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ELECTROKINETIC TREATMENT OF CONTAMINATED SOILS, SLUDGES, AND LAGOONS

Final Report

Contract No. 02112406

By

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Prepared for

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ELECTROKINETIC TREATMENT OF CONTAMINATED SOILS, SLUDGES, AND LAGOONS

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PREFACE

Currently available technology is not adequate to assess environmental contamination at Department of Energy (DOE) sites, take permanent remedial action, and eliminate or minimize the environmental impact of future operations. Technical resources to address these shortcomings exist within the DOE community and the private sector, but the involvement of the private sector in attaining permanent and cost-effective solutions has been limited.

During 1990, on behalf of DOE's Office of Technology Development, Argonne National Laboratory (ANL) conducted a competitive procurement of research and development projects addressing soil remediation, groundwater remediation, site characterization, and contaminant containment. Fifteen contracts were negotiated in these areas.

This report documents work performed as part of the Private Sector Research and Development Program sponsored by the DOE's Office of Technology Development within the Environmental Restoration and Waste Management Program. The research and development work described herein was conducted under contract to ANL.

On behalf of DOE and ANL, I wish to thank the performing contractor and especially the report authors for their cooperation and their contribution to development of new processes for characterization and remediation of DOE's environmental problems. We anticipate that the R&D investment described here will be repaid many-fold in the application of better, faster, safer, and cheaper technologies.

Details of the procurement process and status reports for all 15 of the contractors performing under this program can be found in "Applied Research and Development Private Sector Accomplishments - Interim Report" (Report No. DOE/CH-9216) by Nicholas J. Beskid, Jas S. Devgun, Mitchell D. Erickson and Margaret M. Zielke.

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FOREWORD

The Appendices listed below have not been published due to their length. However, they are available upon request at the following address:

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ABSTRACT

The electrokinetic process is an emerging technology for *in-situ* soil decontamination, in which chemical species, both ionic and nonionic are transported to an electrode site in soil. These products are subsequently removed from the ground via collection systems engineered for each specific application. Electrokinetics refer to movement of water, ions and charged particles relative to one another under the action of an applied direct current electric field. In a porous compact matrix of surface charged particles such as soil, the ion containing pore fluid may be made to flow to collection sites under the applied field.

The work presented here describes the effort undertaken to investigate electrokinetically enhanced transport of soil contaminants in synthetic systems. These systems consisted of clay or clay-sand mixtures containing known concentration of a selected heavy metal salt solution or an organic compound. Metals, surrogate radio nuclides and organic compounds evaluated in the program were representative of those found at a majority of DOE sites. These compounds included the classes of metals (Cd, Hg, Pb, Ni, Zn), surrogate radio nuclides (Co, Cs, Sr, U), anions ($HAsO_4^{=}$, $Cr_2O_7^{=}$), hydrocarbons (chlorobenzene, hexachlorobenzene, phenol, trichloroethylene, acetic acid and acetone). Degree of removal of these metals from soil by the electrokinetic treatment process was assessed through the metal concentration profiles generated across the soil between the electrodes. The best removals, from about 85 to 95% were achieved at the anode side of the soil specimens. Transient pH change had an effect on the metal movement via transient creation of different metal species with different ionic mobilities, as well as changing of the surface characteristics of the soil medium.

The results of the laboratory study presented here show that electrokinetic enhancement of contaminant transport in soils is a viable technology to be developed into an effective *in-situ* remediation process for a wide range of applications.

EXECUTIVE SUMMARY

Introduction

In this project, the feasibility of electrokinetically enhancing the transport of specific heavy metals and organic contaminants in soils was investigated in the laboratory. Electrokinetically enhanced transport of contaminants is perhaps one of the most promising *in-situ* decontamination processes capable of removing heavy metals and organic contaminants from soils, sludges and lagoons. The significance of the technology appears to be in its projected low operation cost and its potential applicability to a wide range of contamination situations. It is also viewed by researchers and industry as a potential "problem solver" when other remedial technologies appear non-workable or fail to remediate a site. Present day urgency to develop innovative technologies to cleanup contaminated soils and ground water makes it necessary to look at the fundamental mechanisms associated with the electrokinetic technology and to develop it into a well-engineered and predictable process for field applications.

