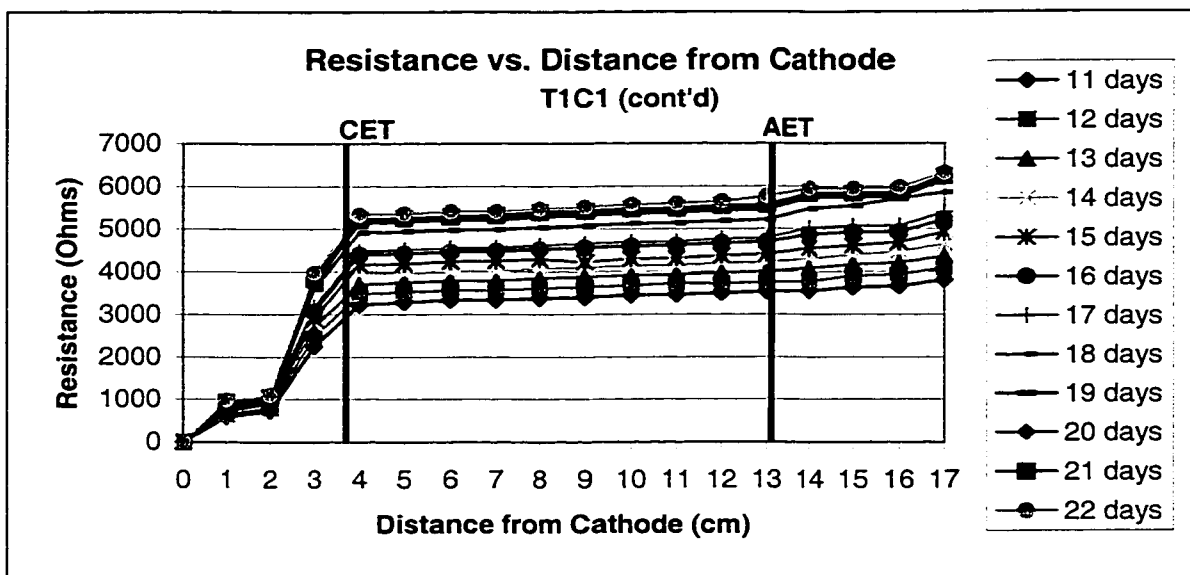
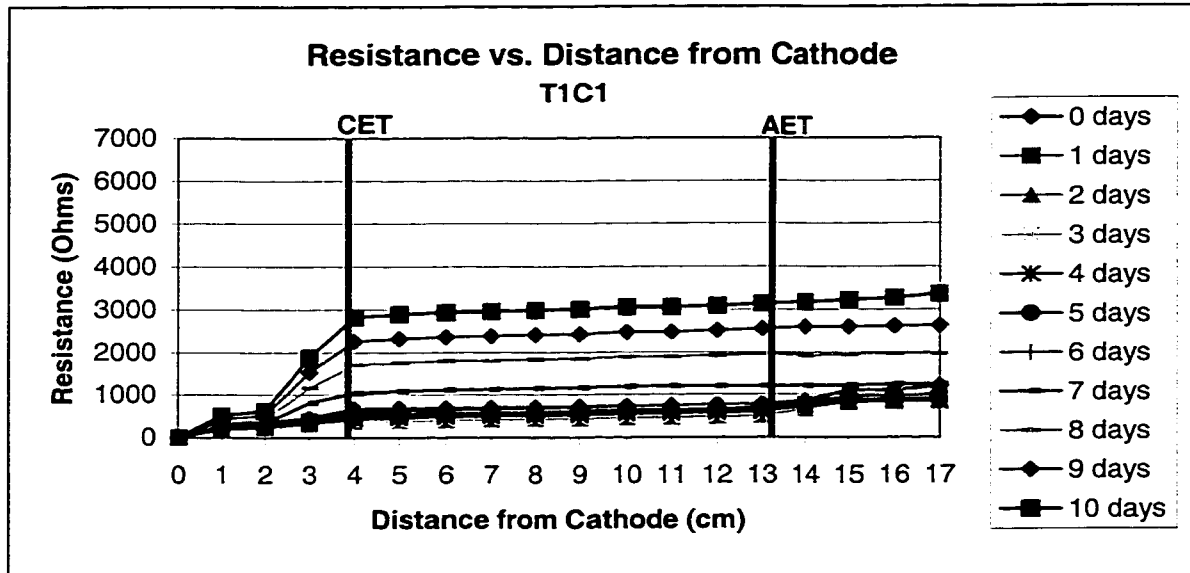


Figure 4.1 Resistance distribution versus distance from the cathode (T1C1)

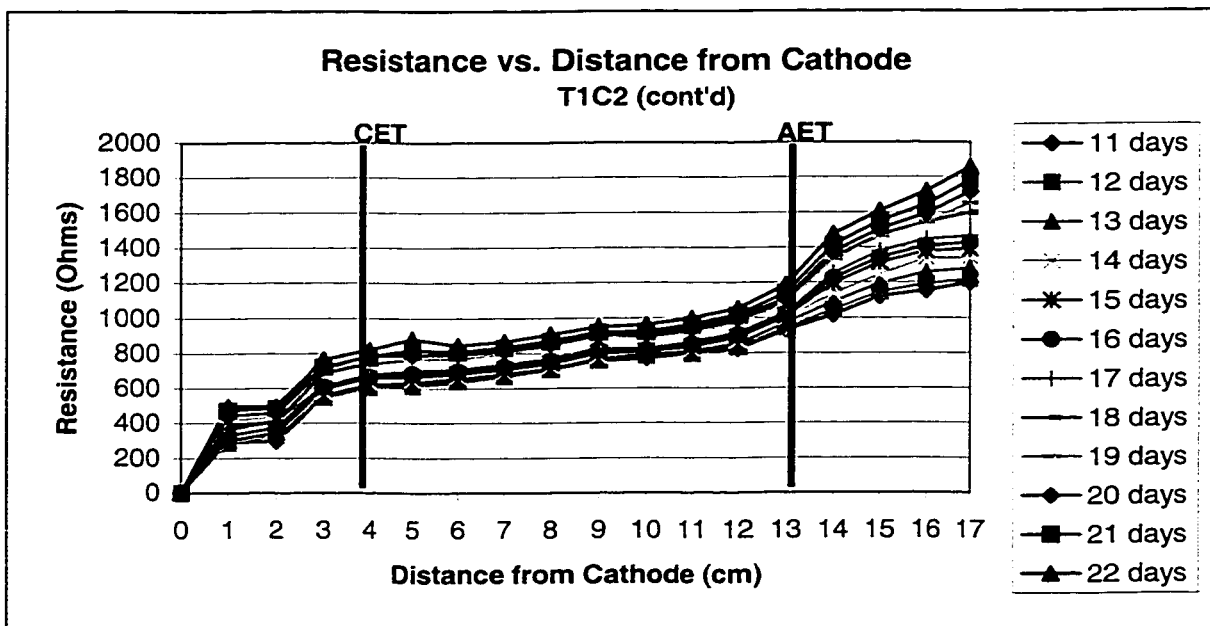
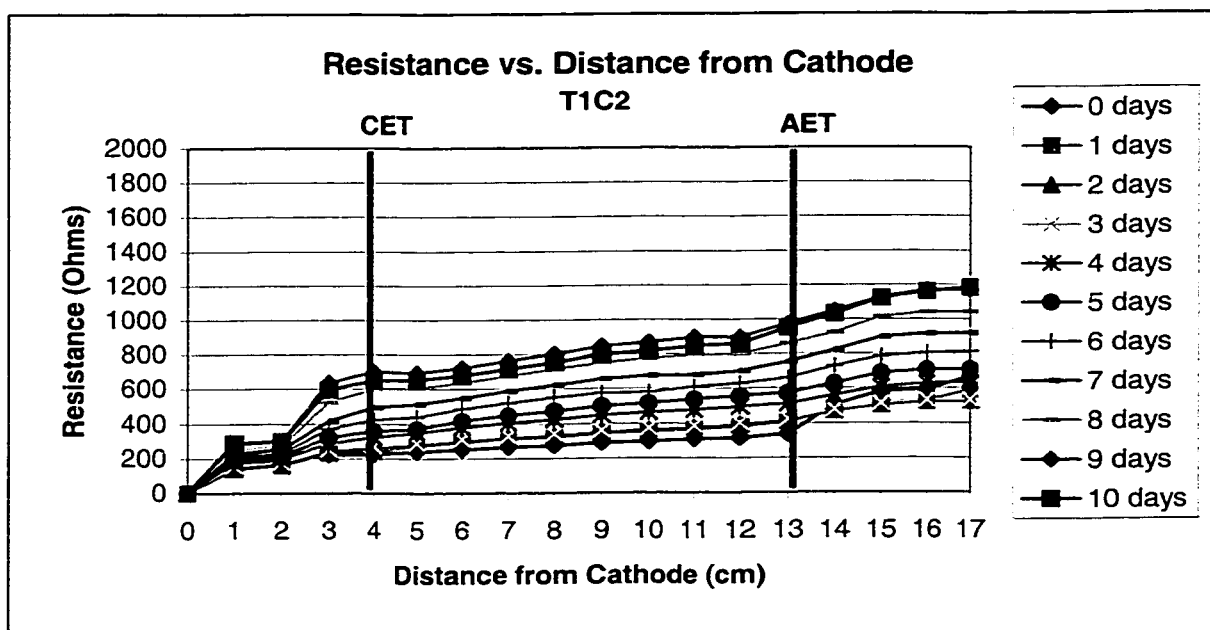


Figure 4.2 Resistance distribution versus distance from the cathode (T1C2)

The total resistance and its variation with the time are displayed graphically in Figure 4.3 for cells T1C1 and T1C2. With time, the total resistance of cell T1C1 increased from 1200 Ohms at the beginning of the experiment to 6315 Ohms at the end. In cell T1C2, the corresponding resistance increased from 667 Ohms to 1860 Ohms. This increase can be attributed to the formation of OH^- ions at the cathodes. This increased the pH and promoted the precipitation of metals, thereby increasing the resistance of the soil close to cathode.

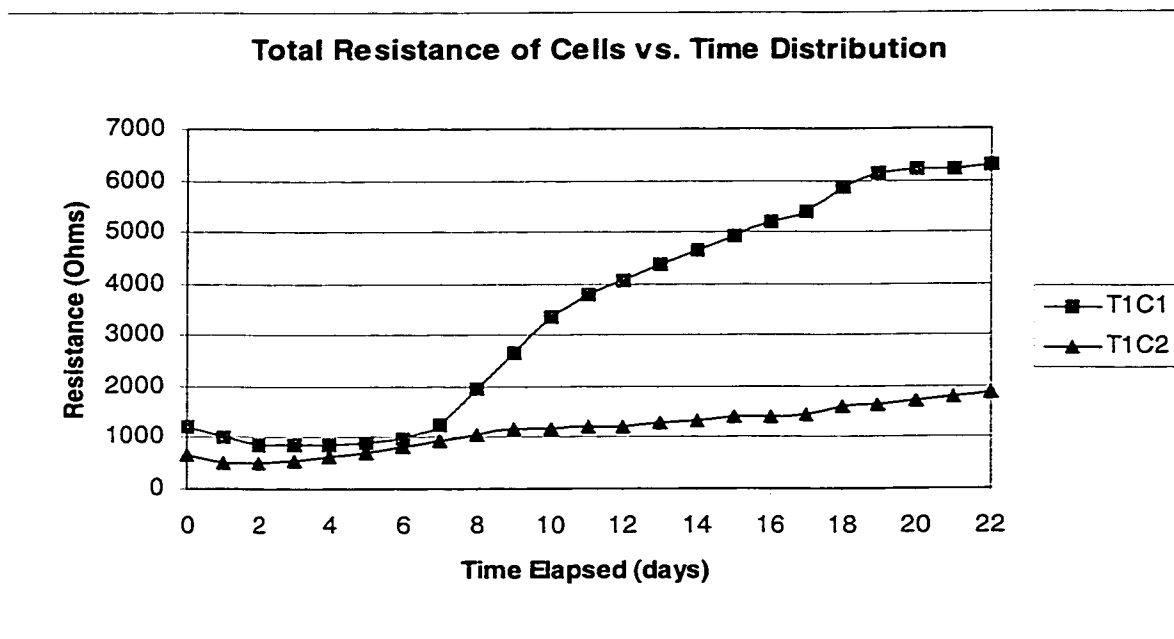


Figure 4.3 Total resistance of soil for cells T1C1 and T1C2

4.1.2. Results Pertaining to Cathode Liquids

The pH of the liquids extracted from the cathode in cells T1C1 and T1C2 on a daily basis are displayed in Figure 4.4. For both cells, a small difference between maximum and minimum pH values was shown. For cell T1C1, the maximum pH (13.06)

was observed after 3 days and minimum pH 12.08 after 17 days. For cell T1C2, the maximum and minimum pH values observed were 13.42 after 1 day and 12.70 after 22 days respectively.

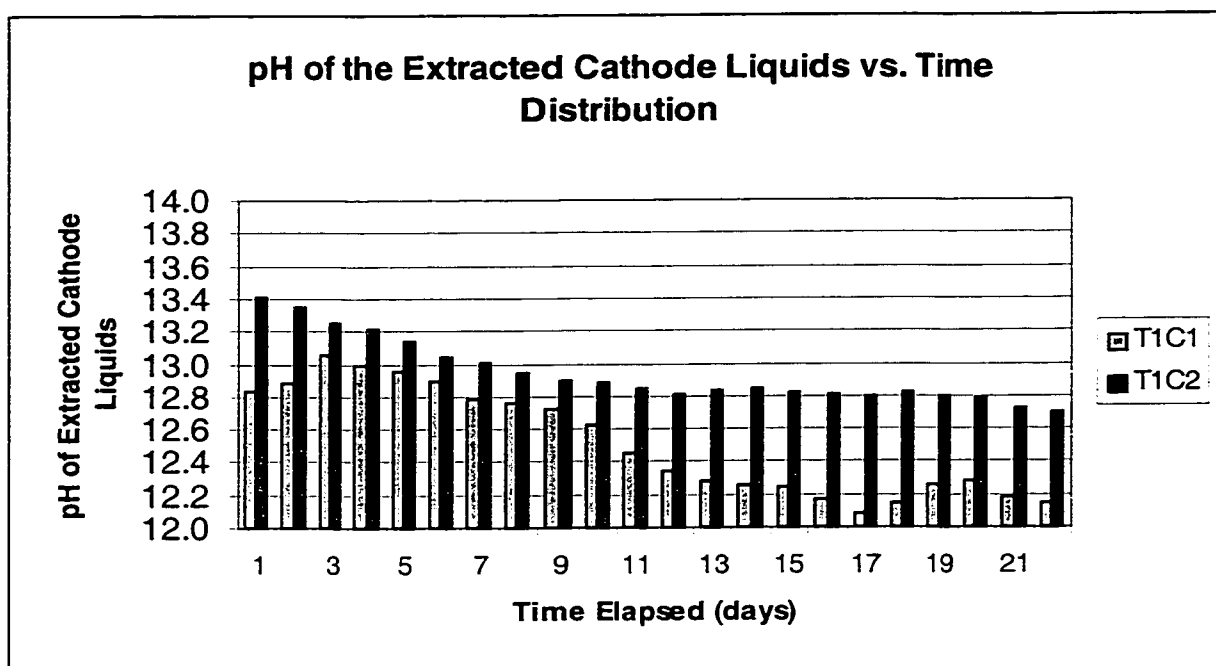


Figure 4.4 pH of the extracted daily cathode liquids (T1C1 and T1C2)

The fluctuation of the liquids extracted daily through the cathode of cell T1C1 and T1C2 is shown in Figure 4.5. The volume extracted from cell T1C1 and cell T1C2 for the entire duration of the experiment were 314.3 mL and 194.1 mL respectively. Maximum and minimum daily volumes for cell T1C1 were 20.4 mL and 8.1 mL respectively. Maximum and minimum daily volumes for cell T1C2 were 12.8 mL and 5.1 mL respectively. The maximum values were observed in the second week of the test in both cells. The maximum liquid collected was 1.6 times lower in the cell with conditioning liquids. The total discharge was also 1.6 times lower in the same cell. Cells

without conditioning liquid expressed higher collected liquid discharge. It was also observed as time progressed, decreased water flow was observed as reflected by a decrease in the volume of collection liquid.

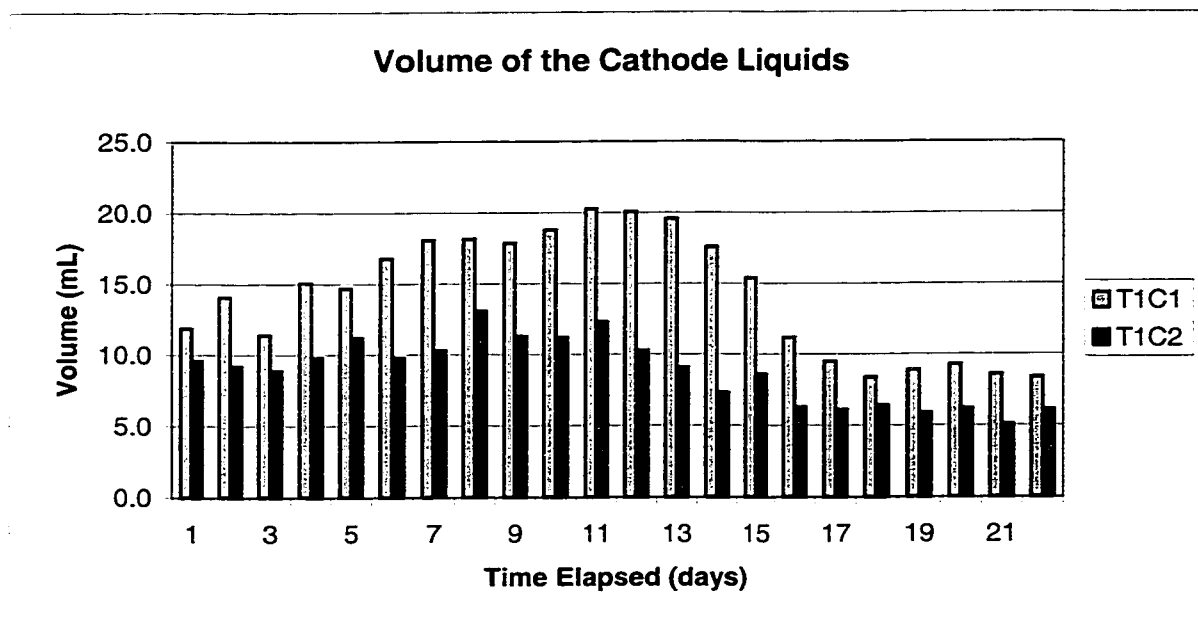


Figure 4.5 Volume of extracted daily cathode liquids (T1C1 and T1C2)

4.1.3. Volume of Supplied Liquids

As stated previously, water was supplied to cell T1C1. Figure 4.6 shows the cumulative volume of water supplied to anode and cathode zones in cell T1C1. Average daily volume supplied to anode and cathode zones were 11.75 mL and 14.75 mL respectively.

Figure 4.7 shows the cumulative volume of surfactant and EDTA supplied in cell T1C2. The average daily volume of surfactant supplied at the anode zone was 10.8 mL. The average daily volume of EDTA supplied in the cathode zone was 2.9 mL.

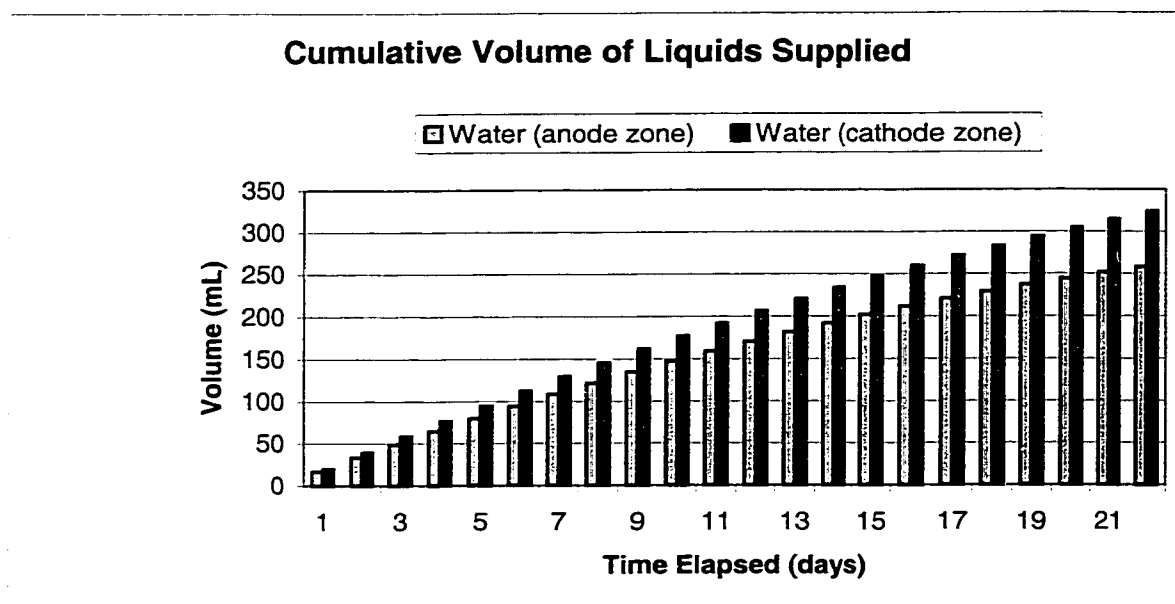


Figure 4.6 Cumulative volume of water supplied to cell T1C1

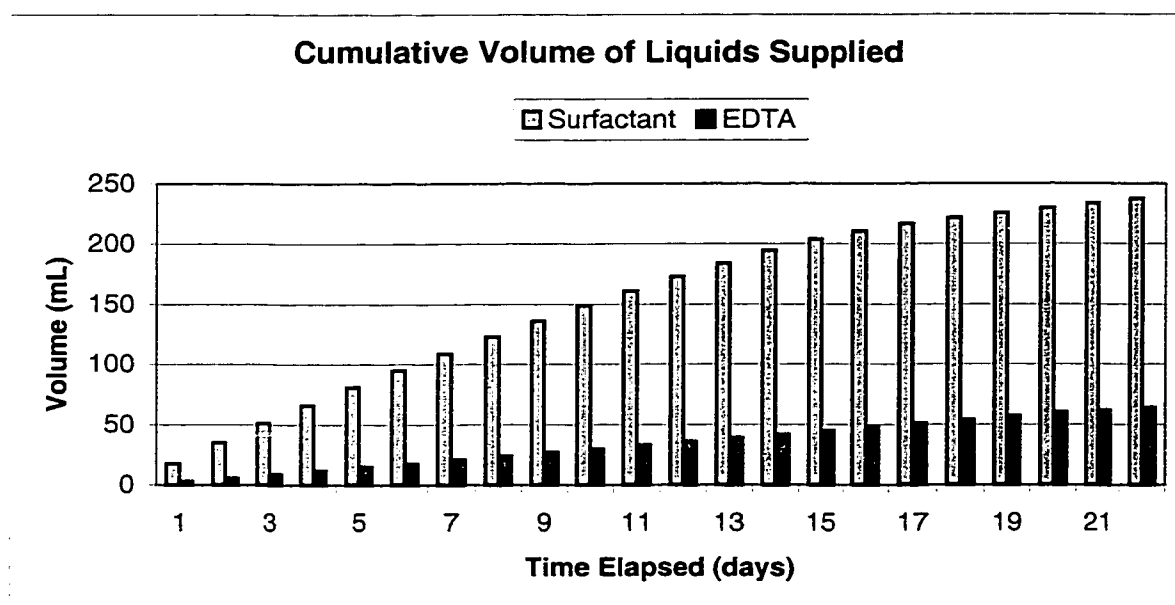


Figure 4.7 Cumulative volumes of surfactant and EDTA supplied in cell T1C2

4.1.4. Soil Samples

4.1.4.1. pH of the Soil

The pH analysis of soil samples and its variation from cathode to anode in cells T1C1 and T1C2 are shown in Figure 4.8. The locations of the anode, the cathode and the ion exchange textiles are superimposed onto this graph in order to give an accurate representation of each cell. Maximum soil pH values that observed in cell T1C1 and T1C2 were similar, 11.48 and 11.47 respectively. As expected, there was a general increase from anode to cathode, which is a typical pH distribution. The initial pH of soil was 7.6 and in cell T1C1 the pH value in anode area was close to initial soil pH. The formation of hydrogen ions at the anode lowered the soil pH to 6.75 in cell T1C2. Usually pH in anode area is much lower in electrokinetic cell. This small decrease in both cells was presumably due to the supply of water directly into the anode.

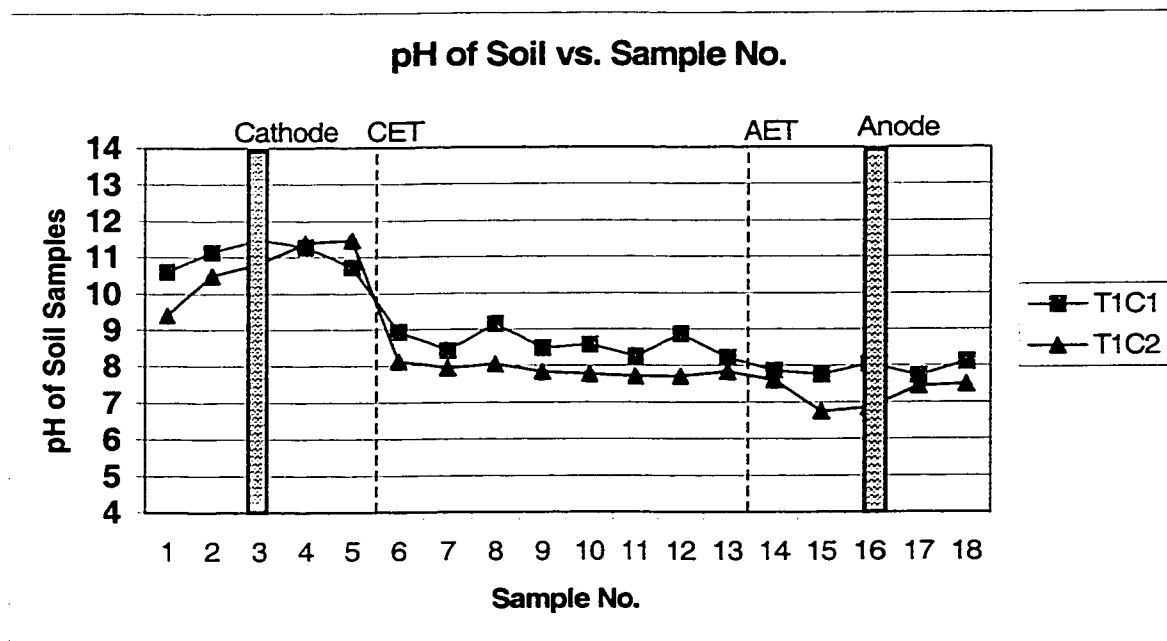


Figure 4.8 pH distribution for cells T1C1 and T1C2 after experiment

The increase of pH in the cathode region was due to the formation of OH^- ions. Typically, it is expected that the pH of the soil in the cathode region would be closer to 11. Probably the formation of hydroxide precipitates removed some hydroxide ions from solution thereby lowering the pH slightly. In general, both cell displayed similar soil pH distributions.

4.1.4.2. Metal Concentration in the Soil

The concentration of lead and nickel in the soil was measured using AA spectrometer (see Chapter 3.7.1.3). The concentration of lead and nickel in the soil samples and its variation with the sample numbers for cells T1C1 and T1C2 are shown in Figure 4.9 and 4.10 respectively, where C is the remaining metal concentration (mg/L) and C_0 is the initial concentration (mg/L). The distribution of lead in the soil for cell T1C1 and T1C2 showed 35 % and 82 % average removal of lead between the ion exchange textiles respectively. The presence of the majority of lead ions in the anode area (Fig 4.9) is directly related to the effectiveness of EDTA in the mobilization of lead and its transport to the anode. Lead has a strong affinity for clay soil and has a higher power of exchange with soils than most of the other metals. The distribution of nickel in the soil for cell T1C1 and T1C2 showed 76 % and 73 % average removal of nickel between the ion exchange textiles respectively. Both cells showed high nickel concentrations in the anode area, which is indicative of significant electrolytic migration to the anode. The relocation of nickel that was achieved, was higher than lead. Nickel is easily subjected to complexation in the presence of various compounds. For example, it is known that nickel bonds with organic compounds (e.g. carbon monoxide and toluene) undergoing anionic complexation, which give it a high mobility in soil. Removal of nickel without EDTA

was excellent as with EDTA. The application of electrokinetics seems to be the best technology to control the transportation of nickel in the clayey soil.

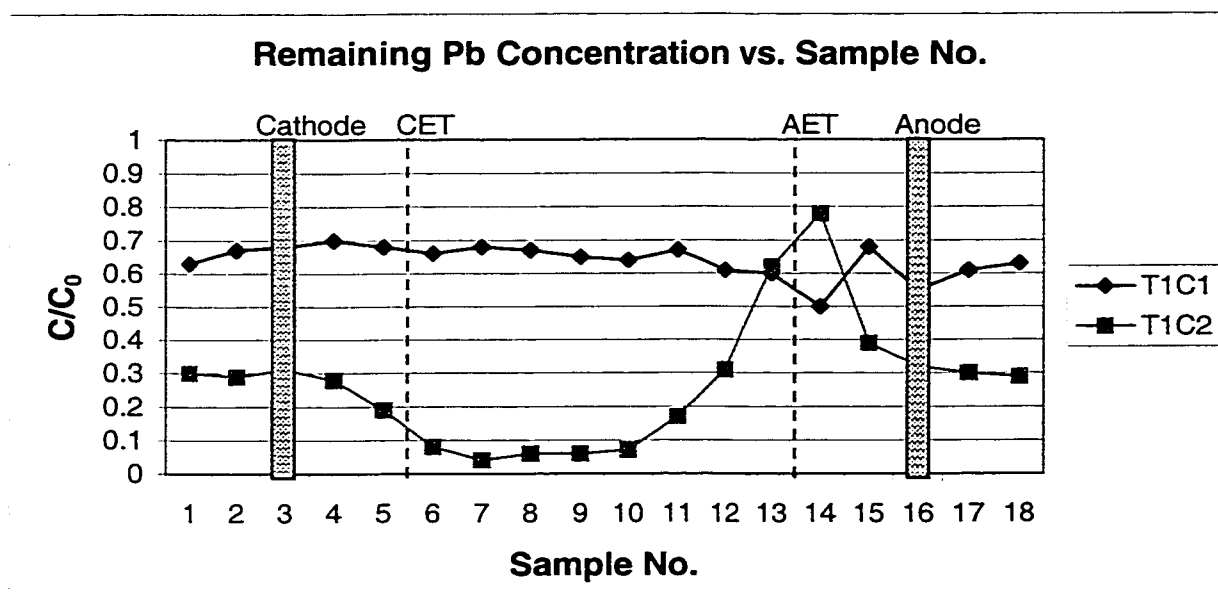


Figure 4.9 Pb distribution in cells T1C1 and T1C2 after experiment

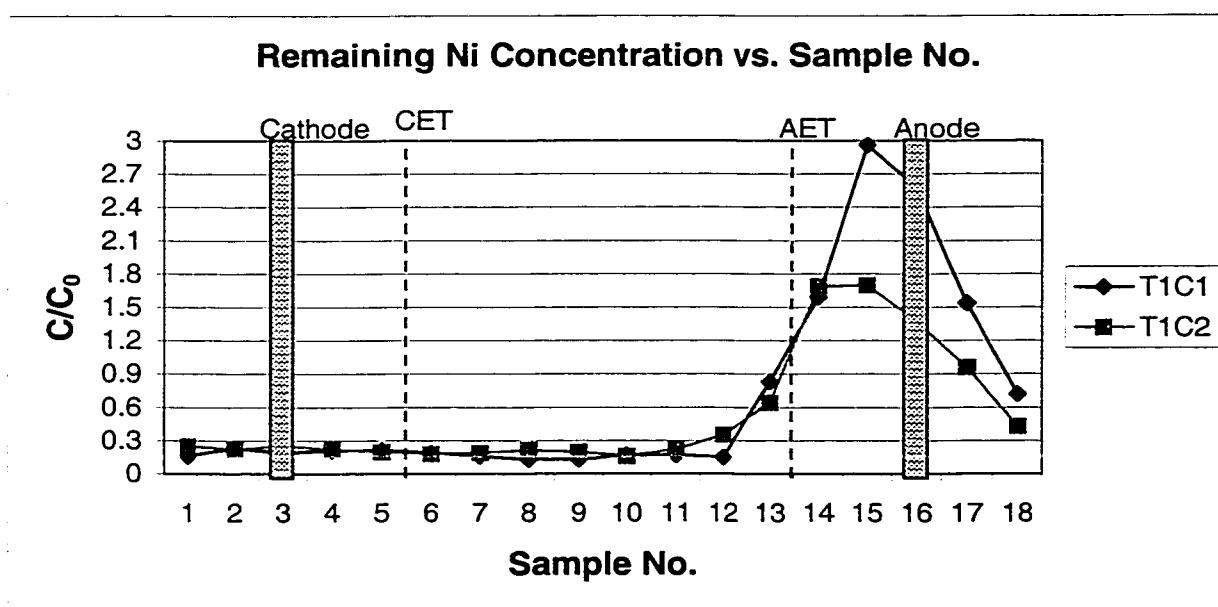


Figure 4.10 Ni distribution in cells T1C1 and T1C2 after experiment

4.1.4.3. Phenanthrene Concentration in the Soil

Soil samples were tested for residual phenanthrene content after the test. Contaminated soil samples, which were not subjected to electrokinetics were tested for phenanthrene content and the results were used as a reference for samples that underwent electrokinetic treatment. The concentration of phenanthrene in soil samples was measured using UV/Vis (see Chapter 3.7.1.4). The phenanthrene concentration in the soil samples and its variation with the sample numbers for cells T1C1 and T1C2 are shown in Figure 4.11. The distribution of phenanthrene in the soil for cell T1C1 and T1C2 showed 55 % and 73 % average removal of phenanthrene between ion exchange textiles respectively. The results showed higher removal efficiency in T1C2, where the surfactant was applied. Electrokinetic phenomena themselves can transport phenanthrene in the direction of cathode. However electrokinetic supply of surfactant enhanced the mobility of phenanthrene by 30 %.

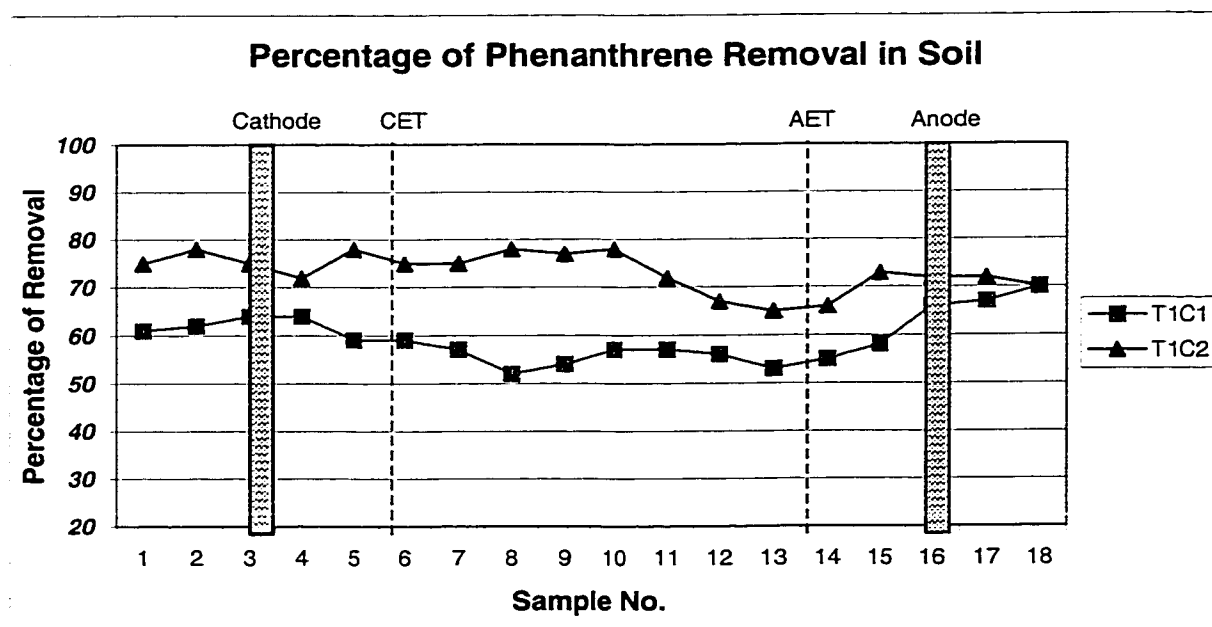


Figure 4.11 Percentage of phenanthrene removal in soil samples (T1C1 and T1C2)

4.1.5. Analysis of Ion Exchange Textiles

The specific concentration (mg/mm^2) of lead, nickel and phenanthrene at particular locations on the textiles in T1C1 and T1C2 are shown in Table 4.1. Both nickel and lead ions were captured by anion exchange textiles (AET) which shows that metal complexes can exchange onto the AET. The capture of cation exchange textiles (CET) was low for both metals. AET and CET captured the same insignificant amount of phenanthrene in both cells.

Table 4.1 Specific concentration of Pb, Ni and phenanthrene in IET (Experiment T1)

Cell Number	Pb (mg/cm^2)		Ni (mg/cm^2)		Phenanthrene (mg/cm^2)	
	AET	CET	AET	CET	AET	CET
T1C1	0.0028	0.0061	0.0072	0.0049	0.0048	0.0058
T1C2	0.1624	0.0050	0.1678	0.0080	0.0043	0.0059

4.2. Experiment T2: Sequential desorption of mix contaminants by applying surfactant and EDTA electrokinetic injections in various orders.

Experiment T2 consisted of four tests, T2C3, T2C4, T2C5 and T2C6. In order to find the optimal desorption conditions for mix contamination the introducing surfactant and EDTA in various periods was tested. Table 4.2 shows the periods of liquid supply. EDTA was supplied at the beginning of tests in cells T2C4 and T2C6. Other two cells T2C3 and T2C5 were subjected to surfactant enhancement from the beginning.

Table 4.2 Supplied periods of EDTA and surfactant (Experiment T2)

Cell No.	EDTA Supply Period	Surfactant Supply Period	Entire Period of Tests (days)
T2C3	11 th -22 nd	1 st -22 nd	22
T2C4	1 st -22 nd	11 th -22 nd	22
T2C5	11 th -22 nd	1 st -11 th	22
T2C6	1 st -11 th	11 th -22 nd	22

4.2.1. Electrical Parameters

Measurements related to potential at each probe and cell current was performed daily. The resistance variation with the distance from the cathode are displayed graphically in Figure 4.12, 4.13, 4.14 and 4.15 for cells T2C3, T2C4, T2C5 and T2C6 respectively. It clearly showed that the resistance tended to decrease from the anode to the cathode in all cells. The resistance gradient increased as EDTA was introduced. The average resistance gradients in cell T2C3 in the first period of 11 days was 12 Ohms/cm and in the second 11 days was 36 Ohms/cm. The average resistance gradients that were observed in cell T2C5 in the first and second 11 day-periods were 14 Ohms/cm and 44 Ohms/cm respectively, which was higher than T2C3. As time progressed, the resistance in both cells increased. In both cells, resistance in the first 11 days was high, but the resistance gradient was low. Injection of EDTA in the second 11 days decreased the resistance in both cells, but a higher gradient observed.

The average resistance gradients that were observed in cell T2C4 in the first and second 11 day-periods were 19 Ohms/cm and 35 Ohms/cm respectively. The average resistance gradients that were observed in cell T2C6 in the first and second 11 day-periods were 24 Ohms/cm and 37 Ohms/cm respectively. As time progressed, the resistance and its gradient in both cells increased. A resistance gradient increase was observed, especially between cathode and CET.

The total resistance of each cell was calculated using the current obtaining daily and the total electrical potential (4.8 V). The total resistance variation with time is displayed graphically in Figure 4.16 for cells T2C3, T2C4, T2C5 and T2C6.

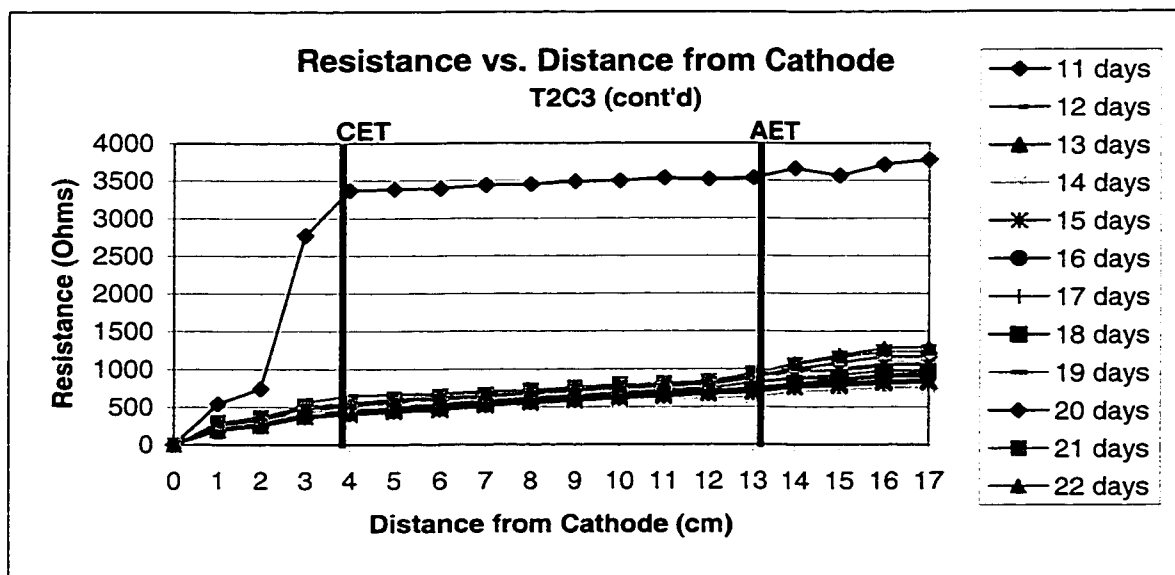
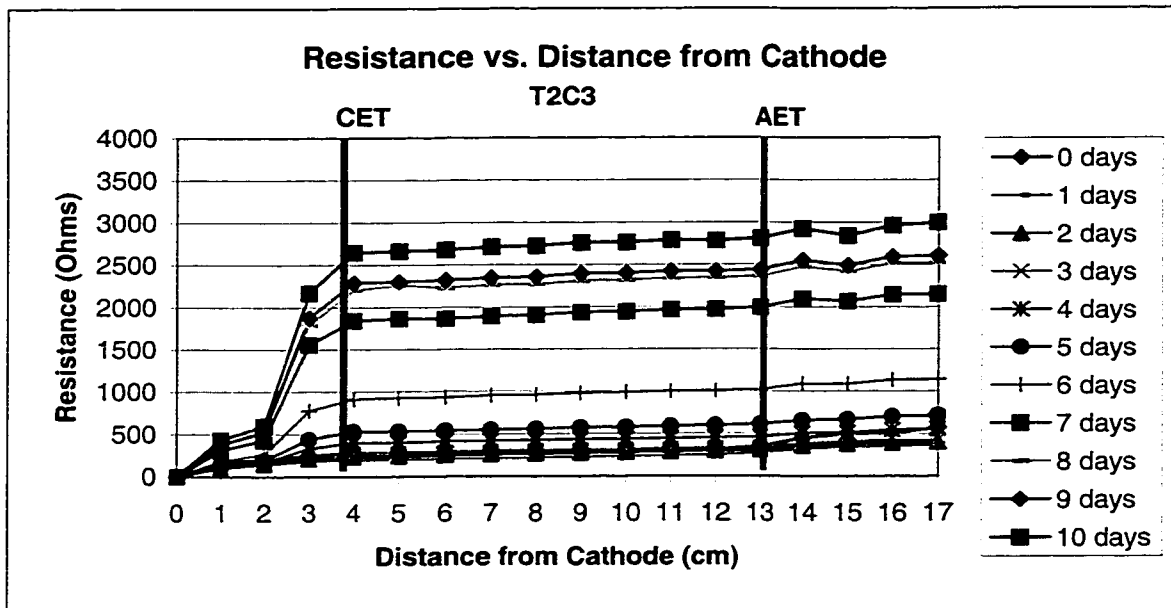


Figure 4.12 Resistance distribution versus distance from the cathode (T2C3)

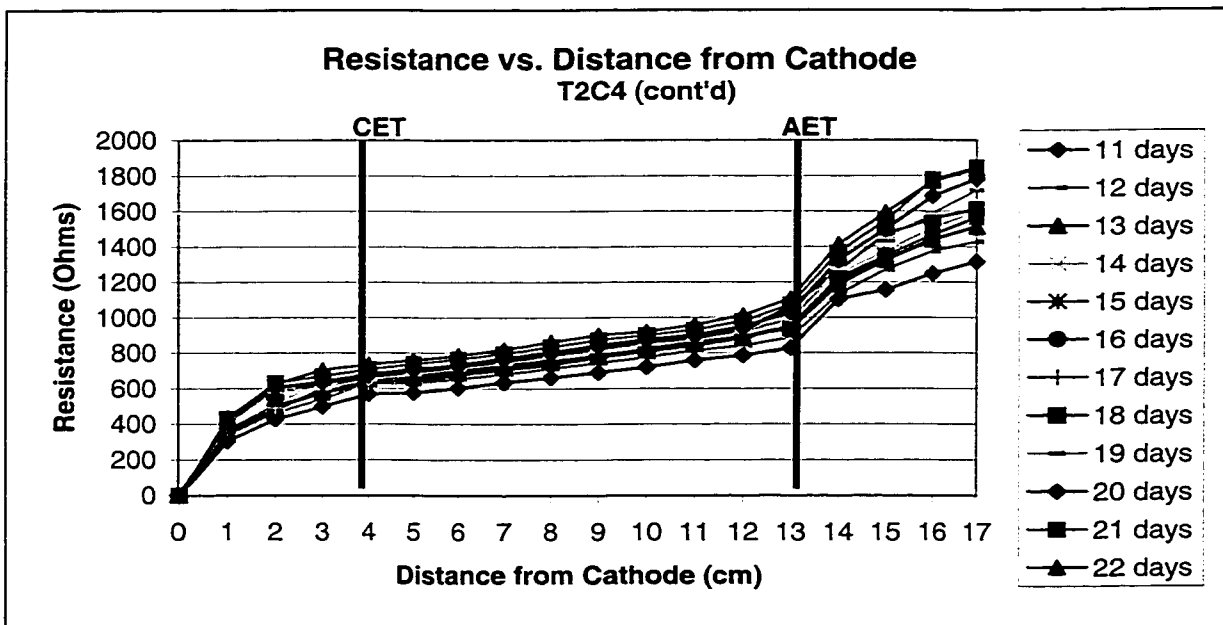
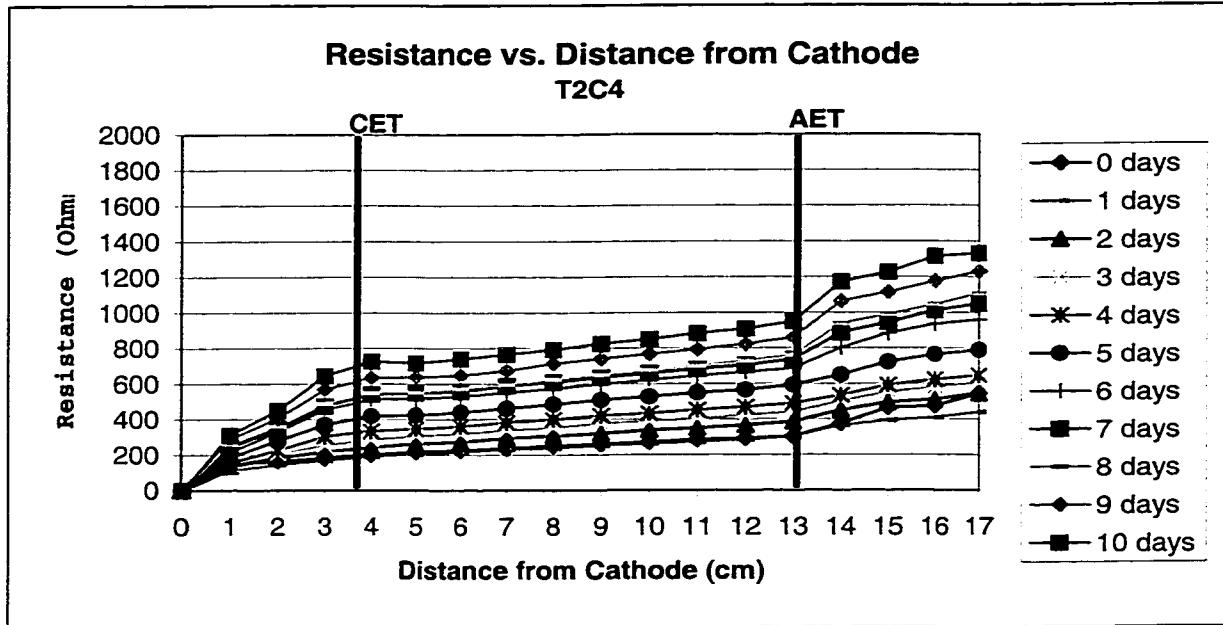


Figure 4.13 Resistance distribution versus distance from the cathode (T2C4)