In this work, successful application of the technique was demonstrated on soil-contaminant mixtures in the laboratory. The results of the work presented here indicated that development of the technology for a wide range of applications in the field hinges upon the understanding of the *transient processes* during the application of direct current through soil. Some of these processes, such as net electroosmotic water flux and transient acid-base distributions, have been studied in the past and were confirmed in this study. The simultaneous interactions between different transient and physical processes that may take place in a complex system of soil, water and contaminant, when subjected to electrical field has been advanced by this program. These processes have been identified as the physical and chemical interactions between soil components and the contaminants; soil surface physico-chemistry and its variation with pore fluid chemistry; speciation and distribution of the contaminants.

In this work, the generated data base, which incorporated combinations of 5 soil types with 11 heavy metal elements and 6 organic compounds, confirmed that electrokinetic treatment of soils is a promising decontamination process that is capable of removing contaminants from clayey saturated soils. The degree of success of decontamination appeared to be parameter specific; more dependent on the type of the contaminant to be removed than the type of the medium being decontaminated. Those contaminants whose chemistry were least affected by the transient chemical and physical processes during electrokinetic treatment exhibited a significantly higher degree of removal than those that were affected. This trend was consistent despite the variations in soil type and properties. The contaminant levels selected in this program were typical of levels to be found at various DOE Sites. High and low concentrations were selected for a few of the soils.

This program has demonstrated in the laboratory the viability of the electrokinetic process to move "contamination" through soil types of permeability as low as 10^{-8} cm/s to a directed location and has identified conditions which have an impact on contaminant mobilization, and, subsequently, potential needs to be addressed in the field. The testing has clarified the need for site specific design and control of the treatment operation so that once the contaminant is mobilized, it is transported to a collection system in the most efficient manner. Chemical (pH control, complexing agents, etc.) and physical enhancement methods may be necessary in some situations to accomplish this goal. These situations are the ones when the contaminant chemistry (speciation, distribution), the oxidation/reduction state of the soil, and/or the adsorption and exchange capacity of the soil solids vary significantly with pH, ion type and concentration. Therefore, at a given site, it is important to acquire as much information as possible on the general state of the contaminants, such as their speciation, distribution and adsorption to the soil. This and other field information , such as soil type, water content and its chemistry and conductivity, are essential for successful site specific engineering of this treatment process.

Technology Description

Electrokinetics is the movement of water (electroosmosis), ions and polar molecules (electromigration) and charged solid particles (electrophoresis) relative to one another between two electrodes under the action of an applied direct current (voltage) electric field. When direct current is passed through soil, the aqueous phase will move toward the negative electrode (cathode) by the phenomenon of electroosmosis. In addition, ion migration takes place; cations (+ charge) migrate to the cathode while anions (- charge) migrate toward the anode. These processes, referred to as electrokinetic processes, can be used to remediate contaminated soil without excavation.

The main objective of the Department of Energy (DOE) project was to investigate the feasibility of the decontamination of soil by means of electrokinetic processes. The project has increased the basic understanding of the components of the electrokinetic phenomena and identified critical parameters to be considered in the subsequent development of large-scale, *in-situ* soil remediation programs. The method is expected to be significantly more efficient and cost effective than other *in-situ* methods of soil decontamination.

The investigation was composed of two phases of laboratory work. In the first phase, short term (24 to 48 hour) electrokinetic tests were performed on samples and the migratory trend of each contaminant was observed. A matrix of organic and inorganic compounds and various soil types constituted the materials for producing artificially contaminated soil systems in the laboratory. Metals, surrogate radio nuclides and organic compounds evaluated in the program were representative of those found at a majority of DOE sites. These compounds included the classes of metals (Cd, Hg, Pb, Ni, Zn) , surrogate radio nuclides (Co, Cs, Sr, U), anions ($HAsO_4^=$, $Cr_2O_7^=$), hydrocarbons (chlorobenzene, hexachlorobenzene, phenol, trichloroethylene, acetic acid and acetone). Five soil types were studied: kaolinite clay, Na-montmorillonite clay, sand with 10% Na-montmorillonite, kaolinite clay with simulated ground water, and kaolinite clay with humic substance solution. The minimum test duration was 24 hours. In order to investigate the time dependent transient behavior of the transport, a number of the replicate tests were extended for longer periods (up to 48 hours). During each test, the systems were monitored for voltage, current, and inflow and outflow of liquid through the soil. After the test, the soil samples were analyzed for metal and organic contaminant concentration profiles and pH profiles across the length of the sample in order to assess the extent of the decontamination. This phase resulted in the development of a large data base by which the efficiency of the electrokinetic removal of 11 metal species and 6 organic compounds, that are of interest to DOE, can be readily assessed. This phase of the research provides an answer to the question "Does a particular contaminant respond to electrokinetically enhanced migration?". The information generated is detailed yet simple enough to assess and compare the efficiencies of removal for different metal and organic species.