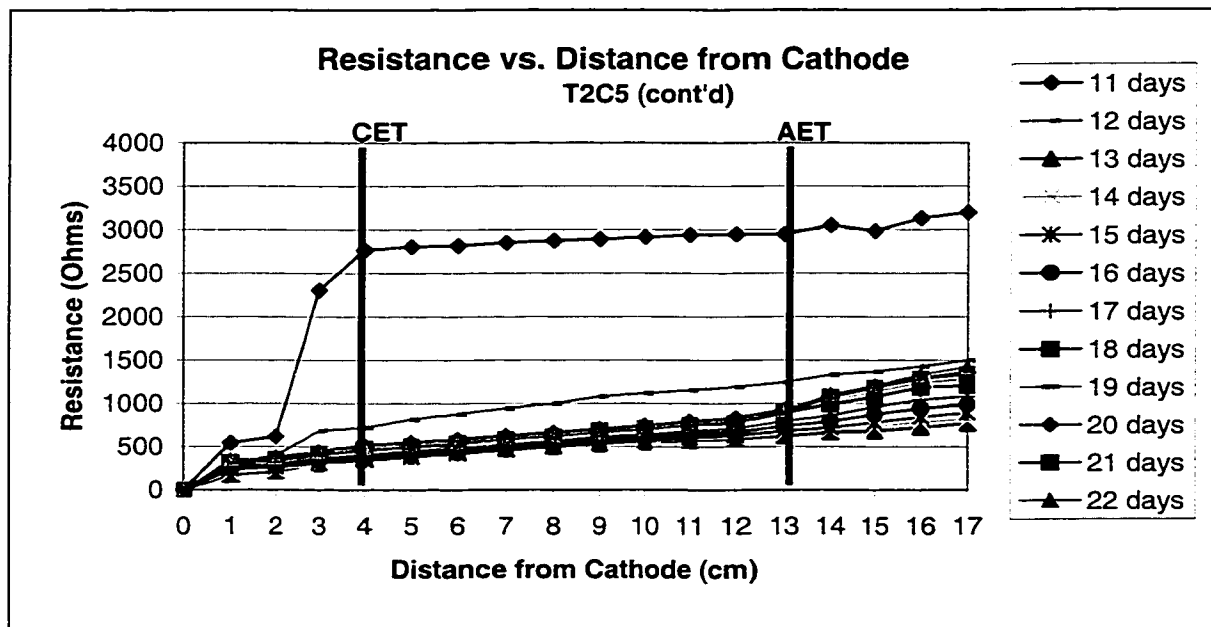
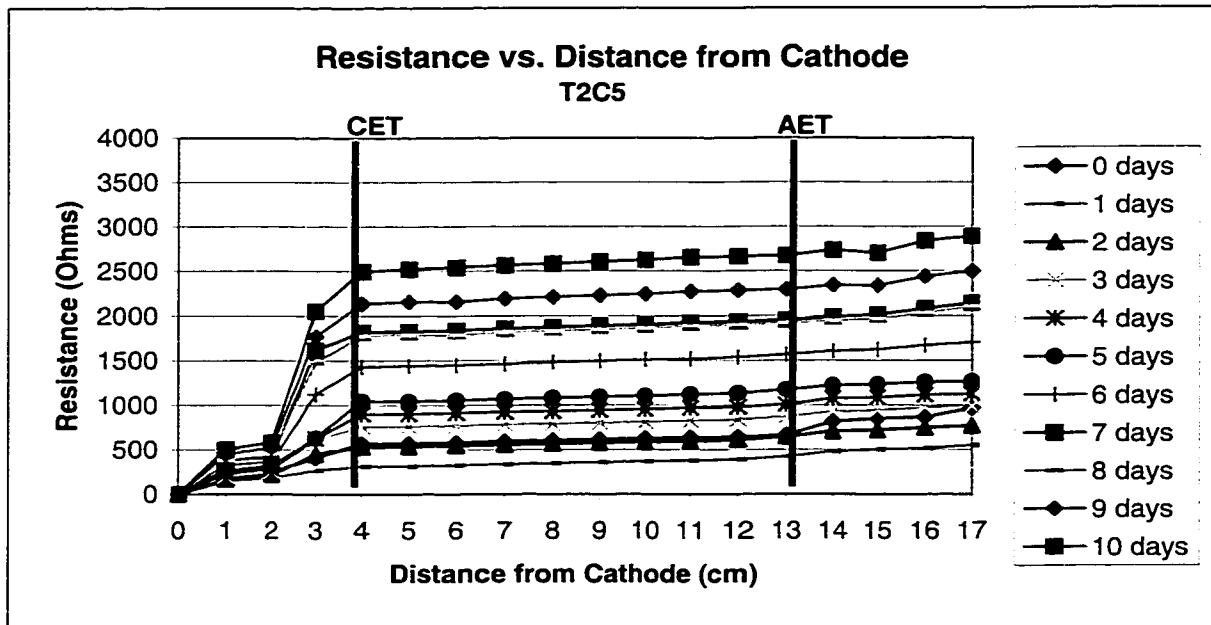


Figure 4.14 Resistance distribution versus distance from the cathode (T2C5)

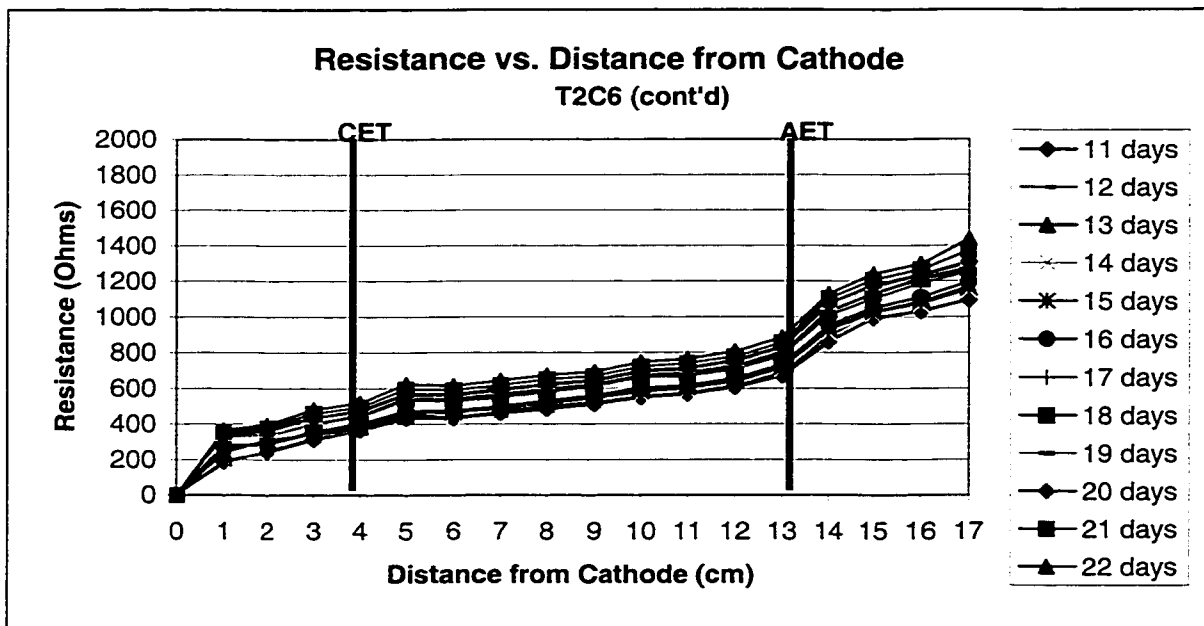
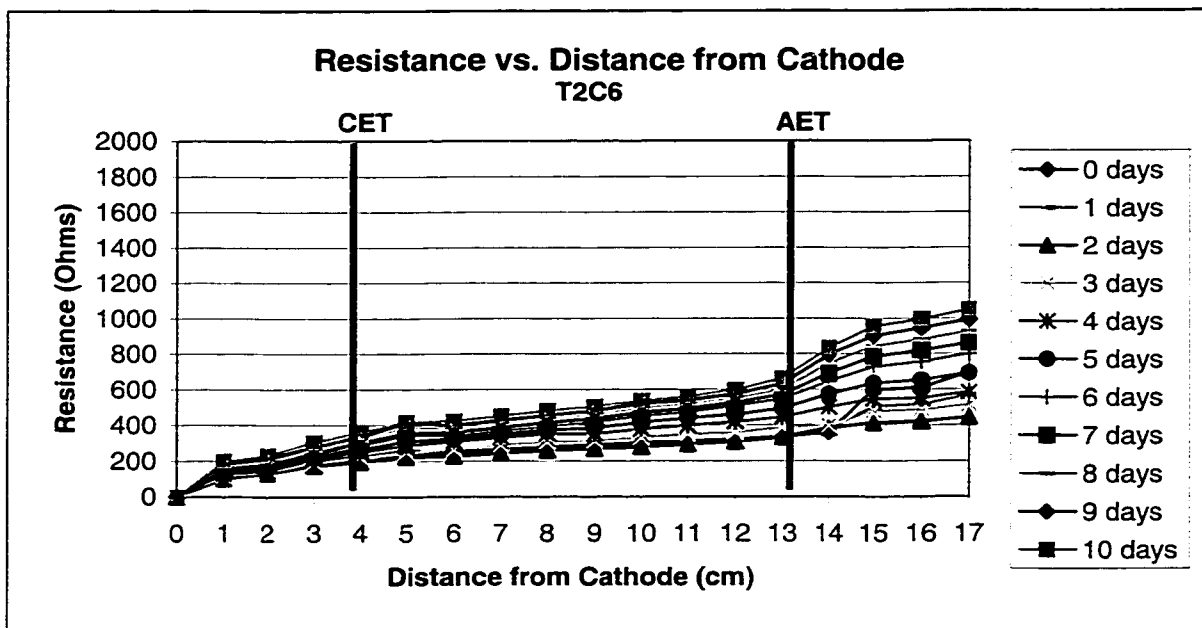


Figure 4.15 Resistance distribution versus distance from the cathode (T2C6)

With time, the total resistance of cells T2C4 and T2C6 increased from 545 Ohms and 696 Ohms at the beginning of the experiment to 1839 Ohms and 1437 Ohms at the end of the experiment respectively. In cells T2C3 and T2C5, the corresponding resistances increased from 571 Ohms and 968 Ohms to 3780 Ohms and 3200 Ohms in the first 11 days respectively. In cells T2C3 and T2C5, because of introducing EDTA in the second 11 days of treatment, the total resistance of soil started to decrease to 762 Ohms and 769 Ohms respectively. The beginning of the electrokinetic process (introducing of surfactant) rapidly increase the resistance of the cells quickly. The introduction of EDTA during the second injection period decreased the resistance 4 times. It seems that introduction of EDTA could be used for control of soil resistance.

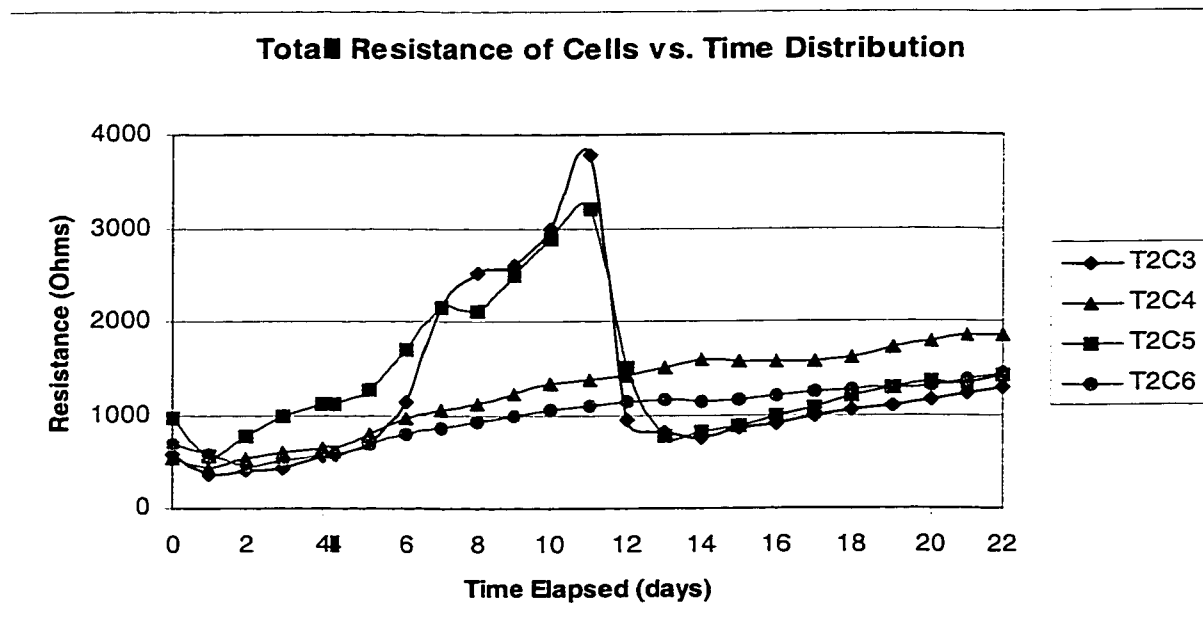


Figure 4.16 Total resistance of soil for cells T2C3, T2C4, T2C5 and T2C6

4.2.2. Results Pertaining to Cathode Liquids

The pH of the liquids extracted daily from the cathodes is displayed in Figure 4.17 and 4.18. As time progressed, the pH of extracted cathode liquids decreased slightly. In cells T2C3 and T2C5, injection of EDTA showed an increase of pH from 12.61 and 12.58 to 13.28 and 13.22 respectively. The highest pH was associated with an introduction of EDTA into the cells.

The fluctuation of the liquids extracted daily through the cathode of cell T2C3 and T2C4 is shown in Figure 4.19. The total volume extracted from cells T2C3, T2C4, T2C5 and T2C6 for the entire duration of the experiments were 307.7 mL, 234.9 mL, 296.8 mL and 228.3 mL respectively. The average daily volume extracted for the corresponding cells were 14.0 mL, 10.7 mL, 13.5 mL and 10.4 mL respectively. The lowest volumes were observed for cells where EDTA was supplied from the beginning of test, independent of the duration of application (11 days or 22 days). When EDTA was introduced, the discharge increased for a few days and decreased thereafter. The test days show almost the same discharges in both cells where conditioning liquid were introduced. The fluctuation of the liquids extracted daily through the cathode of cell T2C5 and T2C6 is shown in Figure 4.20.

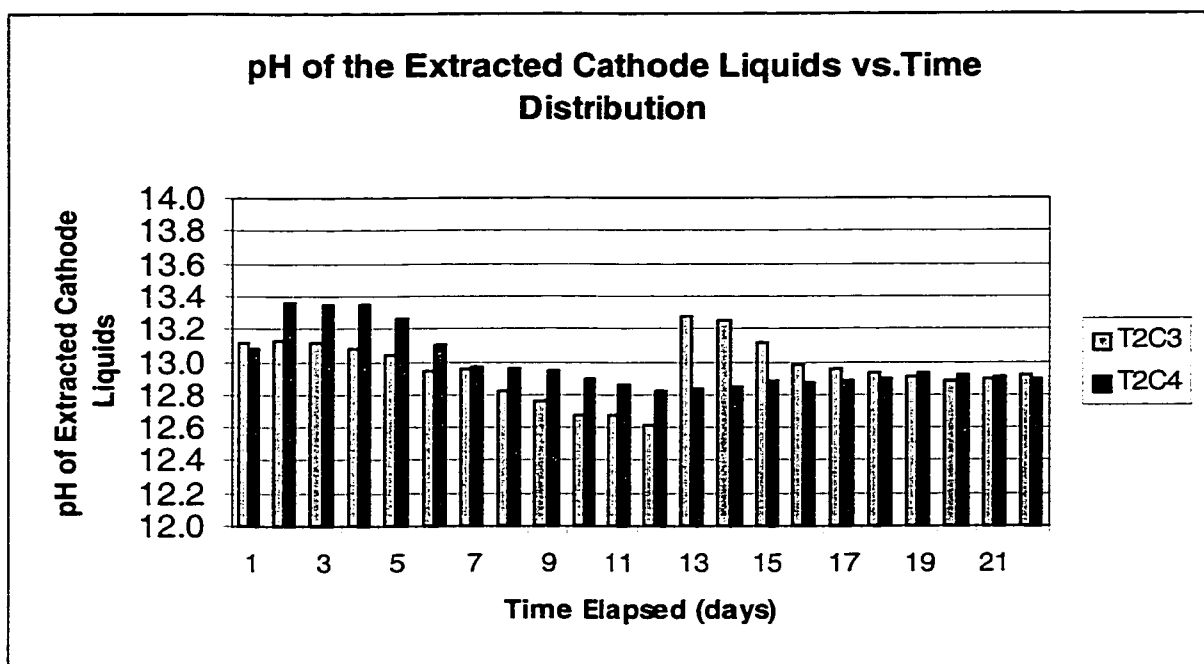


Figure 4.17 pH of the extracted daily cathode liquids (T2C3 and T2C4)

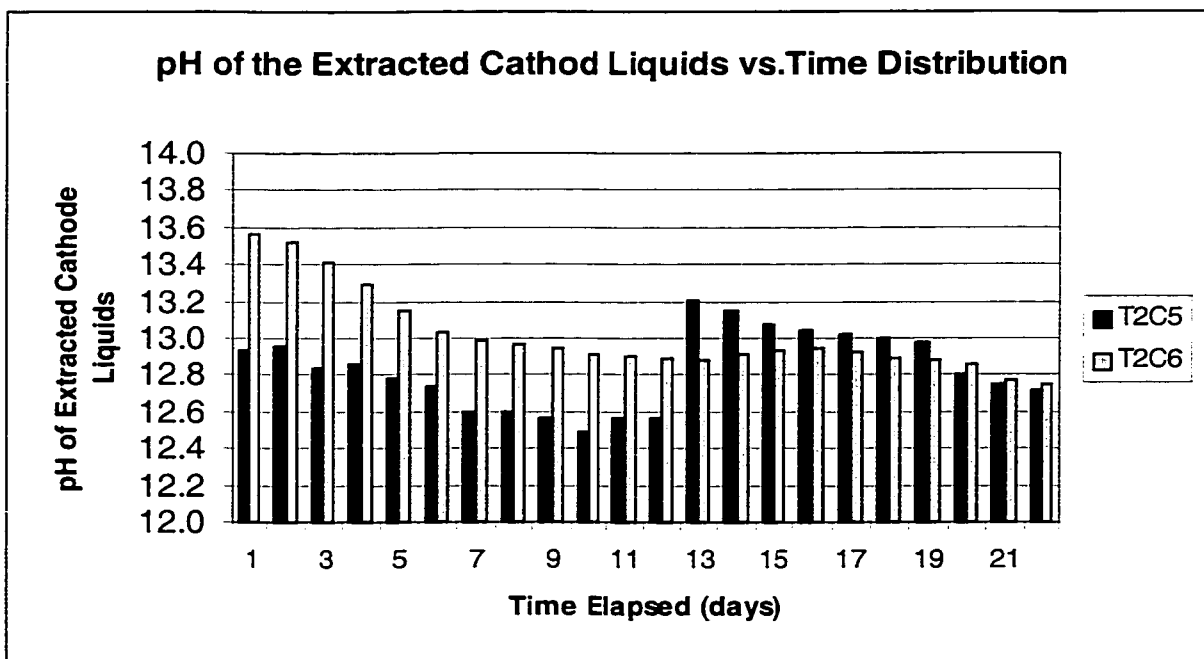


Figure 4.18 pH of the extracted daily cathode liquids (T2C5 and T2C6)

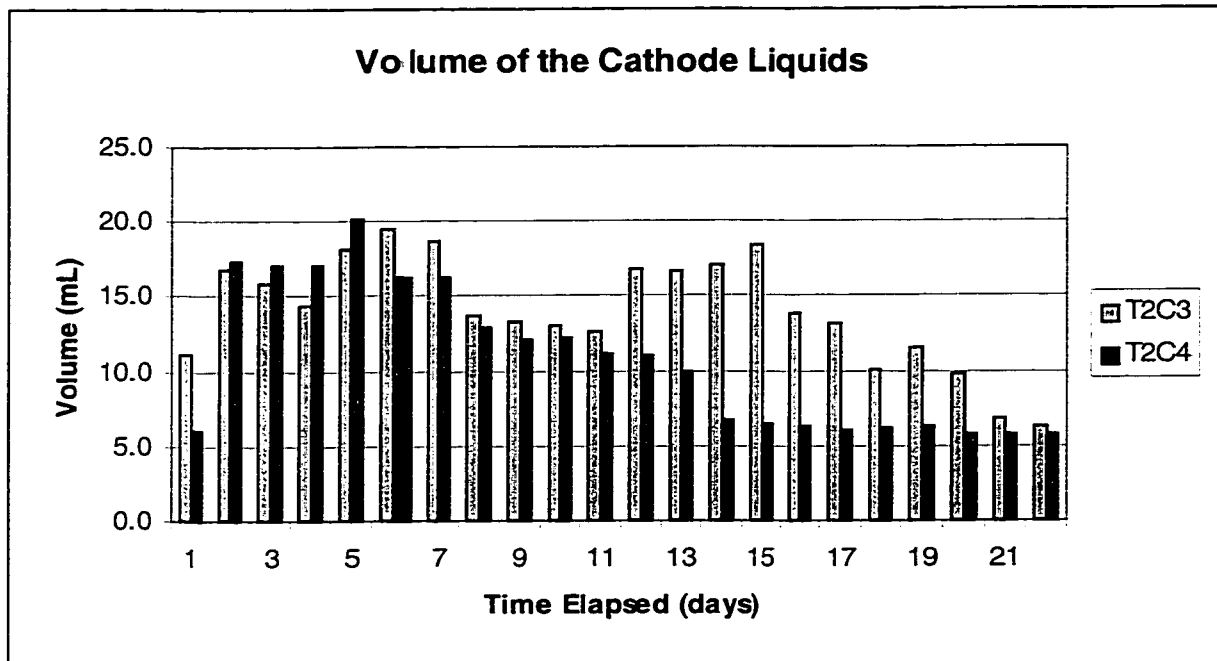


Figure 4.19 Volume of extracted daily cathode liquids (T2C3 and T2C4)

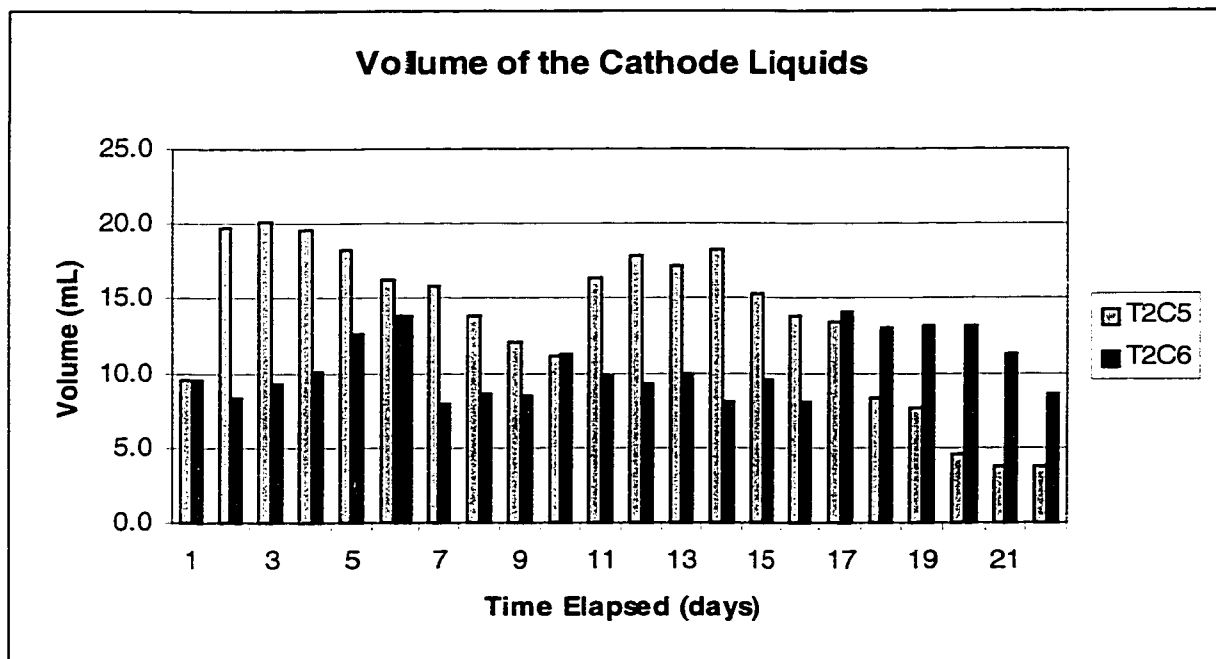


Figure 4.20 Volume of extracted daily cathode liquids (T2C5 and T2C6)

4.2.3. Volume of Liquids Supplied

Figure 4.21 shows the cumulative volume of the surfactant and EDTA supplied in cell T2C3. The average daily volumes of surfactant and EDTA supplied were 11.5 mL and 5.9 mL respectively.

Figure 4.22 shows the cumulative volume of surfactant and EDTA supplied in cell T2C4. Average daily volume supplied of surfactant and EDTA were 10.6 mL and 1.5 mL respectively. Amount of surfactant supplied in cell T2C3 was 4.5 times higher than EDTA. Amount of surfactant supplied in cell T2C4 was 3.5 times higher than EDTA.

Figure 4.23 shows the cumulative volume of the surfactant and EDTA supplied in cell T2C5. The average daily surfactant and EDTA volumes supplied were 2.9 mL and 4.8 mL respectively. Less surfactant was used when supplied during first period of treatment.

Figure 4.24 shows the cumulative volume of the surfactant and EDTA supplied in cell T2C6. The average daily surfactant and EDTA volume supplied were 8.0 mL and 3.9 mL respectively.

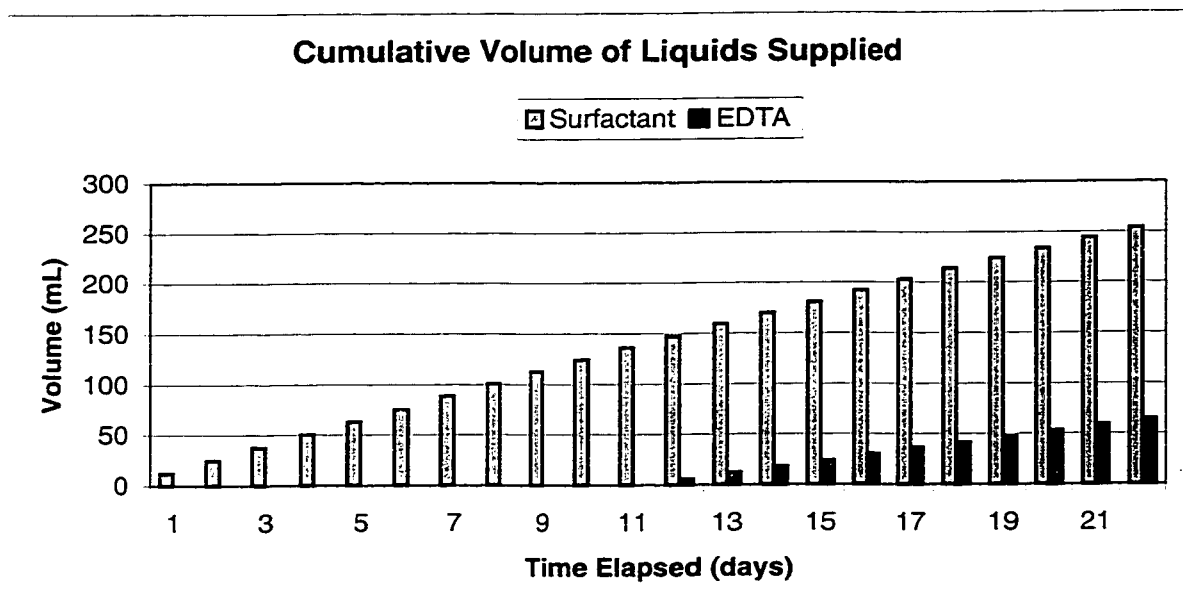


Figure 4.21 Cumulative volume of the surfactant and EDTA supplied in cell T2C3

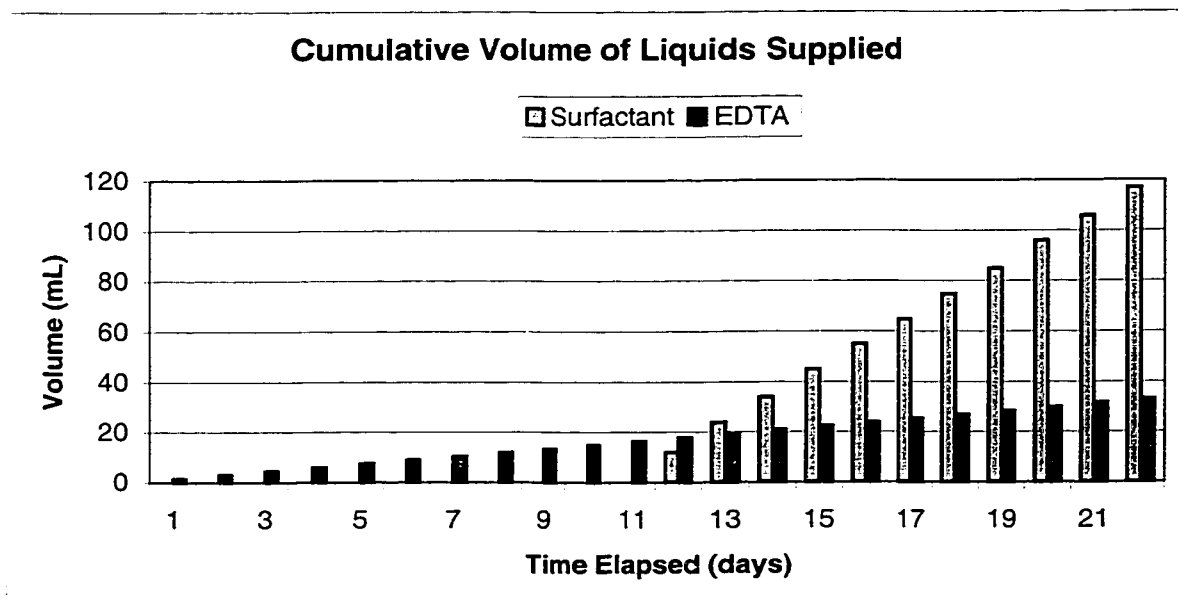


Figure 4.22 Cumulative volume of the surfactant and EDTA supplied in cell T2C4

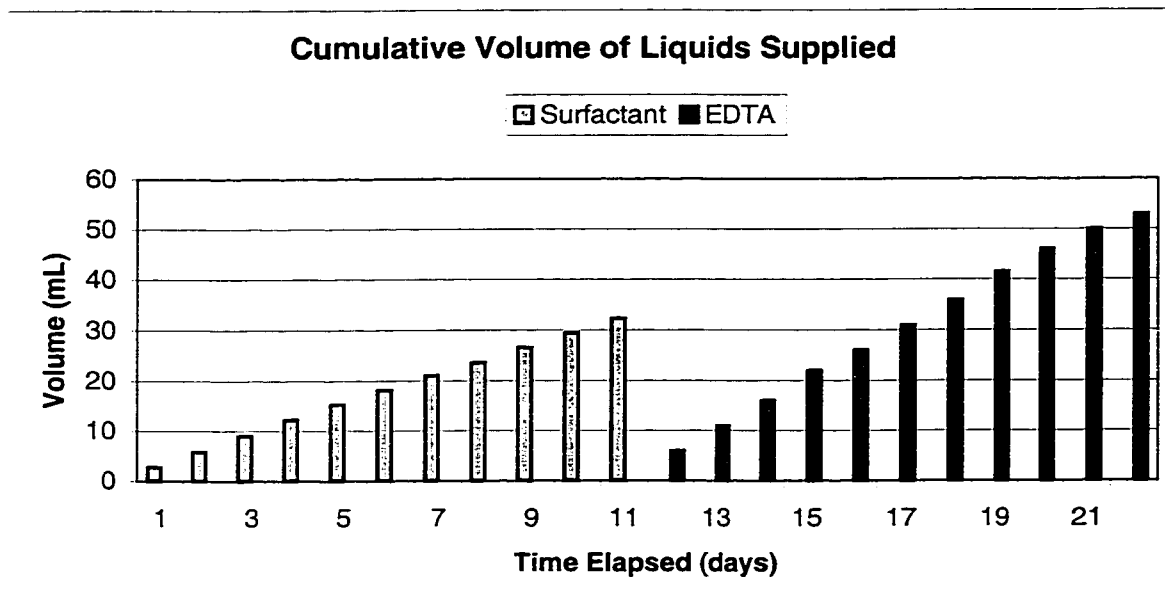


Figure 4.23 Cumulative volume of the surfactant and EDTA supplied in cell T2C45

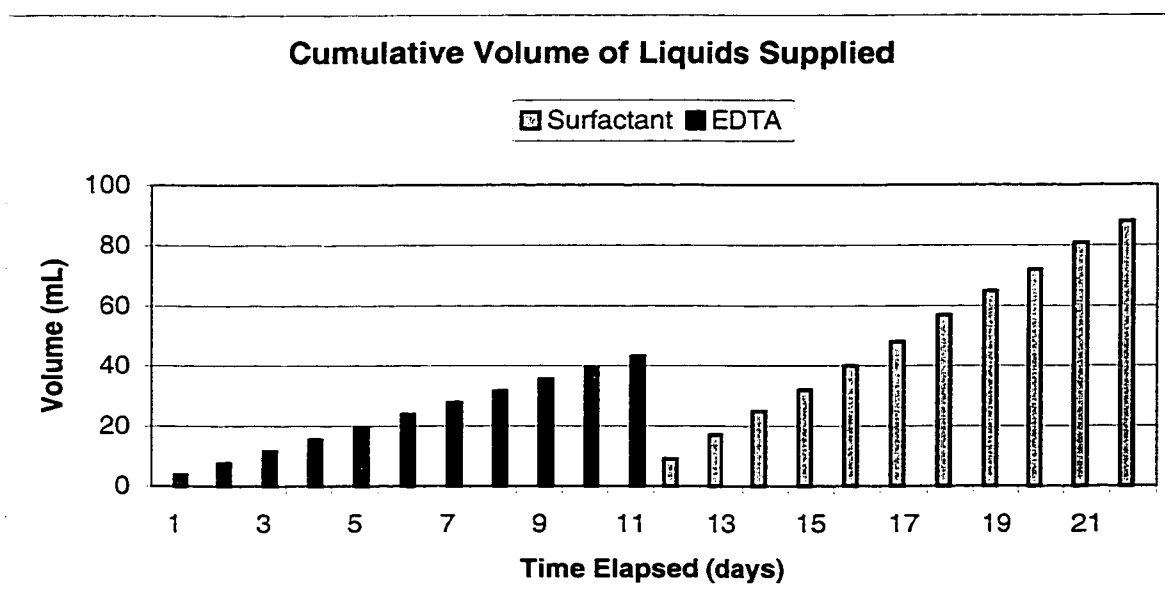


Figure 4.24 Cumulative volume of the surfactant and EDTA supplied in cell T2C6

4.2.4. Soil Samples:

4.2.4.1. pH of the Soil

The pH analysis of the soil samples and its variation with the sample numbers for cells T2C3 and T2C4 are shown in Figure 4.25, and for cells T2C5 and T2C6 are shown in Figure 4.26. Maximum soil pH values observed in cells T2C3, T2C4, T2C5, and T2C6 were 11.03, 10.98, 11.31 and 11.15. As expected, there was a general increase from anode to cathode. The pH of the soil showed a typical distribution from cathode to anode. The initial pH of soil was 7.6 and the formation of hydrogen ions at the anode lowered the soil pH. The small reduction in all cells was due to the supply of water directly into the anode. The increase of pH in the cathode region was due to the formation of OH^- ions. Typically, it is expected that the pH of the soil in the cathode region would be closer to 11; probably the formation of hydroxide precipitates removed some hydroxide ions from the solution thereby lowering the pH slightly. In general both cell T2C5 and T2C6 displayed similar soil pH distributions. It seems that high pH values occur between the cathode and the CET.

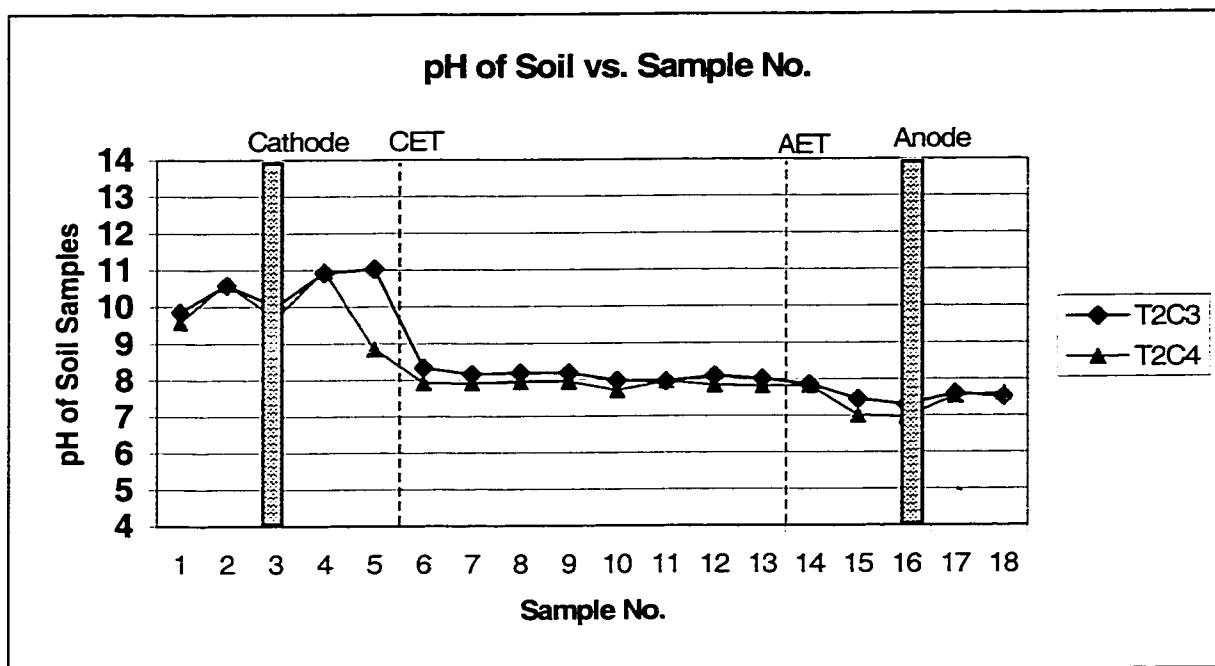


Figure 4.25 pH distribution for cells T2C3 and T2C4 after experiments

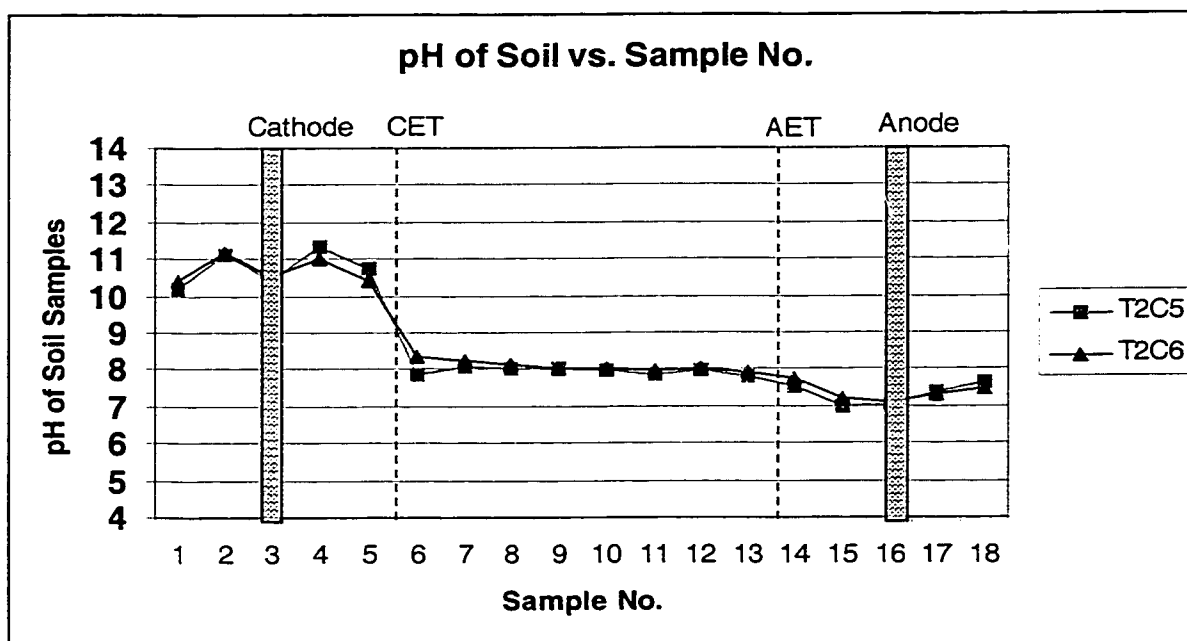


Figure 4.26 pH distribution for cells T2C5 and T2C6 after experiments

4.2.4.2. Metal Concentration in the Soil

The concentration of lead and nickel in the soil was measured using AA spectrometer (see Chapter 3.7.1.3). The concentration of lead and nickel in the soil samples and its variation with the sample numbers for cells T2C3, T2C4, T2C5 and T2C6 are shown in Figure 4.27 and 4.28 respectively, where C is the remaining concentration (mg/L) and C_0 is the initial concentration (mg/L). The lead distribution in the soil for cells T2C3, T2C4, T2C5 and T2C6 showed 70 %, 77 %, 74 % and 85 % average removal of lead between ion exchange textiles respectively. The presence of the majority of lead ions in the anode area (Fig. 4.27) is directly related to the effectiveness of EDTA in the mobilization of lead. Lead has a strong affinity for clay soil and has higher power of exchange with soils than other heavy metals. The highest removal of lead was observed when EDTA was supplied during the first period of treatment in electrokinetic process. The distribution of nickel in the soil for cells T2C3, T2C4, T2C5 and T2C6 showed 57 %, 59 %, 82 % and 84 % average removal of nickel between ion exchange textiles respectively. All four cells showed high nickel concentration in the anode area, which is indicative of significant electrolytic migration from cathode to anode. The relocation of nickel that was achieved, was higher than lead. Nickel is easily subjected easy to complexation in the presence of various compounds. For example it is known that nickel reacts with carbon monoxide and toluene. Therefore, we can find out that nickel undergoes of anionic complexation which gives it a high mobility in soil. The highest removal of nickel was observed when EDTA was supplied during the first period of treatment. Cells T2C5 and T2C6 showed better removal efficiencies and better localization of nickel. It seems that the introduction of surfactant and EDTA

simultaneously is not efficient. The application of electrokinetics seems to be the best technology to control the transportation of nickel in the soil.

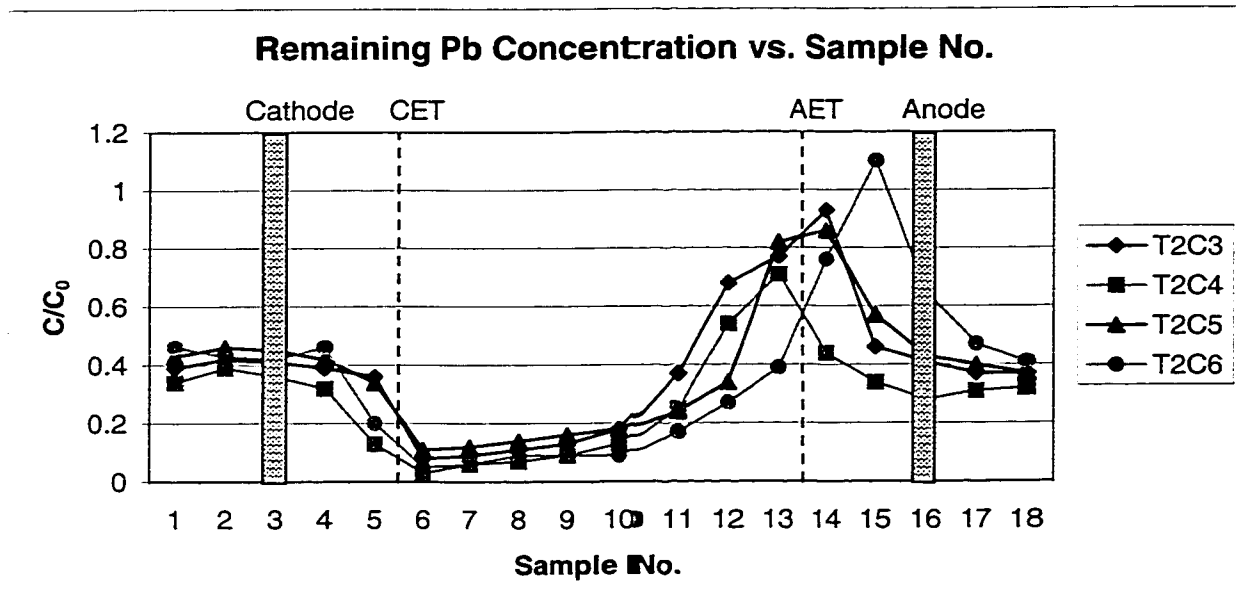


Figure 4.27 Pb distribution in cells T2C3, T2C4, T2C5 and T2C6 after experiments

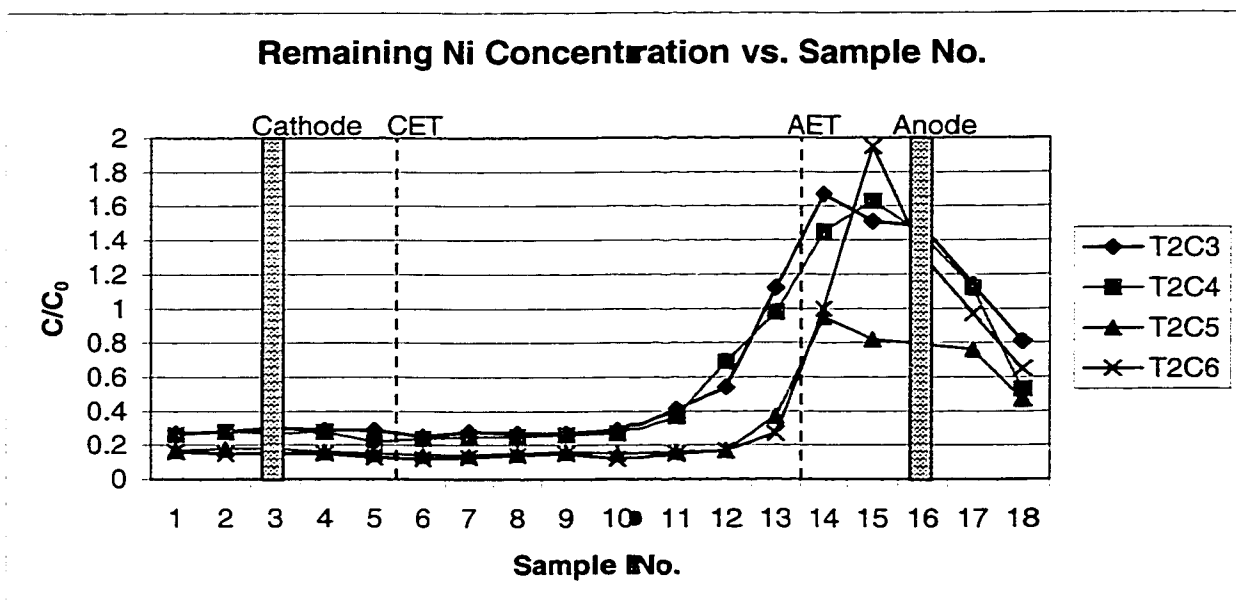


Figure 4.28 Ni distribution in cells T2C3, T2C4, T2C5 and T2C6 after experiments

4.2.4.3. Phenanthrene Concentration in the Soil

Soil samples were tested for the amount of residual phenanthrene after the test. Contaminated soil samples, which were not subjected to electrokinetics, were tested for phenanthrene content and the results were used as a reference for samples undergone electrokinetic tests. The concentration of phenanthrene in soil samples was measured using UV/Vis (see Chapter 3.7.1.4). The concentration of phenanthrene in the soil samples and its variation with the sample numbers for cells T2C3, T2C4, T2C5 and T2C6 are shown in Figure 4.29. The distribution of phenanthrene in the soil for cells T2C3, T2C4, T2C5 and T2C6 showed, 76 %, 70 %, 72 % and 74 % average removal of phenanthrene between ion exchange textiles respectively.

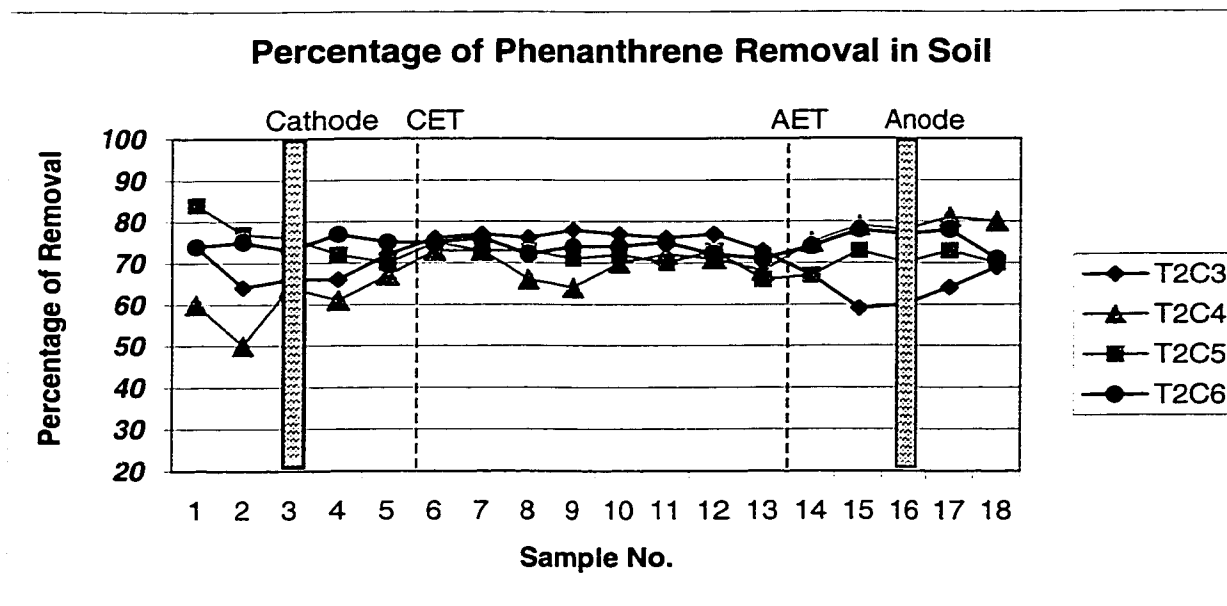


Figure 4.29 Concentration of phenanthrene in cells T2C3, T2C4, T2C5 and T2C6

It can be concluded that coupling the supply of surfactant with electrokinetics, enhanced the mobility of phenanthrene. The highest removal of phenanthrene was achieved in cell T2C3, because the surfactant was supplied for a longer period. A higher removal efficiency was achieved in anode zone when the surfactant was supplied during second period of treatment.