In the second phase of the work, the electrokinetic process was augmented by physical and chemical enhancement methods. The physical enhancement methods were the application of heat and high frequency, low amplitude seismic waves to the contaminated systems. The chemical enhancement techniques constituted pH control at the electrode sites and injection of complexing agents (ethylenediamine and sodium dodecylbenzene sulfonate) into the contaminated systems. For all of these enhancement methods, the net flow of water per mole of electrons transferred increased substantially.

The second phase of the work also involved development of an improved analytical model of contaminant transport in soils. In this modeling effort, variable voltage gradients obtained from long term testing of strontium and short term testing of acetic acid contaminated specimens were used. The model predicted plug flow for either of the contaminants. Laboratory data for strontium clearly deviated from the plug flow prediction of the model. The improved algorithm results agreed well with strontium distribution in soil only after 4 pore volumes of water flow through soil. The model predicted slower rate of removal for strontium and faster rate of removal for acetic acid than actually were observed in the laboratory tests.

Results from the tests demonstrated that electrokinetics can be an effective method of transporting metals and poorly adsorbed organic compounds in soils. Electroosmotic flow could be induced and sustained in all soil types with all of the contaminants investigated. Two mechanisms for the movement of the contaminants are predicted. For constituents of ionic nature, transport takes place by ion migration. For nonionic species, such as organic compounds, the mobilization is by electroosmotic transport. In ion migration, electrochemical behavior of the species forced to migrate plays a predominant role. Electroosmotic flushing is dependent on soil mineralogy. The effectiveness of the process demonstrated that up to 99% of initial concentrations of metals can be removed from soil. In this process the pH and metal type was found to influence the removal rather than the electroosmotic flow. For instance, when high concentration zinc, which exists as both anionic and cationic species, contaminated soils were tested, despite very little net flow of water through soil, significant removal of zinc was achieved at either end of the soil. In general, hydronium ions produced at the anode due to electrolysis of water migrated through the soil and enhanced metal transport by dissolution and exchange reactions. The basic conditions at the cathode, however, caused most of the metals to precipitate in the soil near the cathode. pH adjustment at the cathode compartment appeared to minimize precipitation and to enhance the removal of some, such as lead. For organic contaminated soils, when the organic compounds are undissociated and poorly adsorbed onto soil, they are transported by electroosmosic water flow. The approximate time for electroosmotic removal can then be estimated based on tracer analysis of these organic compounds in a given soil of specific electroosmotic flow rate. This was demonstrated in kaolinite clay using o-nitrophenol as a tracer substance.

Enhancement methods improved removal efficiencies for some of the contaminants tested. The three metals tested (Co, Pb, Hg) responded well to pH control, thus removal efficiency was increased. The use of complexing agent, ethylenediamine (EDA), appeared to decrease electrolytic migration thus promoting plug flow type transport of the metals. This is especially beneficial for metals with pH dependent speciation and solubility. The results of the surfactant enhancement for organic contaminant transport indicated the need for further study in this area. Four organic compounds were studied: chlorobenzene, hexachlorobenzene, phenol and trichloroethylene (TCE) in kaolinite soil systems. In the chlorobenzene and hexachlorobenzene soil systems, the addition of the surfactant (sodium dodecylbenzene sulfonate) appeared to increase the organic contaminant mobility towards the cathode chamber of the cell. In the trichloroethylene and phenol soil systems, organic contaminant mobility was less affected by the addition of this surfactant.