4.2.5. Analysis of Ion Exchange Textiles

The specific concentration (mg/mm^2) of lead, nickel and phenanthrene at particular locations on the textiles in T2C3, T2C4, T2C5 and T2C6 are shown in Table 4.3. Both nickel and lead ions were captured by anion exchange textiles (AET) which showed that metal-EDTA complexes can enter in exchange processes with AET. The capture of cation exchange textiles (CET) was low for both metals. AET and CET captured almost the same amount of phenanthrene in all cells.

Table 4.3 Specific concentration of Pb, Ni and phenanthrene in textiles (Test T2)

Cell Number	Pb (mg/cm^2)		Ni (mg/cm^2)		Phenanthrene (mg/cm^2)	
	AET	CET	AET	CET	AET	CET
T2C3	0.1523	0.0068	0.1479	0.0065	0.0054	0.0059
T2C4	0.1149	0.0083	0.1416	0.0076	0.0055	0.0041
T2C5	0.2136	0.0072	0.0874	0.0062	0.0040	0.0056
T2C6	0.1147	0.0087	0.0968	0.0055	0.0043	0.0047

4.3. Experiments T3: Effect of injection time on contaminant removal and energy consumption.

Experiment T3 consisted of two experiments, T3C7 and T3C8. The investigation of injection time was tested. Table 4.4 shows the different periods of liquid supplied and duration of experiments.

Table 4.4 Supplied periods of EDTA and surfactant (Test T3)

Cell No	EDTA Supplied Period	Surfactant Supplied Period	Entire Period of Tests (days)
T3C7	21 st -42 nd	1 st -21 st	42
T3C8	1 st -21 st	21 st -42 nd	42

4.3.1. Electrical Parameters

Measurements related to potential at each probe and cell current was performed daily. The resistance variation with the distance from the cathode is displayed graphically in Figure 4.30 and Figure 4.31 for cell T2C7 and cell T3C8 respectively. It clearly showed that the resistance tended to decrease from the anode to the cathode. The average resistance gradients that were observed in cell T3C7 in the first and second 21-day periods were 17 Ohms/cm and 43 Ohms/cm respectively. At time progressed, the resistance in cell T3C7 increased faster than T3C8. During the first 21 days of treatment the resistance in cell T3C7 was higher than T3C8, but the resistance gradient was lower. Injection of EDTA in the second 21 days decreased the resistance in cell T3C7, but a higher resistance gradient was observed thereafter. The average resistance gradients that were observed in cell T3C8 in the first and second 21-day periods were 30 Ohms/cm and 34 Ohms/cm respectively. Generally an increase in resistance gradient was observed, particularly between the cathode and the CET.

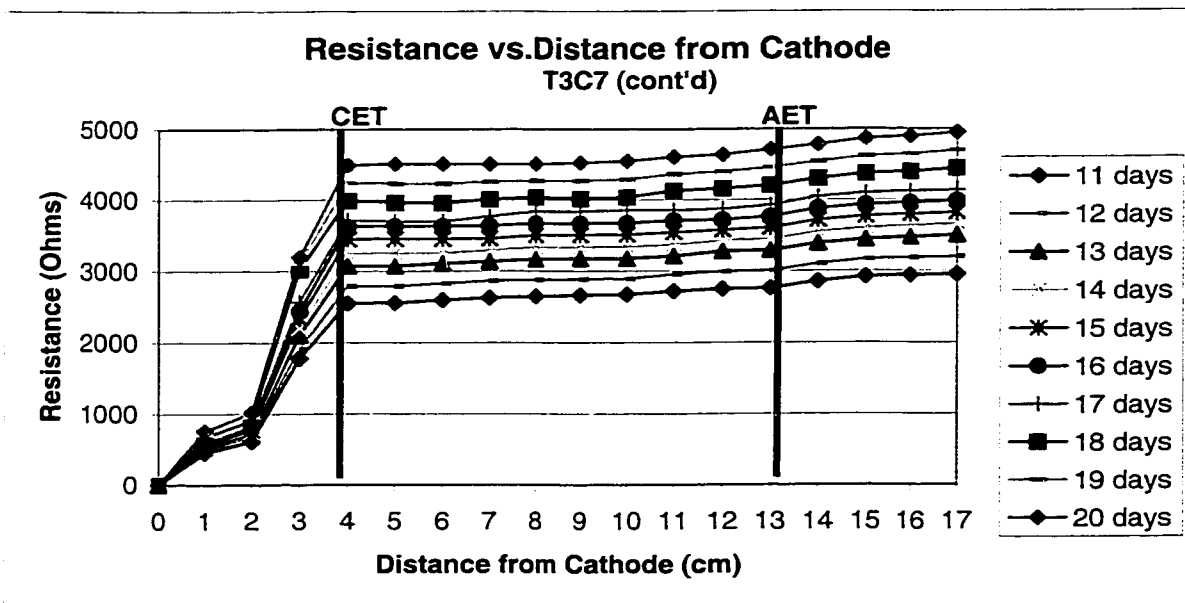
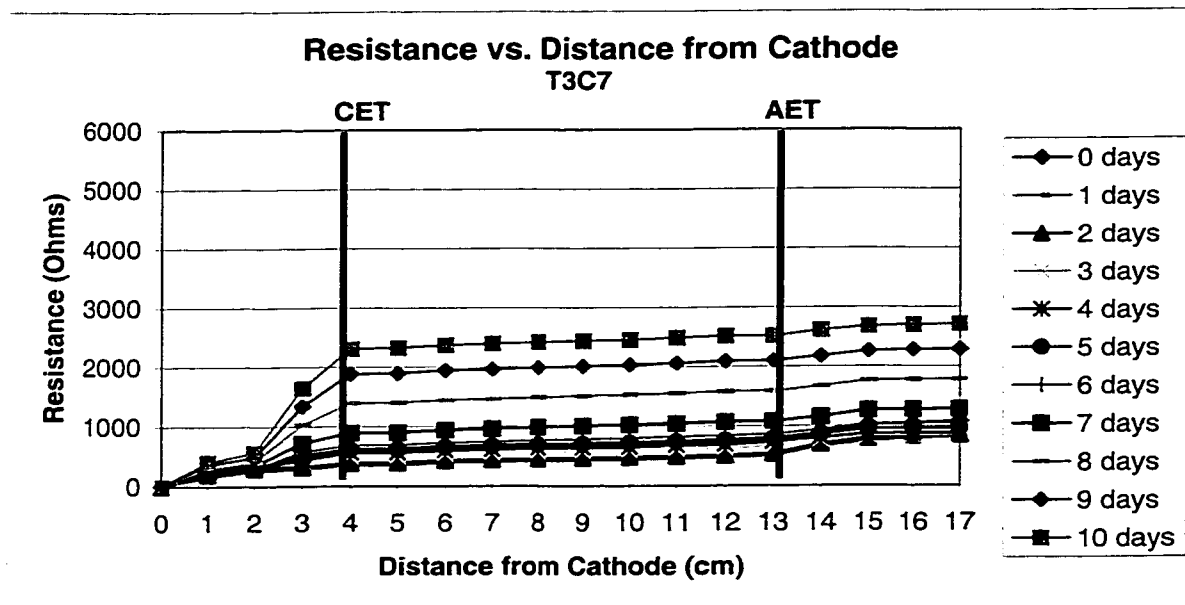


Figure 4.30 Resistance distribution versus distance from the cathode (T3C7)

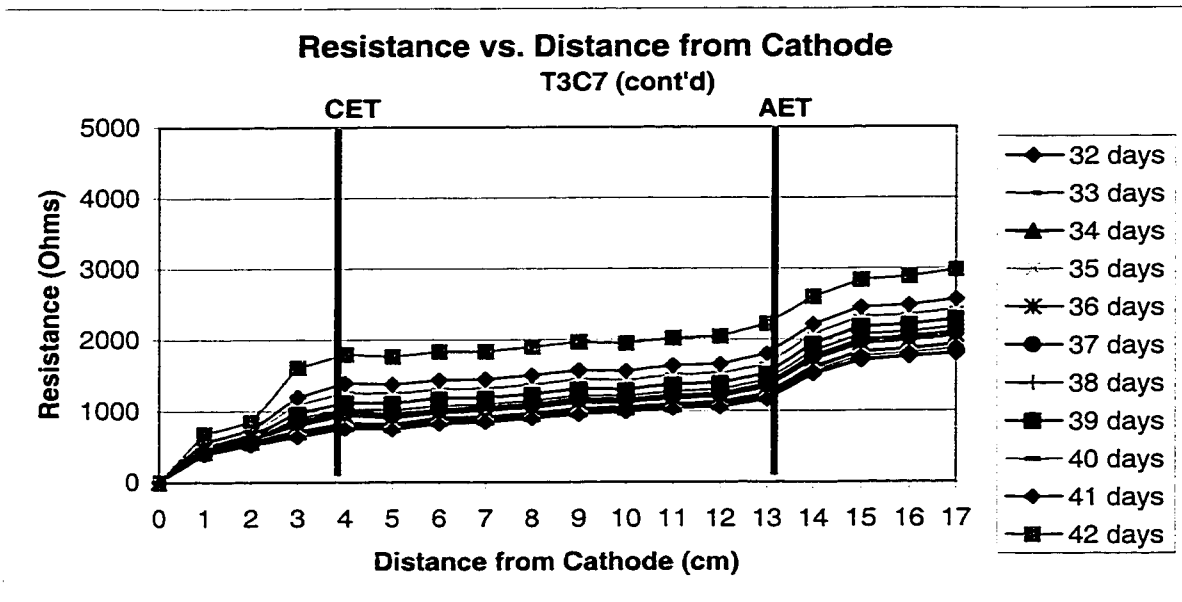
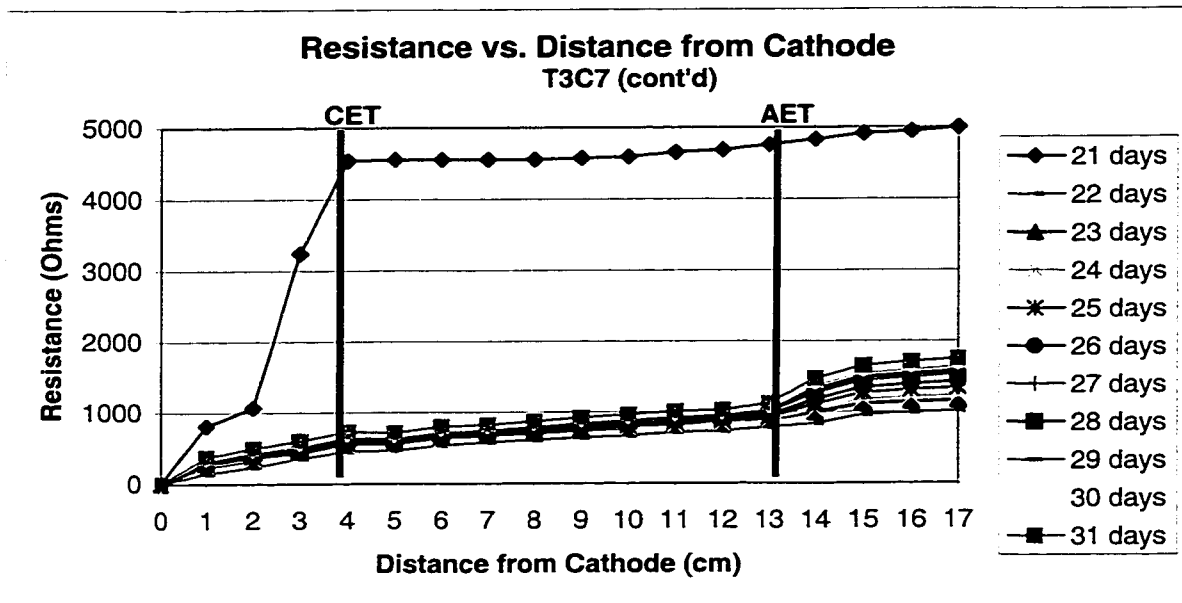


Figure 4.30 Resistance distribution versus distance from the cathode (T3C7) (cont'd)

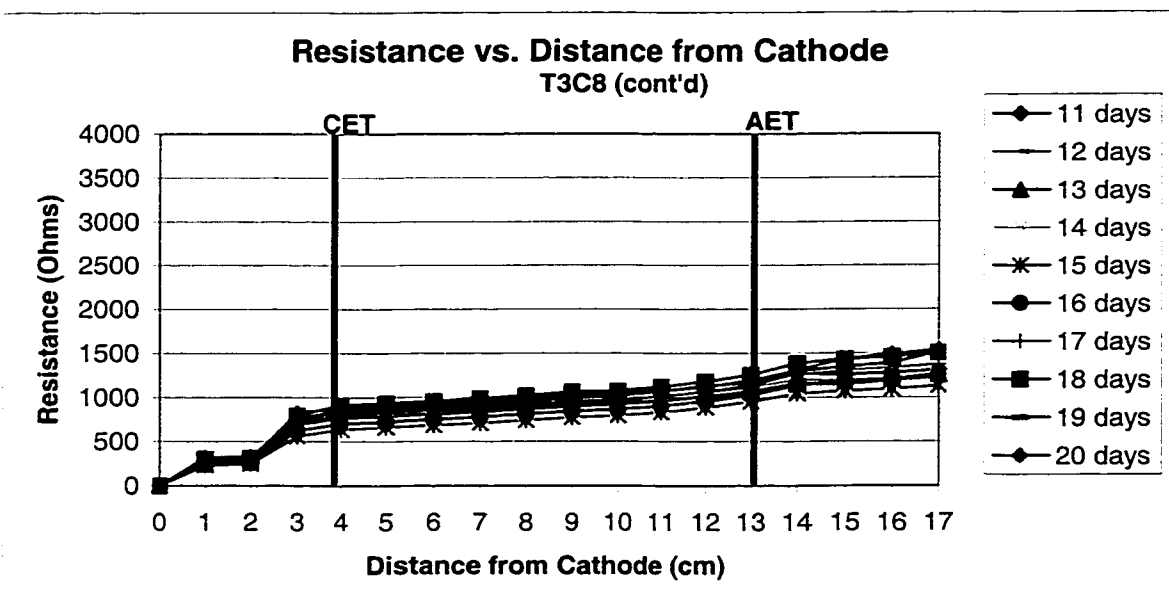
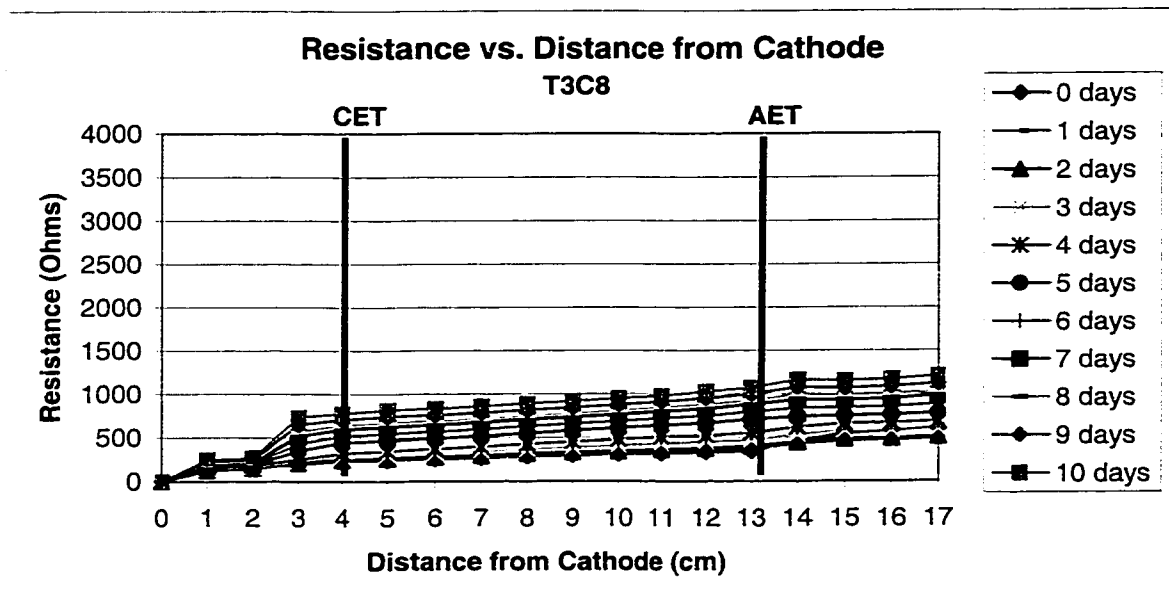


Figure 4.31 Resistance distribution versus distance from the cathode (T3C8)

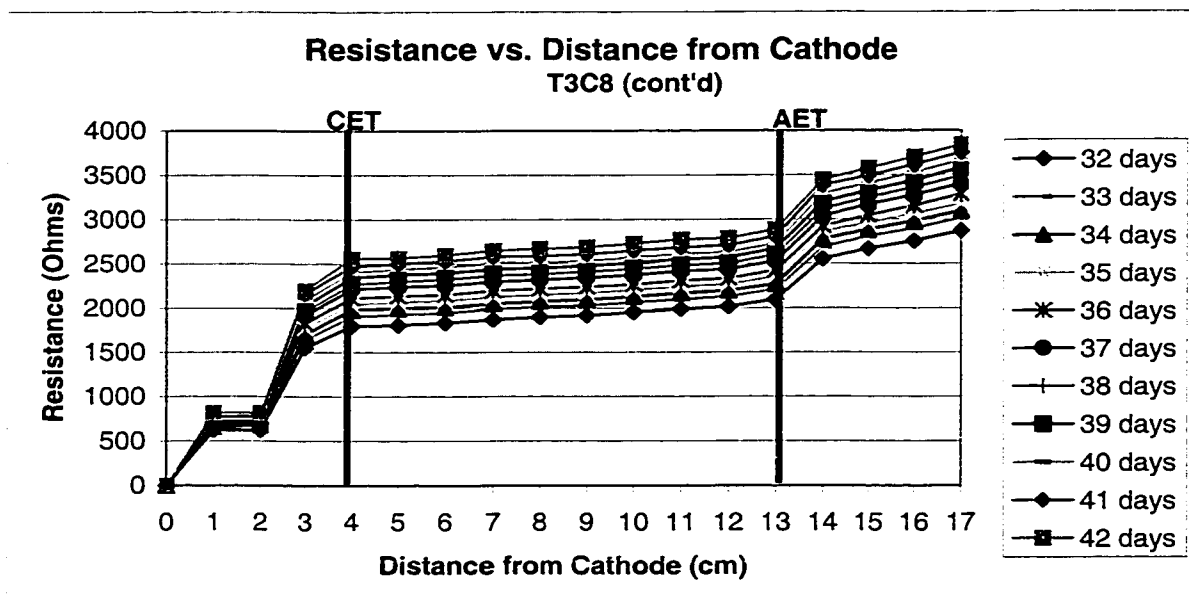
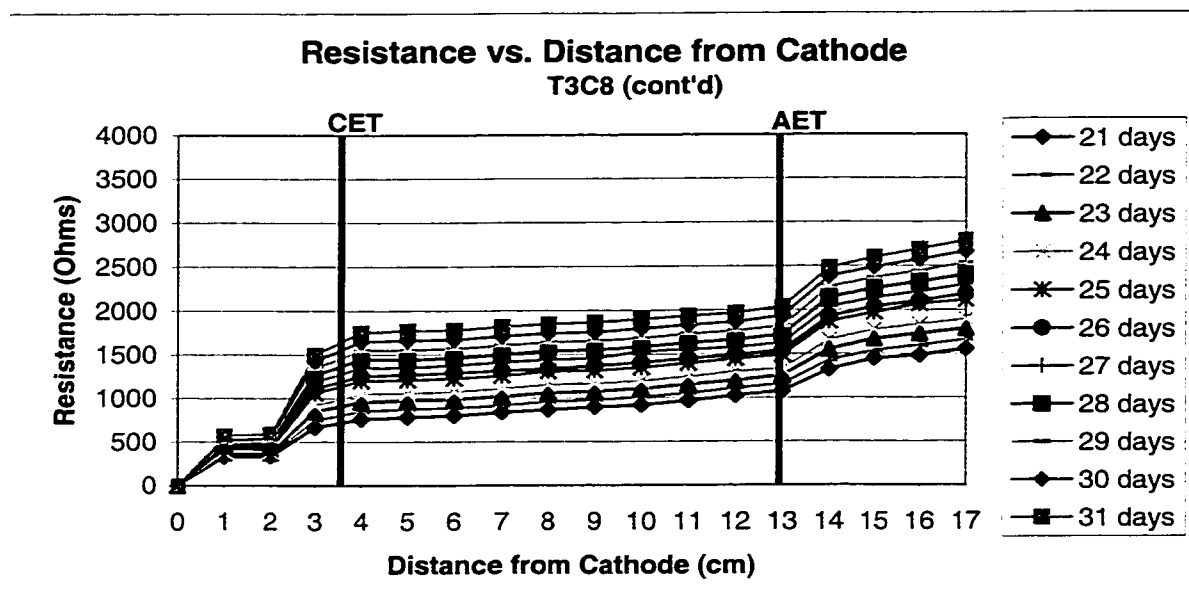


Figure 4.31 Resistance distribution versus distance from the cathode (T3C8) (cont'd)

The total resistance variation with time is displayed graphically in Figure 4.32 for cells T3C7 and T3C8. With time, the total resistance of cell T3C8 increased from 600 Ohms at the beginning of the experiment to 3840 Ohms at the end of experiment. In cell T3C7, the corresponding resistances increased from 1076 Ohms to 4998 Ohms in the first 21 days. In cell T3C7, by introducing EDTA in the second 21 days, the total resistance of the soil decreased five times. It seems that EDTA could be used for control of resistance.

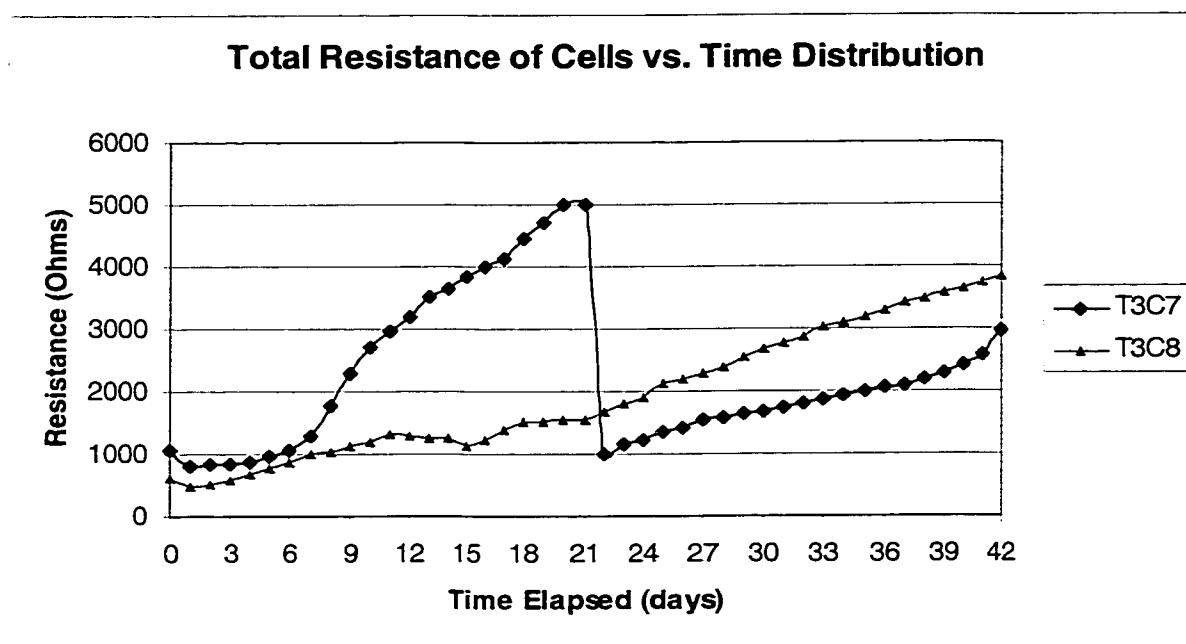


Figure 4.32 Total resistance of soil for cells T3C7 and T3C8

4.3.2. Results Pertaining to Cathode Liquids

The pH of the liquids extracted from the cathode is displayed in Figure 4.33. As time progressed, the pH of the cathode liquids decreased slightly. The highest pH was associated with the initiation of EDTA supply. As time progressed, the total resistance of the soil increased and the pH of the soil decreased.

The fluctuation of the liquids extracted through the cathode of cell T3C7 and T3C8 is shown in Figure 4.34. The total volume extracted from cells T3C7 and T3C8 for the entire duration of the experiments were 387.3 mL and 382.4 mL respectively. The average daily volume extracted for corresponding cells were 9.2 mL and 9.1 mL respectively. The lowest volumes were observed for cells where EDTA was supplied at the beginning of test, independent of the duration of application. When EDTA was introduced, the discharge increased for a few days and decreased thereafter. Each cell shows almost the same discharge in both cells.

4.3.3. Volume of Liquids Supplied

Figure 4.35 shows the cumulative volume of surfactant and EDTA supplied in cell T3C7. The average daily surfactant and EDTA volume supplied were 15.4 mL and 2.1 mL respectively. The amount of surfactant supplied in cell T3C7 was 6.5 times higher than EDTA. Figure 4.36 shows the cumulative volume of surfactant and EDTA supplied in cell T3C8. The average daily surfactant and EDTA volume supplied were 9.0 mL and 1.0 mL respectively. The amount of surfactant supplied in cell T3C8 was 7 times higher than EDTA.

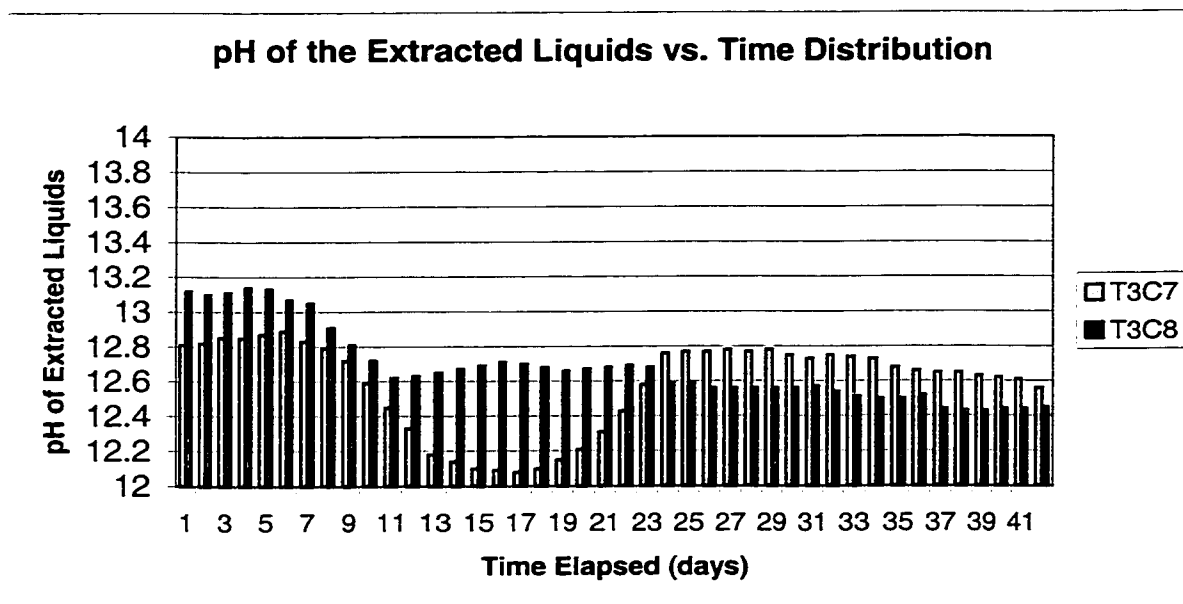


Figure 4.33 pH of the extracted daily cathode liquids (T3C7 and T3C8)

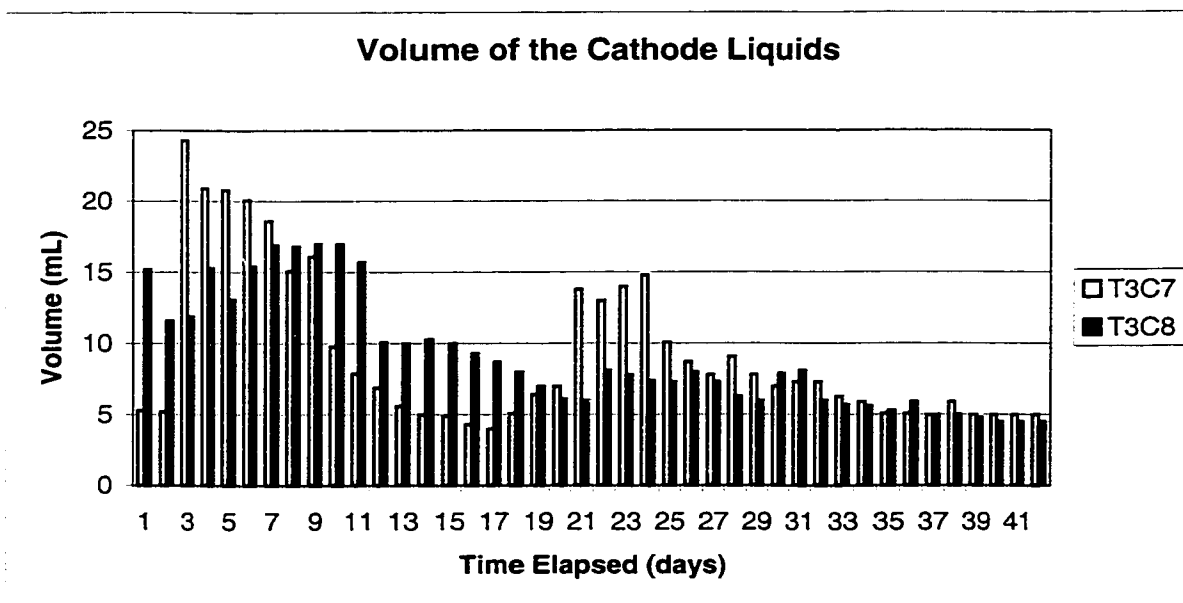


Figure 4.34 Volume of extracted daily cathode liquids (T3C7 and T3C8)

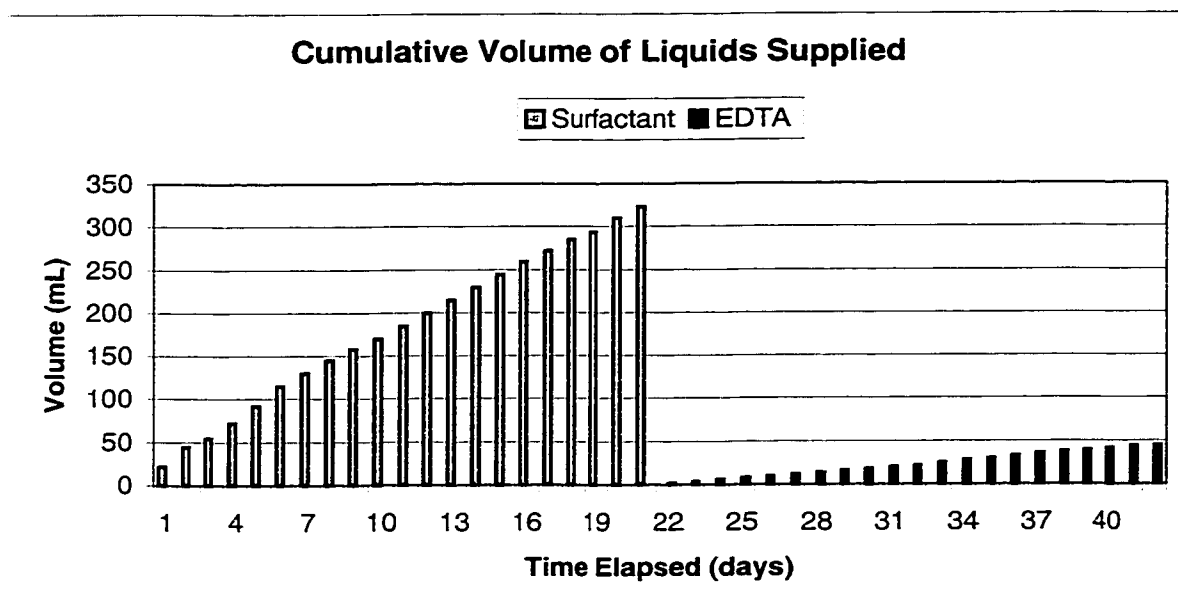


Figure 4.35 Cumulative volume of surfactant and EDTA supplied in cell T3C7

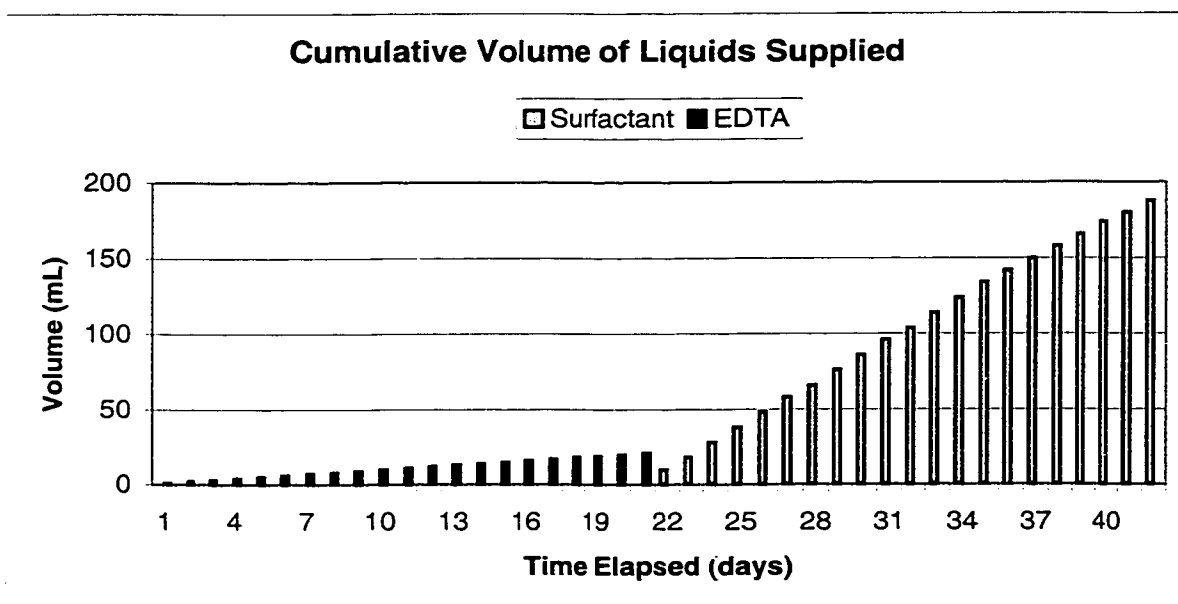


Figure 4.36 Cumulative volume of surfactant and EDTA supplied in cell T3C8

4.3.4. Soil Samples:

4.3.4.1. pH of the Soil

The pH analysis of the soil samples and its variation with the sample numbers for cells T3C7 and T3C8 are shown in Figure 4.37. Maximum soil pH values that were observed in cell T3C7 and T3C8 were 11.61 and 11.88 respectively. As expected, there was a general increase from anode to cathode. The pH of the soil showed a typical distribution from cathode to anode. The initial pH of soil was 7.6 and the formation of hydrogen ions at the anode lowered the soil pH. The small reduction was due to the supply of water directly into the anode. The increase of pH in the cathode region was due to the formation of OH^- ions.

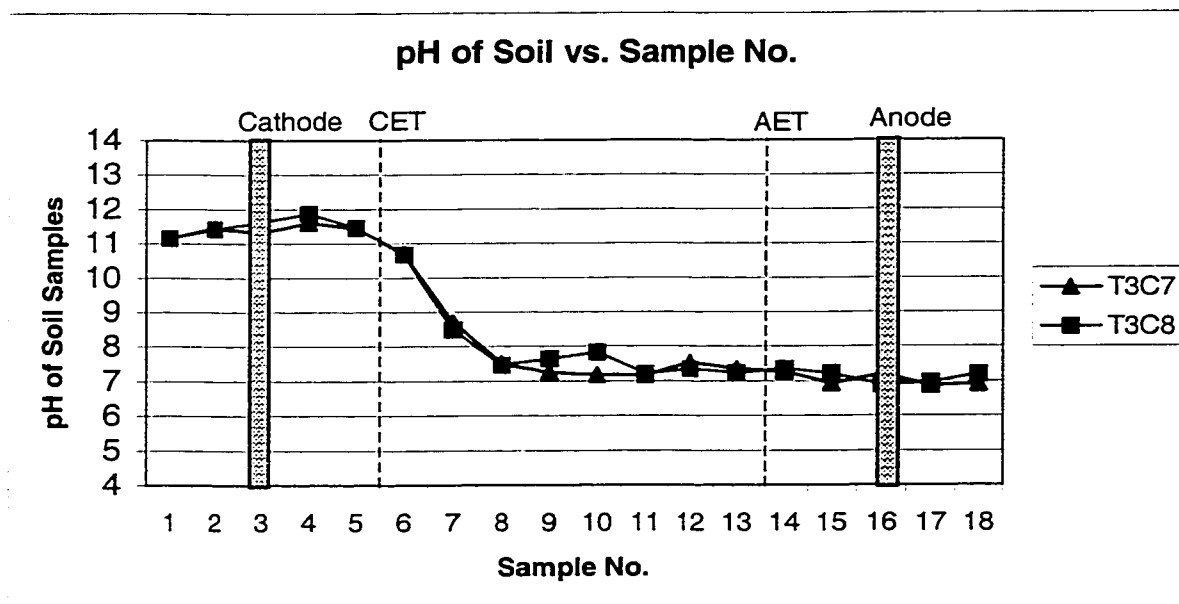


Figure 4.37 pH distribution for cells T3C7 and T3C8 after experiment

Typically, it is expected that the pH of the soil in the cathode region would be closer to 11.8. The formation of hydroxide precipitates removed some hydroxide ions from solution, thereby lowering the pH slightly. In general, both cells T3C7 and T3C8 displayed similar soil pH distributions.

4.3.4.2. Metal Concentration in the Soil

The concentration of lead and nickel in the soil was measured using AA spectrometer (see Chapter 3.7.1.3). The concentration of lead and nickel in the soil samples and its variation with the sample numbers for cells T3C7 and T3C8 are shown in Figure 4.38 and 4.39 where C is the remaining concentration (mg/L) and C_0 is the initial concentration (mg/L). The distribution of lead in the soil for cells T3C7 and T3C8 showed 79 % and 85 % average removal of lead between ion exchange textiles respectively. The presence of the majority of the lead ions in the anode area (Fig. 4.38) is directly related to the effectiveness of EDTA in the mobilization of lead. Lead has a strong affinity for clay soil and has higher power of exchange with soils than other heavy metals. The highest removal of lead was observed when EDTA was supplied during the first period of treatment in electrokinetic process. The distribution of nickel in the soil for cells T3C7 and T3C8 showed 87 % and 74 % average removal of nickel between ion exchange textiles respectively. Both cells showed high nickel concentrations in the anode area, which is indicative of significant electrolytic migration from cathode to anode. The relocation of nickel that was achieved, was higher than lead. Nickel is easily subjected to complexation in the presence of various compounds.

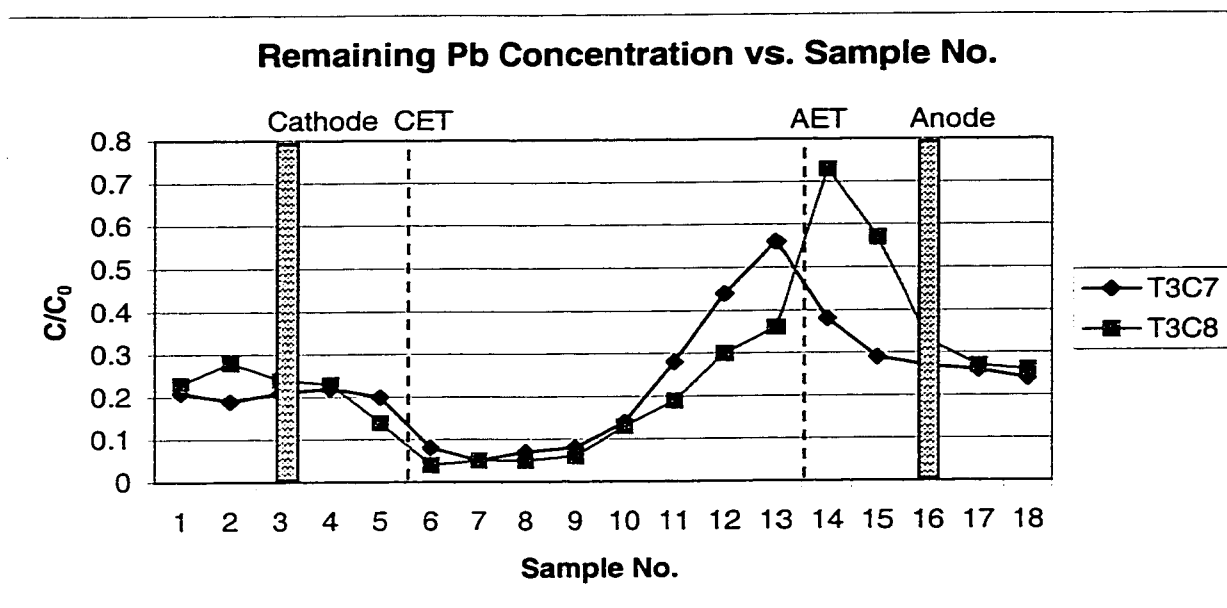


Figure 4.38 Pb distribution in cells T3C7 and T3C8 after experiments

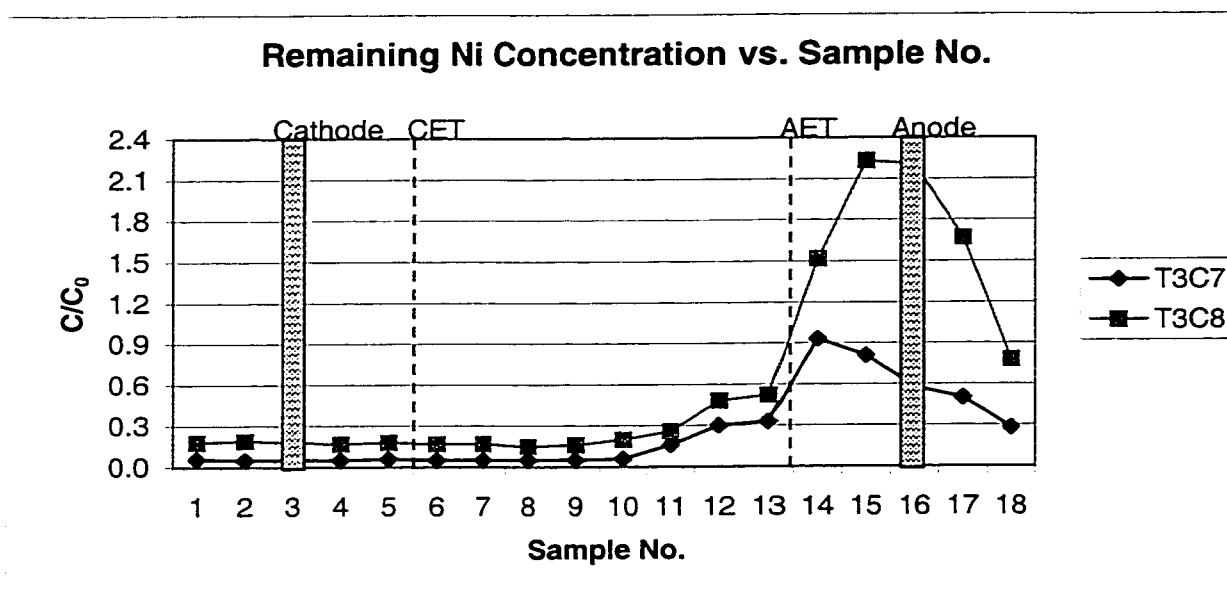


Figure 4.39 Ni distribution in cells T3C7 and T3C8 after experiments

The highest removal of nickel was observed when EDTA was supplied during the first period of treatment. Cell T3C8 showed higher nickel concentrations in the anode area, which is indicative of significant electrolytic migration from cathode to anode.

4.3.4.3. Phenanthrene Concentration in the Soil

Soil samples were tested for the amount of residual phenanthrene after the test. Contaminated soil samples, which were not subjected to electrokinetics, were tested for phenanthrene content and the results were used as a reference for samples undergone electrokinetic tests. The concentration of phenanthrene in the soil was measured using UV/Vis (see chapter 3.7.1.4). The concentration of phenanthrene in the soil samples and its variation with the sample numbers for cells T3C7 and T3C8 are shown in Figure 4.40. The distribution of phenanthrene in the soil for cells T3C7 and T3C8 showed 60 % and 62 % average removal of phenanthrene between ion exchange textiles respectively. Higher removal efficiency was achieved in the anode zone when the surfactant was supplied during the second period of treatment.

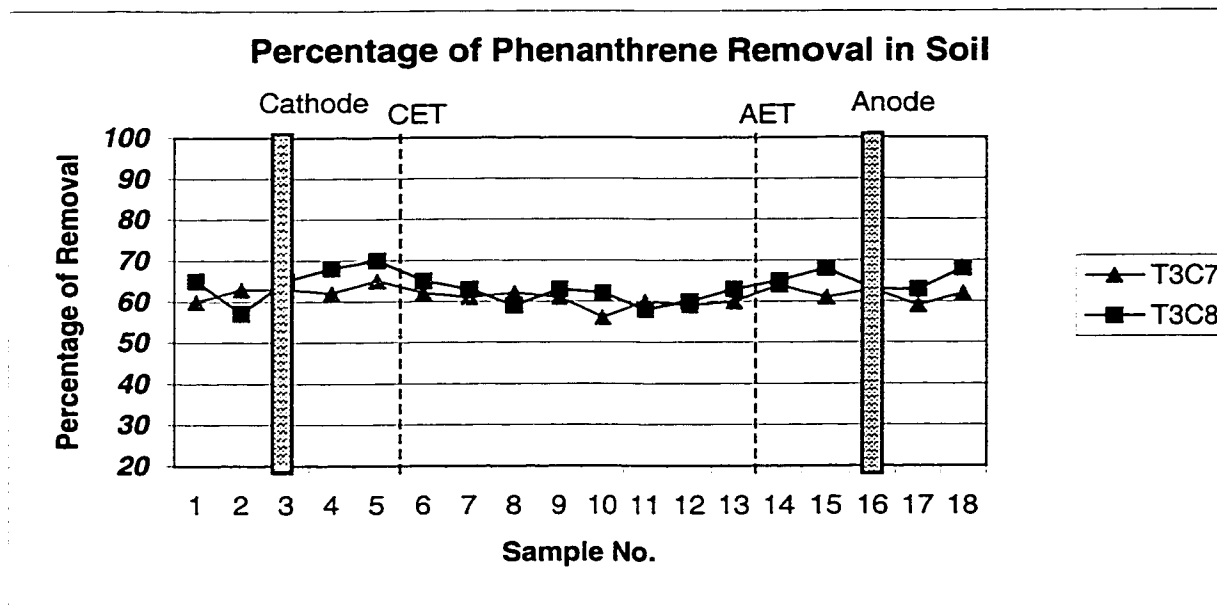


Figure 4.40 Concentration of phenanthrene in cells T3C7 and T3C8

4.3.5. Analysis of Ion Exchange Textiles

The specific concentration (mg/mm^2) of lead, nickel and phenanthrene at particular locations on the textiles in T3C7 and T3C8 are shown in Table 4.5. Both nickel and lead ions were captured by anion exchange textiles (AET) which shows that metal-EDTA complexes can enter in exchange processes with AET. The capture of cation exchange textiles (CET) was low for nickel. It was observed that the longer period of the electrokinetic treatment, the nickel removal via the AET increased when surfactant was introduced the first. The AET and CET captured almost the same amount of phenanthrene in both cells. Textiles did not capture phenanthrene micelles. The above mentioned result permitted to speculate the presence of surfactant micelles avoided the situation which, phenanthrene can covers partially textile and provoke decreasing their capacity.

Table 4.5 Specific concentration of Pb, Ni and phenanthrene in textiles (Test T3)

Cell Number	Pb (mg/cm^2)		Ni (mg/cm^2)		Phenanthrene (mg/cm^2)	
	AET	CET	AET	CET	AET	CET
T3C7	0.0337	0.0365	0.1112	0.0090	0.0035	0.0024
T3C8	0.0711	0.0379	0.0562	0.0098	0.0042	0.0033

4.4. Results and Discussion for All Experiments

4.4.1. Contaminant Removal

The percentage of contaminant removal (Pb, Ni, phenanthrene) between anode and cathode in each cell is shown in Figure 4.41.