The application of thermal enhancement was investigated on blank and TCE-contaminated samples in the kaolinite soil system. The results showed significant increase in the electroosmotic water flow and current efficiency. The detected organic contaminant removal efficiency was promising. Low amplitude, high-frequency shear waves were also applied on contaminated systems. Ongoing experiments demonstrate the need for further study to determine the best possible combination of amplitude, frequency and duration of shear wave application for improved results. The range of frequencies (1500 to 4000 Hz) and duration (20 to 48 hours) of shear wave application in this part of the work showed no appreciable enhancement.

The results with mixed waste soils showed consistent and uniform reduction of the 4 metals and 3 organic contaminants investigated with increasing duration of electrokinetic treatment. This occurrence was unlike the concentration accumulation of the metals at the cathode end of the single contaminant and clay systems. The difference was attributed to the high buffering capacity of the soil matrix used in the mixed waste case which helped to maintain a uniform neutral pH throughout the treatment up to 72 hours.

1.0 INTRODUCTION

1.1 Technology Scope

1.1.1 Purpose and Objectives Accomplished

The main objective of this work was to investigate *electrokinetically enhanced contaminant transport* in soils with specific attention given to soil contaminants that are of interest to the Department of Energy (DOE), under controlled conditions. The majority of the investigation hinged upon developing a basic understanding of the potential response of these selected metal and organic species to electrokinetic treatment in different soils. A specific sub task of the work was to augment electrokinetically enhanced transport with other in-situ methods to increase the efficiency of decontamination, such as application of heat, shear waves, and complexing agents to the contaminated soil, and maintaining an adjusted pH at the electrode sites. Another sub task was to attempt to modify an existing electrokinetic transport model with respect to time and space dependent electric field data obtained from long term tests to demonstrate improvement in the prediction of process efficiency.

Laboratory studies that addressed fundamental aspects of the process can help to improve the technology, and the predictions of decontamination for complex site specific situations. The work presented here undertook such a task. The results of this task should bring about better engineered electrokinetic systems which can be applied to soil decontamination at sites of interest to the DOE.

1.1.2 General Background

Electrokinetic decontamination invokes three processes: electroosmosis, electrophoresis and electrolytic migration of ionic or polar species. Electroosmosis produces rapid flow of water in low permeability soils and probably contributes significantly to the decontamination process in clay soils (Figure 1.1.2.1). Electrophoresis is the migration of the charged colloids in the soil-liquid mixture. In a compact system, electrophoresis should be of less significance since the solid phase is restrained from movement. In some cases, however, electrophoresis may play a major role in decontamination if the migrating colloids contain the chemical species of interest. Electrolytic migration is the movement of ionic species present in the pore fluid under the influence of an electric field as well as the migration of H^+ (produced at anode) and OH^- (produced at cathode). Electrolytic migration is responsible for conducting the major portion of the current in a soil-water system. As ions migrate toward an electrode, they can drag layers of water molecules, which may be of significant quantity if the ionic concentration is high. In electrolytic migration, the ionic velocity of each ion under the electric field plays an important role in the rate of extraction. Other reactions inherent to electrokinetics are ionic diffusion, electrolysis of water in soil pores and electrolytic reactions at the electrode sites. These reactions may or may not play significant roles in decontamination depending on the specific field process implemented and the process control.

Extraction of contaminants by the electrokinetic method is based on the assumption that the contaminants are in the liquid phase in the soil pores and they are not strongly adsorbed to soil. The flux of water produced by electroosmosis should be able to move both non-ionic and ionic species through the soil towards the cathode. This transport is perhaps best achieved when the state of the contaminant (dissolved, suspended, emulsified, etc.) is suited for the flowing water to carry it through the tight pores of soil without causing accumulation of an immovable plug of concentrated substance in the soil before reaching the cathode. Polar organic molecules should orient themselves in the direction of the electric field, and the movement towards one of the electrode sites is dependent upon their polarity, mobility and the surface charge characteristics of the soil medium. Removal of cationic species occurs due to the combined effect of electroosmotic flow of water and the electrolytic migration of the cation toward the cathode electrode. The movement of anionic species is mostly governed by electromigration. The relative magnitude of contribution