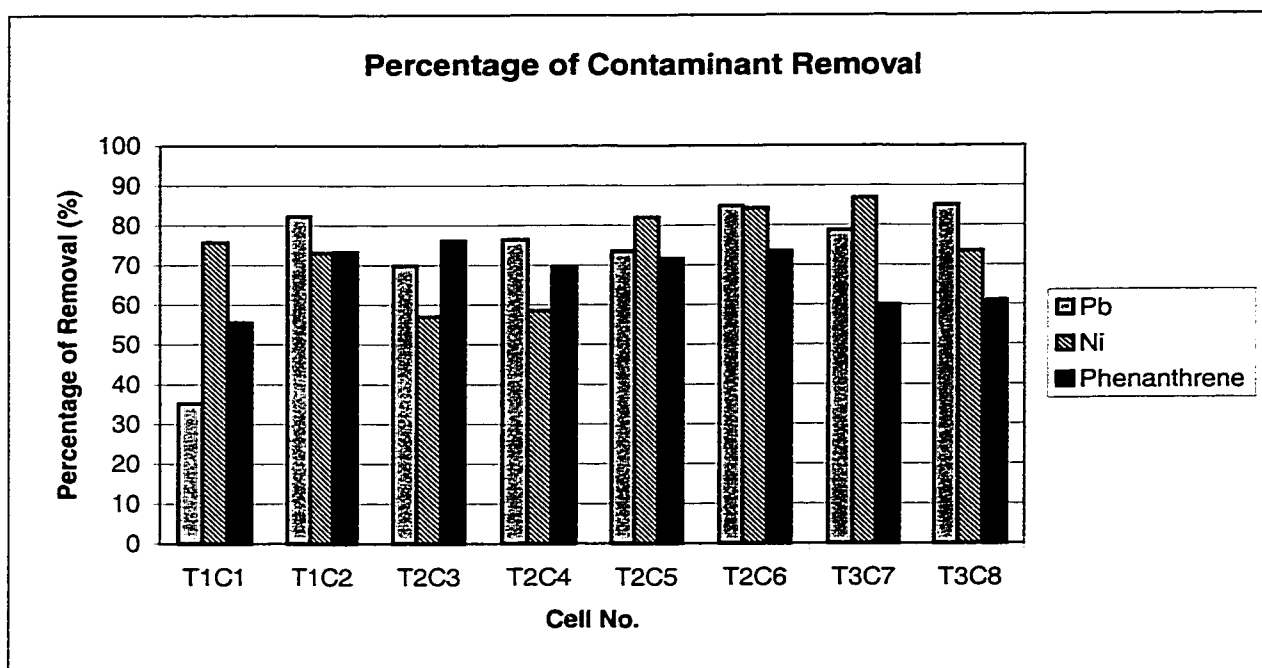


Figure 4.41 Percentage of the average removal of lead, nickel and phenanthrene in electrokinetic cells.

Maximum (85 %) and minimum (35 %) lead removals were observed in cells T3C8 and T1C1 respectively. Maximum and minimum nickel removal was 87 % (T3C7) and 57 % (T2C3) respectively. Maximum (76 %) and minimum (56 %) phenanthrene removals were observed in cells T2C3 and T1C1 respectively. The highest lead removal was observed when EDTA was first supplied for 21 days. A high nickel removal was observed in several cells. The long period of removal seems to be an important factor for nickel. Phenanthrene removal was observed when the surfactant was applied for the entire period of experiment (22 days). Among all of experimental sets, cell T2C6 had best results for mixed contamination removal. The electrokinetic cell T2C6 was capable of removing an average of 85 % of lead, 84 % of nickel and 74 % of phenanthrene.

4.4.2. Power Consumption

The energy consumption is another parameter, which demonstrates the effectiveness of a particular set-up. The power consumption in the electrokinetic cells

was an important parameter to calculate the energy consumption by each cell. Figure 4.42 shows the power consumption for all electrokinetic cells (T1C1 to T2C6) versus time elapsed. As time progressed, the power used in all cells increased in the beginning and then decreased slightly. Because of introducing EDTA in cells T2C3 and T2C5 during the second period of treatment, the power consumption again increased from 7 mW to 30 mW for both cells.

Figure 4.43 shows the power consumption for cells T3C7 and T3C8 versus time elapsed. As time progressed, the power consumption in both cells increased in the beginning and then decreased slightly. Due to the introduction of EDTA in cell T3C7 during the second period of treatment, the power consumption again increased from 5 mW to 23 mW. In comparison, cell T3C8 had 25 % more power consumption, and also had better result in lead removal. Twice of the operation time increases the power consumption by 20-27 %.

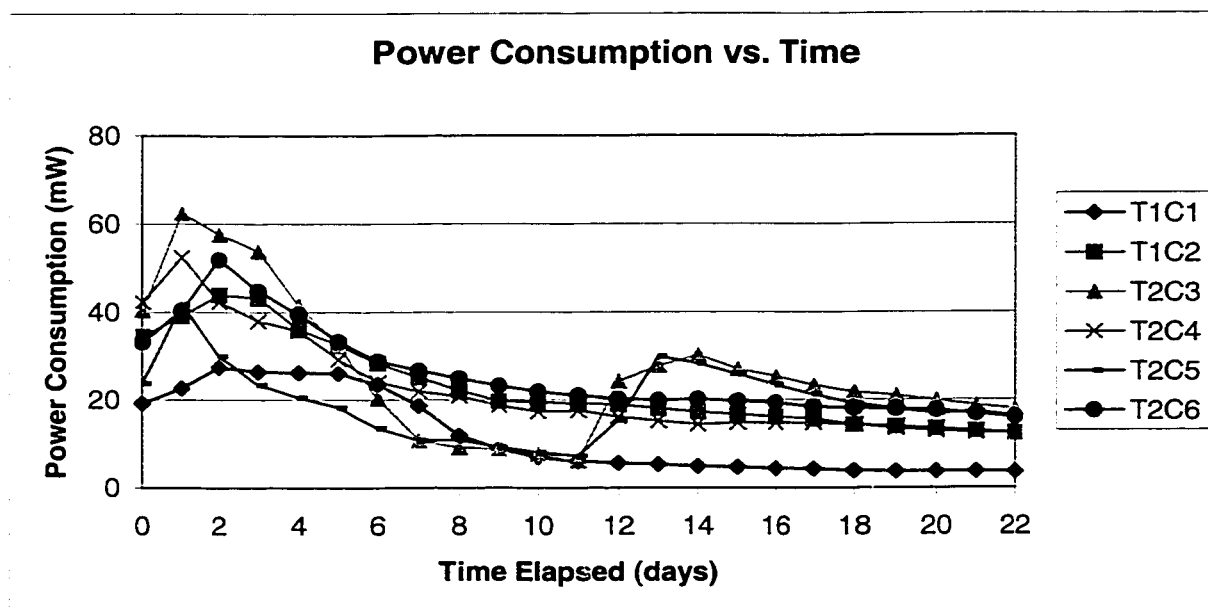


Figure 4.42 Power consumption for all electrokinetic cells with 22 days test period

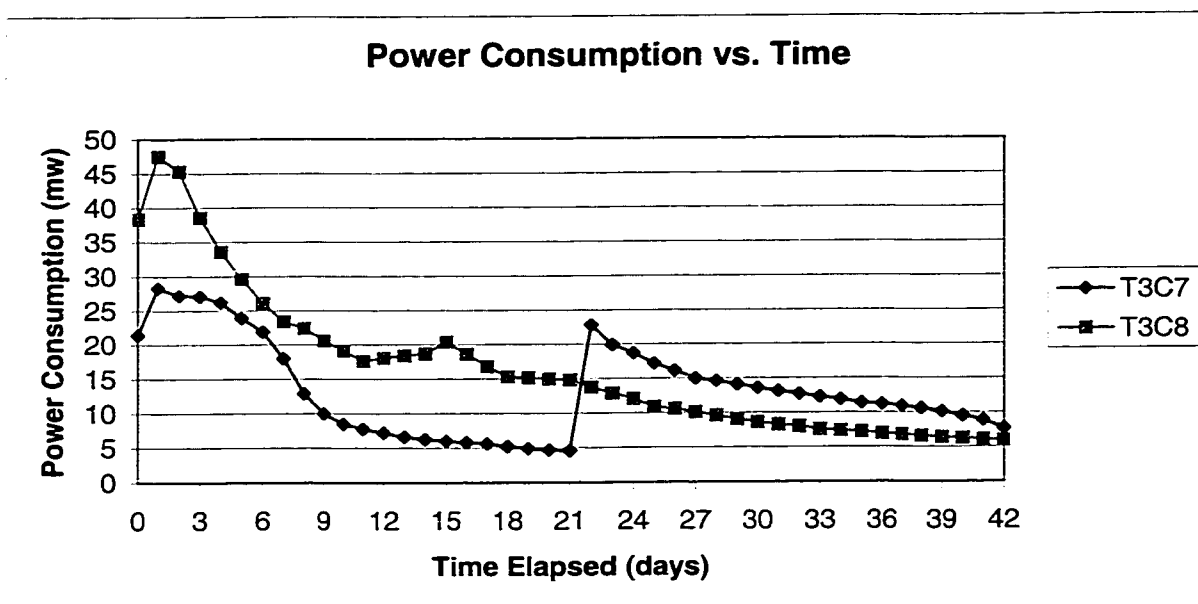


Figure 4.43 Power consumption in electrokinetic cells T3C7 and T3C8

4.4.3. Energy Consumption

The total energy consumption in electrokinetic cells was obtained from having power consumption and duration of treatment for each cell. Figure 4.44 shows the total energy consumption in the cells. The order of amount of energy consumption was as follows:

$$T1C1 < T2C5 < T2C4 < T1C2 < T3C7 < T2C6 < T2C3 < T3C8$$

As mentioned previously, cell T2C6 had the best results in mixed contaminant removal. In comparing between cells T2C6 and T1C1, T2C6 had 2.4 times the Pb removal, 1.1 times the Ni removal and 1.3 times the phenanthrene removal. It was also observed that cell T2C6 had 3% and 21% less energy consumption in comparing with cells T2C3 and T3C8 respectively.

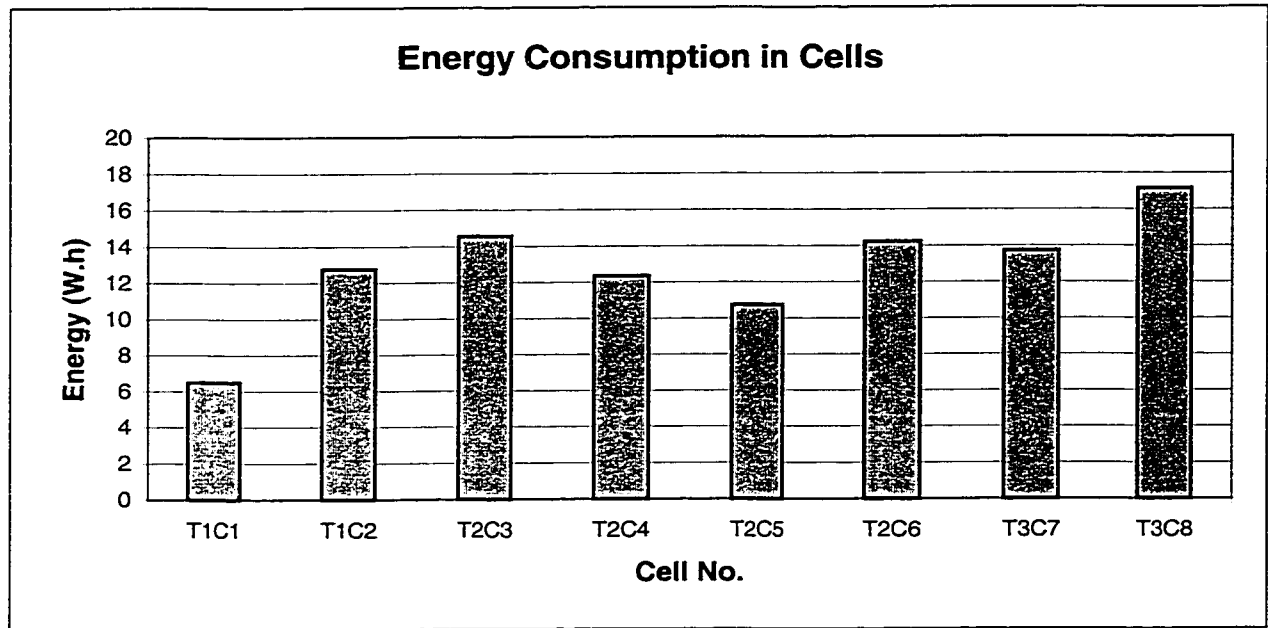


Figure 4.44 The total energy consumption in electrokinetic cells

CHAPTER 5 CONCLUSIONS

The investigation of a new technology for in-situ remediation of clayey soil contaminated with heavy metals and PAHs consisted on coupling, correlating and optimizing of several physico-chemical processes. The electrokinetic transport, PAHs desorption enhanced by surfactant, metal complexation, and capture by ion exchange textile were applied in lab scale in order to study:

- The response of mixed contaminated sites for the simultaneous use of surfactant, EDTA and ion exchange textiles (T1).
- The contaminant mobilization through the application of surfactant and EDTA in various sequences (T2).
- The effect of the injection time on the contaminant removal and energy consumption (T3).

The results from three series of tests (T1, T2 and T3) permitted to make the following conclusions:

- 1- The study achieved simultaneous treatment of organic and inorganic contaminants in the soil.
- 2- The development of a new methodology applied in-situ for clay contaminated with organic and inorganic compounds was successful.
- 3- The results show a successful use of the electrokinetic system (connected to low DC current) for transport of surfactant, EDTA, phenanthrene micelles and metal compounds into removal zones protected with ion exchange textiles.

- 4- The simultaneous removal of organic and inorganic contaminants was satisfied in all experiments. The optimal simultaneous average removal was 85 % for lead, 84 % for nickel, and 74 % for phenanthrene.
- 5- The optimal removal of mixed contaminants was achieved when EDTA was introduced for the first period of removal and surfactant in the second period.
- 6- The maximum local removals from soil were found to be 96 %, 95 %, and 84 % for lead, nickel, and phenanthrene respectively.
- 7- The best local average removal of lead was achieved where EDTA was introduced for the first period of experiments.
- 8- The best local average removal of phenanthrene was achieved where surfactant was introduced as the first conditioning liquid into the cell.
- 9- The nickel removal was only slightly related to the application of the conditioning liquids.
- 10- The introduction of EDTA decreased instantaneously the resistance in the electrokinetic cells.
- 11- The introduction of the surfactant at the beginning of the experiments increased the resistance in the electrokinetic cells.
- 12- The increase of test duration did not improve the phenanthrene removal.
- 13- During the long submission to electrokinetic test, the better removal of nickel through AET was observed when surfactant was first introduced.
- 14- The results showed a low capture of lead and nickel by cation exchange textiles (CET).
- 15- Anionic exchange textiles (AET) were sensitive to both lead and nickel complexes.

16- Neither AET nor CET were not fouled or clogged by phenanthrene micelles.

17- For the optimal removal condition, the consumption of energy was 28.4 kWh/m³.

18- Results showed that the new developed method could achieve a two-fold decrease in energy consumption comparing to the optimal conditions.

The development of the above described hybrid method permits to clean up a high spectra of contaminated soil, particularly those characterized with low permeability. The results from the research can be applied to the various municipal and industrial sites where petroleum products contaminated soil contains heavy metals.

REFERENCES

- Abdul, A. S., Gibson, T. L., Ang, C. C., Smith, J. C. and Sobczynski, R. E., 1992, "In-Situ Surfactant Washing of Polychlorinated Biphenyls and Oils from Contaminated Site", *Ground Water*, Vol. 30, No.2, pp. 219- 231.
- Acar, Y. B., A.N. Alshabwabkeh, 1993, "Principles of Electrokinetic Remediation", *Environmental Science and Technology*, Vol. 27, No.13, pp. 2638-2647.
- Acar, Y. B., A.N. Alshabwabkeh, 1996, "Electrokinetic Remediation I: Pilot-Scale Tests with Lead-Spiked Kaolinite", *Geotechnical Engineering*, Vol.122, No.3, pp. 173.
- Acar, Y. B., A.N. Alshabwabkeh., and Gale, R. J., 1993, "Fundamental of Extracting Species from Soils by Electrokinetics", *Waste Management*, Pergamon Press, London, Vol. 12, No. 3, pp. 141-151.
- Allen, H. E., P. Chen, 1993, "Remediation of Metal Contaminated Soil by Incorporating Electrochemical Recovery of Metal and EDTA", *Environmental Progress*, Vol. 12, No.4, pp. 284-293.
- Brown, R. A., Mahaffey, W., and Norris, R. D., 1993, "In-Situ Bioremediation: The State of the Particle", in *In-Situ Bioremediation*. National Research Council. Water Science and Technology Board, Com. Eng. Tech. Systems. National Academy Press, Washington, D. C. pp. 121-135.
- Brusseau, M. L., Wang, X., 1997, " Simultaneous Elution of Heavy Metals and Organic Compounds from Soil by Cyclodextrin", *Environmental Science and Technology*, Vol. 31, No. 4, pp. 1087-1092.
- Cain. R. B., 1994, "Bioremediation of Detergents", *Current Opinion in Biology*, Vol. 5, pp. 226-274.
- Choudhury, A., 1998, "Removal of Nickel and Lead from Natural Clay Soil through the Introduction of EDTA and Coupling Ion Exchange Processes with Electrokinetic Methodology", M.Sc., thesis.
- Choudhury, A., Elektorowicz, M., 1997, "Enhanced Electrokinetic Methods for Lead and Nickel Removal from Natural Clayey Soil", 32nd Central Symposium on Water Pollution Research, 1997, Burlington, ON.
- Edwards, D. A., Luthy, R. G. and Liu, Z., 1991 a, "Solubilization of Polycyclic Aromatic Hydrocarbons in Micellar Nonionic Surfactant Solution", *Environmental Science and Technology*, Vol. 25, No. 1, pp. 127- 133.
- Elektorowicz, M., Boeva, V., 1996, "Electrokinetic Supply of Nutrients in Soil Bioremediation", *Environmental Technology*, Vol. 17, pp. 1339-1349.

Elektorowicz, M., and Hatim, G., 2000, "Hydrophobic Organic Compound Removal from Clayey Soil due to Surfactant Enhanced Electrokinetic System", 53rd Canadian Geotechnical Conference, Montreal, Canada.

Elektorowicz, M., and Hatim, G., 1999, "Design of the Electrokinetic System to Supply Surfactant in Pilot Scale Condition", 2nd Symposium on Heavy Metals in the Environment and Electromigration Applied to Soil Remediation, Lyngby, Denmark, July 1999.

Elektorowicz, M., McCluren, N., 2000, Increase Efficiency of the Contaminated Site Management by Application of the Post Bioremediation Soil Improvement Using Electrokinetics, Toward Better Management of Waste and Contaminated Site in Australia-Pacific Region Adelaide, Australia, May, 2000.

Elektorowicz, M., Chifrina, R., Jahanbakhshi, P., Hatim, G., Lombardi, G., 1996a, "Phenol Removal from Groundwater Using Electrokinetic", International Conference on Municipal and Rural Water Supply and Water Quality, Vol. 2, pp. 105-116, Poznan, Poland.

Elektorowicz, M., Chifrina, R., Kozak, M., Hatim, G., 1996b, "The Behavior of Ion Exchange Membranes in the Process of Heavy Metals Removal from Contaminated soil", CSCE-4th Environmental Engineering Specialty Conference, Edmonton, Canada.

Elektorowicz, M., 1995, "Technical Requirements Related to the Electrokinetic Removal of Contaminants from Soil", ASCE/CSCE Joint Conference on Environmental Engineering, July 1995, Pittsburgh, U.S.A.

Elektorowicz, M., Chifrina, R., Konyukhov, B., 1995, "Enhanced Removal of Diesel Fuel from Soil by Electrokinetic Method", 30th Annual Central Canadian Symposium on Water Pollution Research, 1995, Burlington, ON.

Elektorowicz, M., Ju, L., Smaragiewicz, W. and Dube, L., 1999, "Behavior of Biosurfactant-producing Bacteria upon the Application of Electrokinetics. 27th Annual CSCE-ASCE, Environmental Engineering Conference, Regina, Saskatchewan, Canada.

Ellis, W. D., Payre, J. R. and McNabb, G. D., 1985, Treatment of Contaminated Soils with Aqueous Surfactant, EPA/600/2-85/129.

Environment Quebec, "Dix Ans de Restauration des Terrains Contamines", 1994, Envirodoq EN950098.

Eykholt, G. R., Daniel, D. E., 1994, "Impact of System Chemistry on Electroosmosis in Contaminated Soil", Geotechnical Engineering, Vol. 120, No.5, pp. 797-815.

Hamblin, W. K., 1992, Earth's Dynamic Systems, 6th ed., Maxwell Macmillian Canada, Toronto, Canada, pp. 202-206.

Hatim, G., 1999, "Design of the Surfactant Enhanced Electrokinetic System for Hydrocarbons Removal from Clayey Soils in Pilot Scale Conditions", M.Sc., thesis.

Hunter, R. J., 1982, "Zeta Potential of Colloid Science", Academic Press, London.

Johns, F. J., II and Nyer, E. K., 1996, "In-situ Treatment Technologies", In In-situ Treatment Technology, Nyer, E. K., Kidd, D. F., Palmer, P. I., CRC Press, Boca Raton, FL, pp. 289- 319.

Joseph, S. H., Wong, R., Hicks, E., Probst, R. F., 1997, "EDTA-Enhanced Electrokinetic of Metal-Contaminated Soils", Hazardous Materials, Vol. 55, pp. 61-79.

Ju Lin., Elektorowicz, M., 2000, In-situ Phenanthrene Removal Provoked by Electrokinetic Transport of on-site Produced Biosurfactant, CSCE 6th Conference on Environmental Engineering, May 2000, London, ON.

Kendorff, H. and Schnitzer, M., 1980, "Sorption of Metal Ions on Humic Acid, Geochim. Cosmochim. Acta, 44, 1701.

Kim, S. O., Moon, S. H., Kim, K. W., 2000, "Enhanced Electrokinetic Soil Remediation for Removal of Organic Contaminants", Environmental Technology, Vol. 21, No. 4, pp. 417-426.

Lageman, R., 1989, "Electrokinetic Reclamation: State of the Art", Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater, Geokinetics, Poortweg, the Netherlands.

Legret, M., Raimbault, G., "Etude de la modelisation des fonctions assurees par une decharge Caracterisation Hydrodynamique et etude du devenir des metaux lourds dans un dechet-type", Bulletin Liason Physique et Chimique, Vol. 175, pp. 77-91.

Maini, G., Sharman, A. K., Knowles, C. J., Jackman, S. A., 2000, "An Integrated Method Incorporating Sulfur-Oxidizing Bacteria and Electrokinetic to Enhance Removal of Copper from Contaminated Soil", Environmental Science and Technology, Vol. 34, No. 6, pp. 1081-1087.

Merian, P. D., 1991, Metals and their Compounds in the Environment: Occurrence. Analysis and Biological Relevance, VCH Publishing, New York, 1438 pages.

Miller, R. M., 1995, "Biosurfactant-Facilitated Remediation of Metal-Contaminated Soils", Environmental Health Perspectives, Vol. 103, pp. 59-62.

Mitchell, J. K., 1976, Fundamental of Soil Behavior, In: Series in Soil Engineering, Lambe, T. W. and Whitman, R. V. Ed., Berkeley, California.

- Moroi, Y., 1992, *Micelles Theoretical and Applied Aspects*, Plenum Press, New York.
- Myers, D., 1992, *Surfactant Science and Technology*, 2nd Edition, VCH Publishers, Inc. USA.
- Pamukcu, S, J. K. Wittle, 1992, "Electrokinetic Removal of Selected Heavy Metals from Soil", *Environmental Progress*, Vol. 11, No.3, pp. 241-250.
- Pamukcu, S., Filipova, I. And Wittle, J. K. 1995, "The Role of Electroosmosis in Transporting PAH Compounds in Contaminated Soils", *Electrochemical Society Proceeding*, Vol. 12, pp. 252-263.
- Petruzzelli, D. and Helfferich, F. G., 1993, "Migration and Fate of Pollutants in Soils and Subsoils", New York.
- Ram, N. M., Bass, D. H., Falotico, R., and Leahy, M., 1993, "A Decision Frame Work for Selecting Remediation Technologies at Hydrocarbon-Contaminated sites", *Soil Contamination*, Vol. 2, No. 2, pp. 167-189.
- Ruggiero, P., 1999, "Abiotic Transformation of Organic Xenobiotics in Soils: A Compounding Factor in the Assessment of Bioavailability", In *Bioavailability of Organic Xenobiotics in the Environment*, Baveye, Ph., Block, J. C., Goncharuk, V. V., 1999, Kluwer Publishers, Netherlands.
- Senseri, M. and Miano, T. M., 1995, "Environmental Impact of Soil Component Interactions. pp. 311-335.
- Taha, M. R., 1996, "Micellar Electrokinetic Remediation of TNT from Soil", Louisiana State University.
- US EPA, 1997, "Recent Development for In-situ Treatment of Metal Contaminated Soils", EPA-542-R-97-004.
- US EPA, 1998, "Innovative Site Remediation Technology: Thermal Desorption", EPA-542-B-97-008.
- US EPA, 1997, "Innovative Site Remediation Technology: Chemical Treatment", EPA-424-b-97-005.
- US EPA, 1997, "Best Management Practices (BMPs) for Soil Treatment Technologies: Suggested Operational Guidelines to Prevent Cross-media Transfer of Contaminants During Clean-up Activities", EPA-530-R-97-007.

Weisman, R. J., Falatko, S. M., Kuo, B. P., and Eby, E., 1994, "Effectiveness of Innovative Technologies for Treatment of Hazardous Soils", In Remediation of Petroleum Contaminated Soils, Roderts, E. R., 1998, Lewis Publishers, Boca Raton Boston London New York Washington D.C.

Wilson, S. C., and Jones, K. C., 1993, "Bioremediation of Soil Contaminated with Polynuclear Hydrocarbons", Environmental Pollution, Vol. 81, pp. 229-249.

Yeung, A. T., and Menon, R. M., 1996, "EDTA-Enhanced Electrokinetic Extraction of Lead", Geotechnical Engineering, Vol. 122, No.8, pp. 666-673.

Yong, R. N., Mohamed, A. M., Warkentin, B. P., 1992, Principles of Contaminant Transport in Soils, Elsevier Publishing, New York, 327 p.

APPENDIX

Photographs of All Experiments

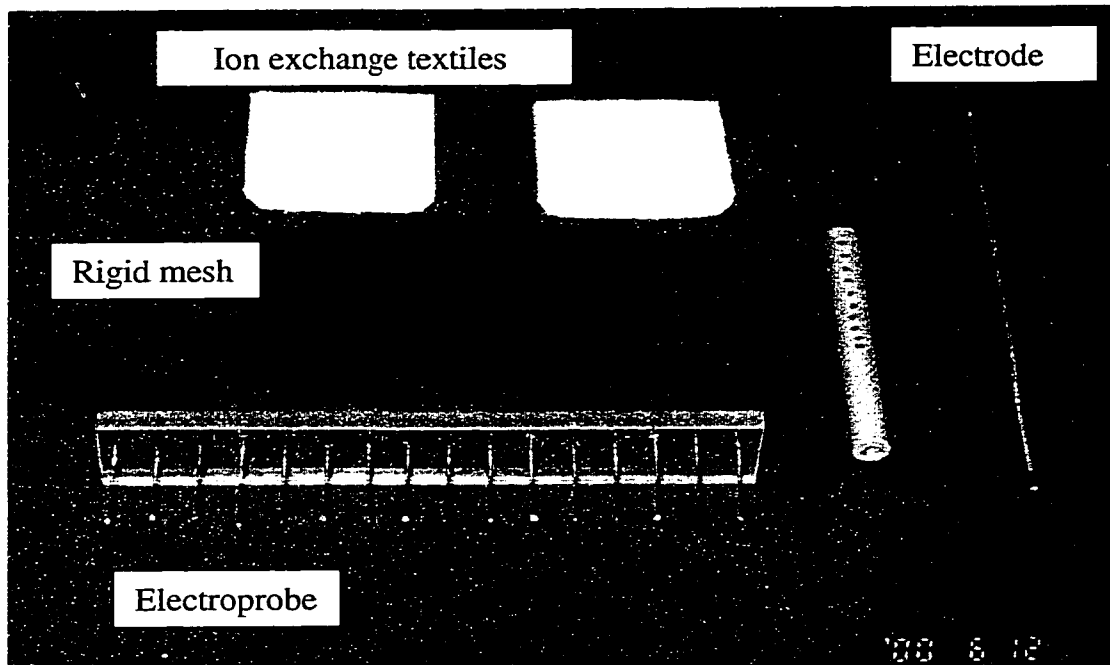


Figure A-1 Materials used to setup of the electrokinetic cell

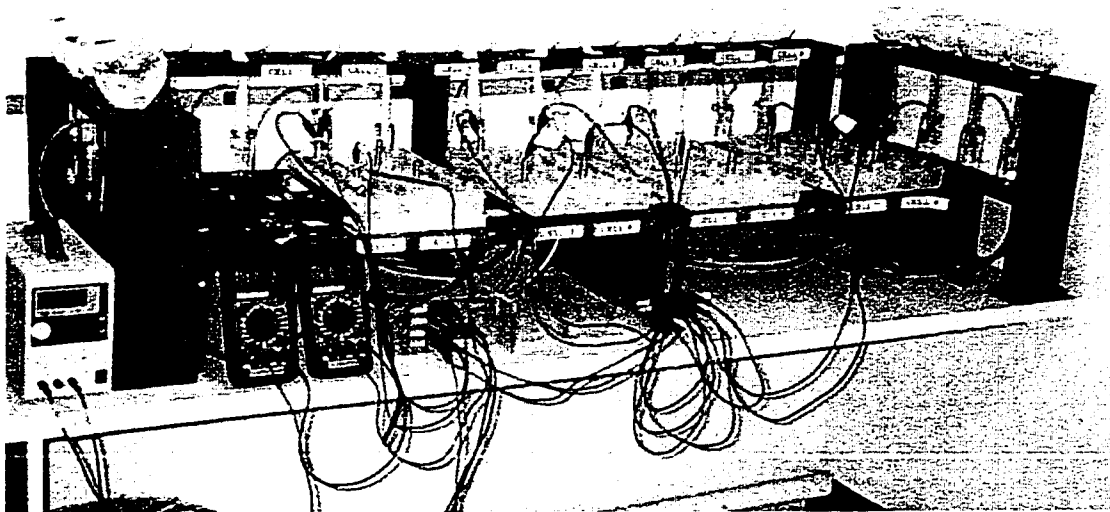


Figure A-2 Setup of all installations

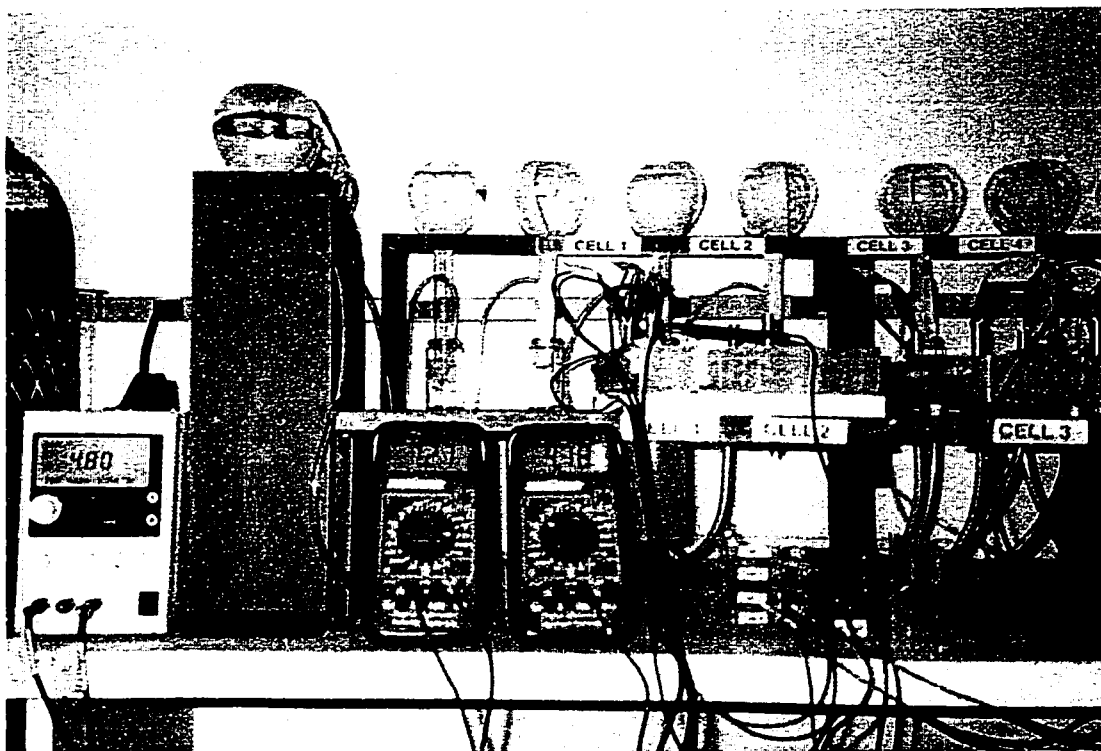


Figure A-3 Electrical system. DC power supply, multimeters and connections

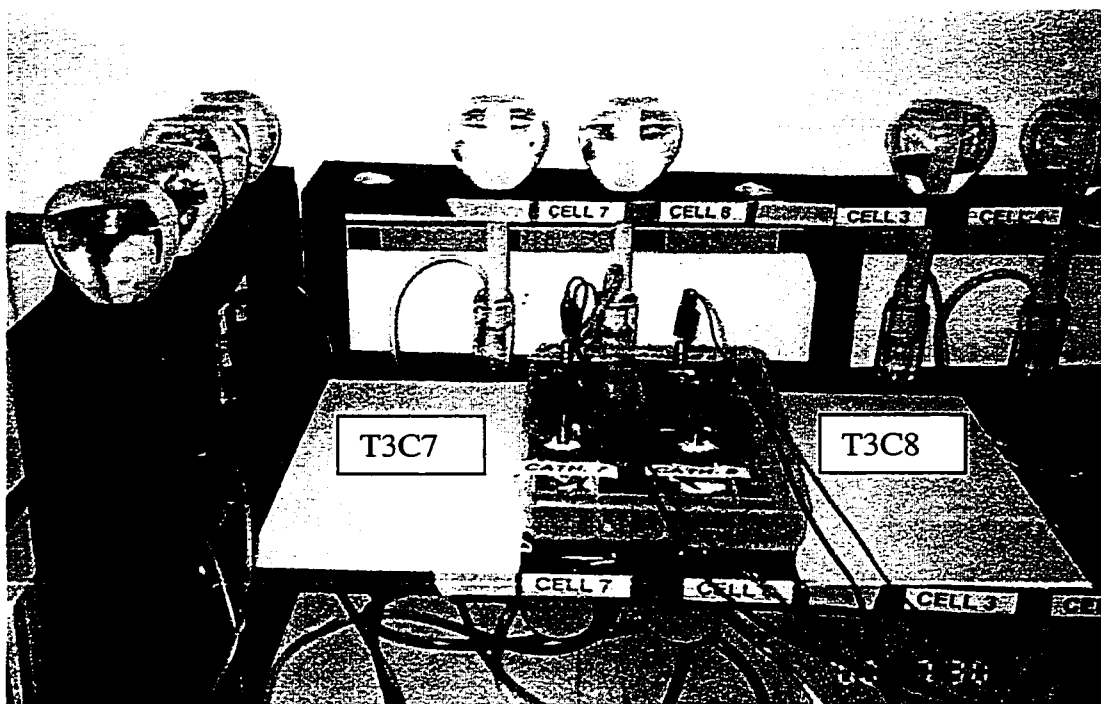


Figure A-4 Electrokinetic cells T3C7 and T3C8 after setup

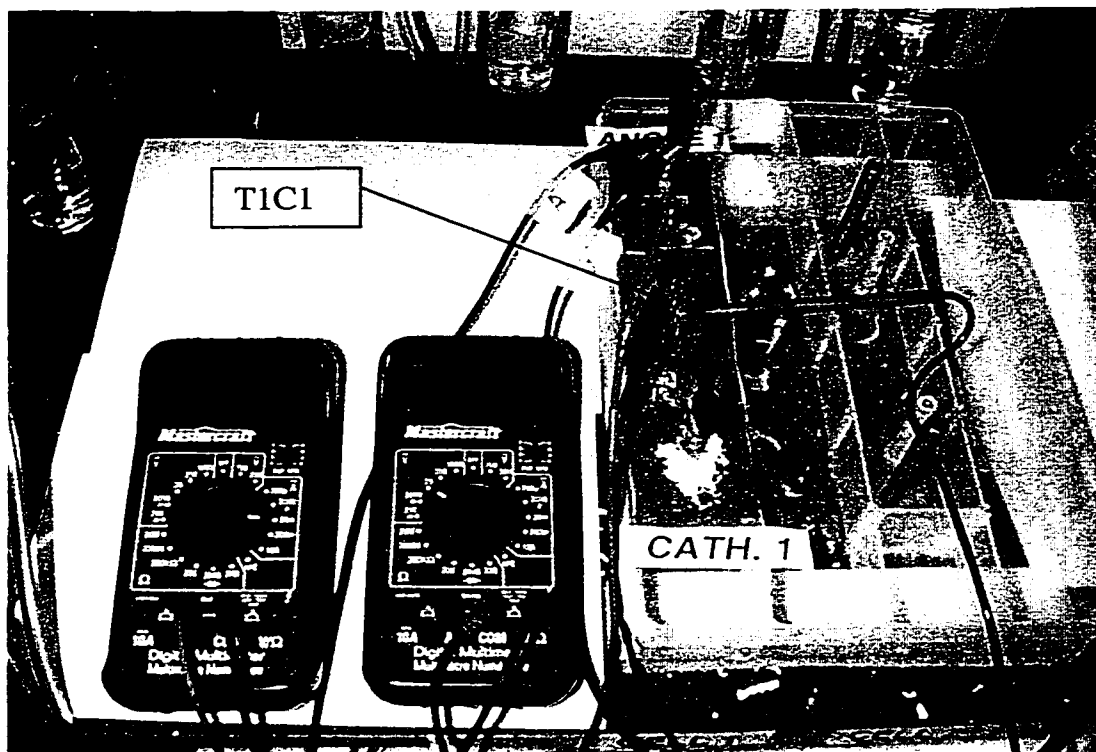


Figure A-5 Electrical measurement of cell T1C1

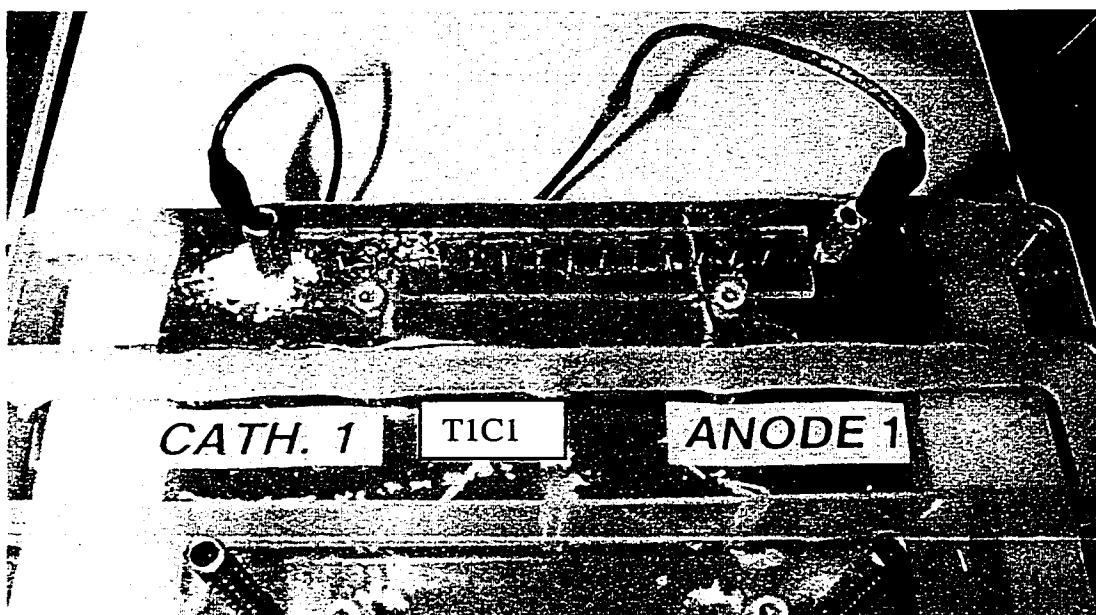


Figure A-6 Cell T1C1 during experimentation

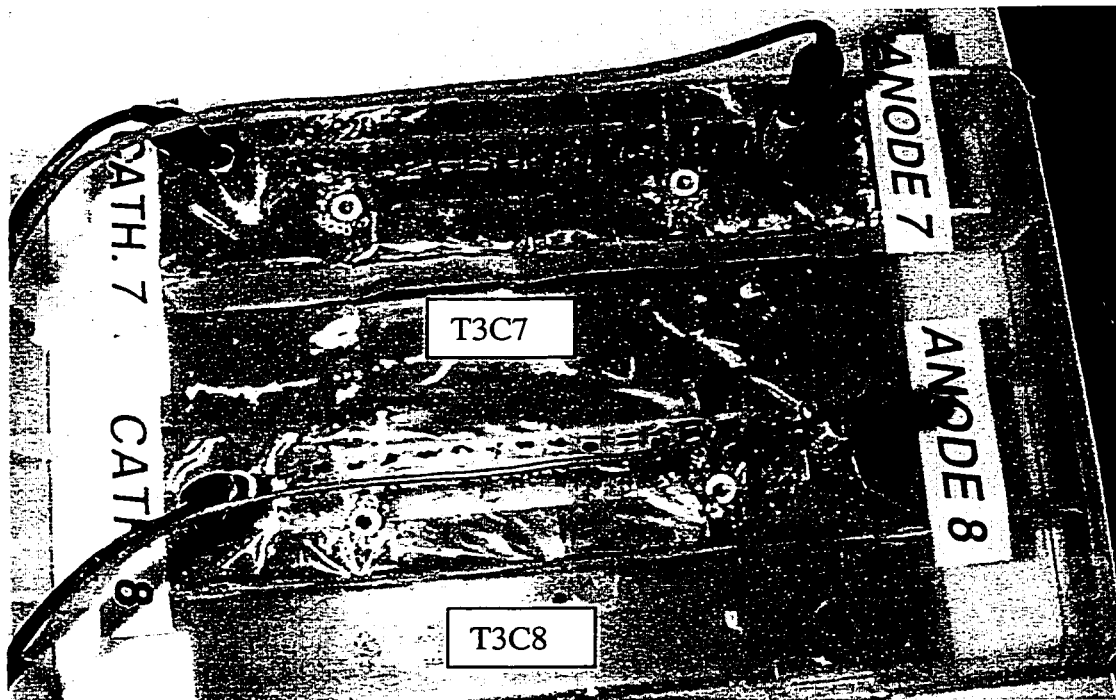


Figure A-7 Cells T3C7 and T3C8 during the experimentation

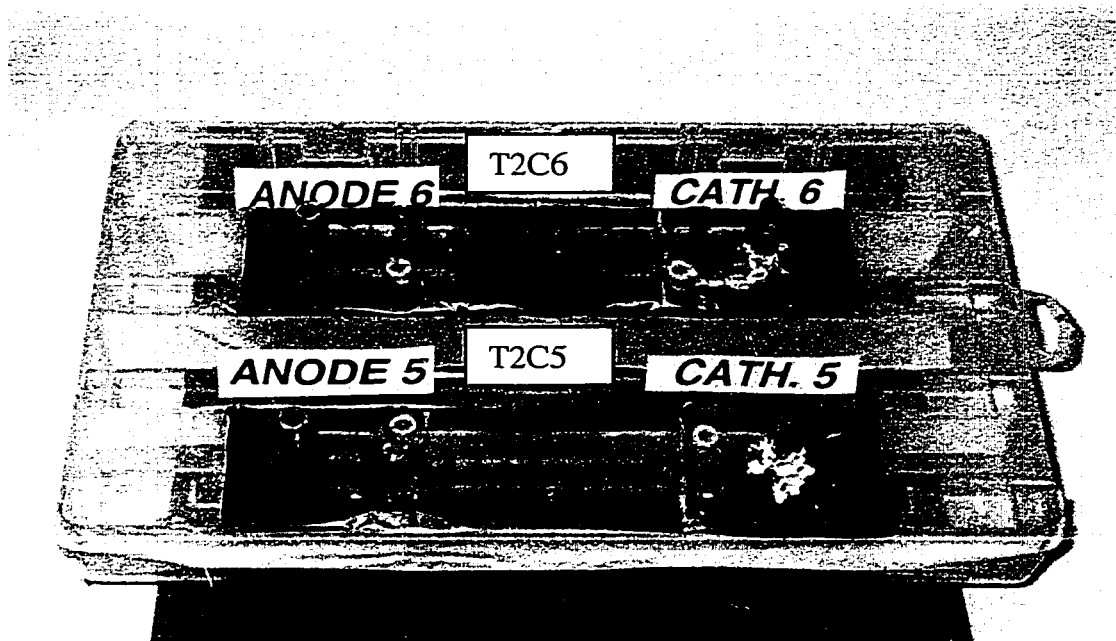


Figure A-8 Cells T2C5 and T2C6 after the experimentation

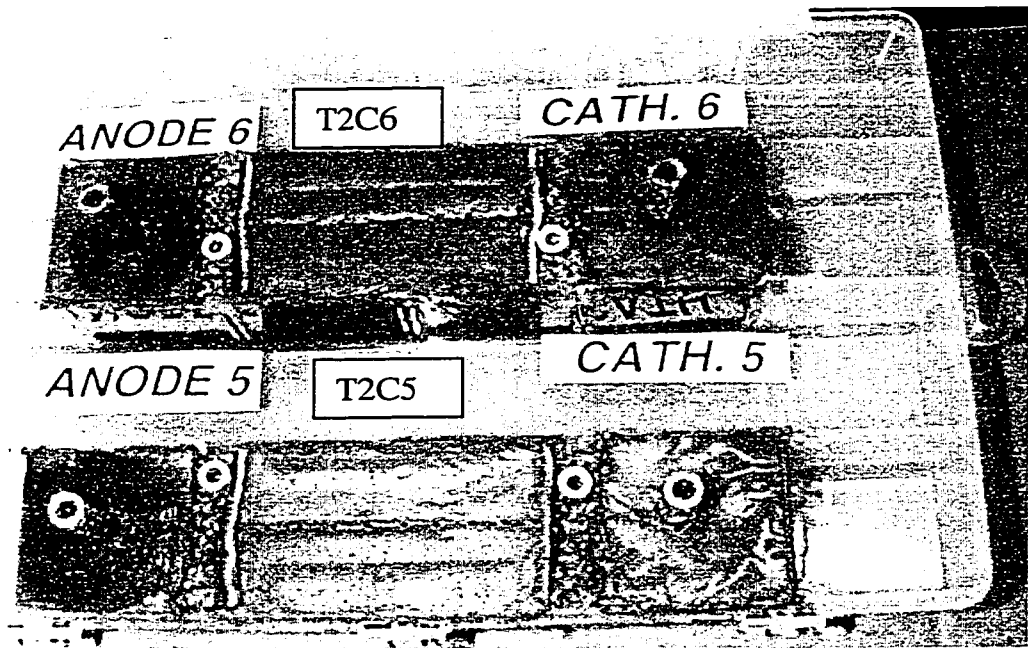


Figure A-9 Cells T2C5 and T2C6 ready for sampling

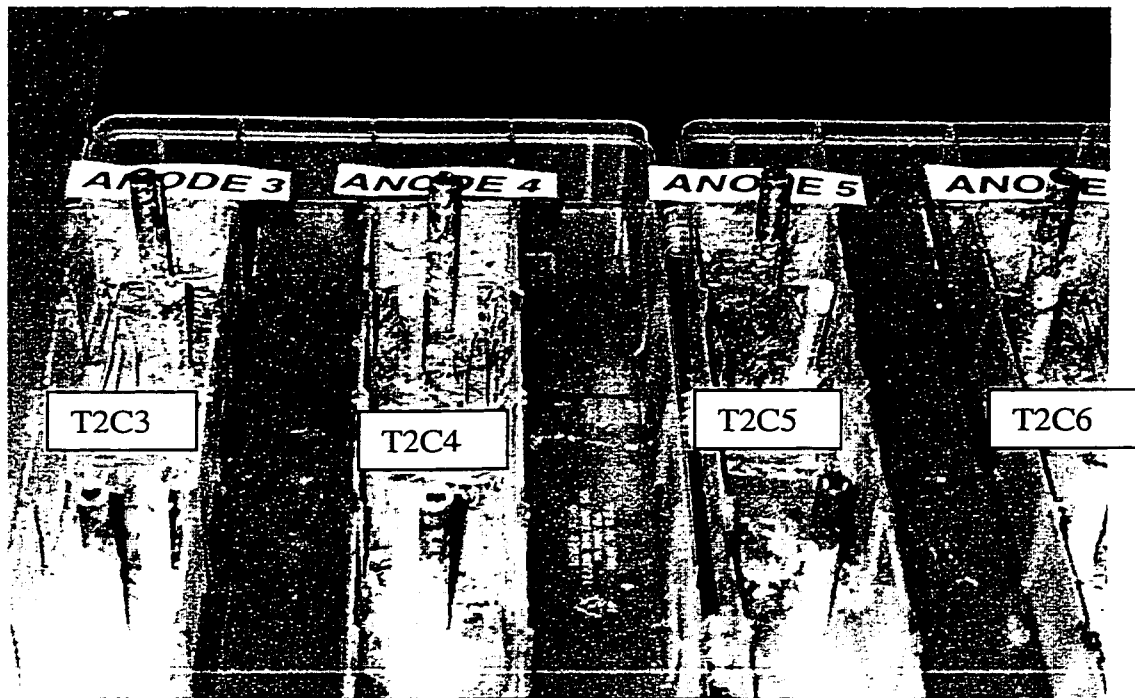


Figure A-10 Test series T2; after the experimentation