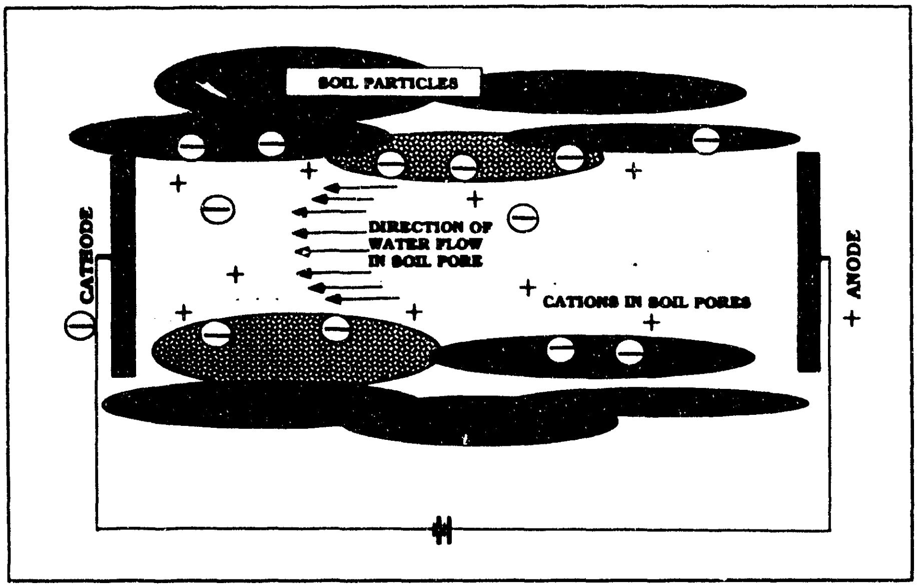

Figure 1.1.2.1 Schematic Representation of Electrokinetic Process in Soil

of either process (electromigration and electroosmosis) to cation movement remains unclear. Recent findings (Khan, 1991, and Khan et al., 1993) indicate that at low concentrations of the ionic species, electroosmotic flow may contribute a significant percentage, if not all, to the overall decontamination process. At high concentrations of the ionic species, electrolytic migration, electrochemical reactions, and auxiliary water movement by hydraulic drag exerted on the hydrated ions (cations and anions) may play more important roles than electroosmosis in the decontamination process. Earlier experimental observations by others (Probstein and Renaud, 1986; Liang, 1977; Gray and Mitchell, 1967) support this conclusion. These investigators have shown significantly higher current efficiencies (volume of flow per quantity of electricity) at lower ionic or organic concentrations in the pore fluid. Others (Lockhart, 1983) have argued that current efficiencies increase with increased ionic concentration in clay suspensions. This observation is valid for colloidal suspensions in which *true electroosmotic flow* is probably not the predominant mechanism of water transport, but is the hydraulic drag caused by the migrating ions. Lockhart (1983) calculated a maximum dewatering current efficiency of 5.6 ml/mA.hr in a clay suspension of 37% solids. This value corresponds to approximately 8300 moles of water per Faraday of electricity, which far exceeds the quantity of water that can be transported by hydration of any cation. On the basis of the Donnan theory, a high water to cation concentration ratio promotes higher current efficiency. Therefore, in slurried systems, increased transport of water with increased cation concentration should hold true provided that the water concentration remains constant throughout the process. In a compact system of soil, the rate of frictional dragging of water by ionic species through the pores is limited by the size of the pores and pore throats. Therefore the ions may move as fast as they would in a loose suspension, however water will not. Under these conditions, increased ionic concentration at constant water content should decrease current efficiency according to the Donnan concept and observations made by Gray and Mitchell (1967), and by the principal investigators of this project.

One of the important aspects of electrokinetics in soil-water systems is the transient migration of an acid front from the anode to the cathode during treatment (Acar et al, 1989, 1990; Shapiro et al. 1989). When water decomposes , it is reduced to hydrogen gas at the cathode and oxidized to oxygen gas at the anode. This process results in progressive reduction of pH at the anode and increase of pH at the cathode. Subsequently the hydronium ions produced at the anode migrate toward the cathode and the hydroxide ions produced at the cathode migrate toward the anode. Since the ionic velocity of hydrogen ion is about twice as high as that of the hydroxide ion, H^+ would move faster into the soil. This movement would further be enhanced by the electroosmotic flow of water toward the cathode. Acid front migration is beneficial for metal extraction from soils, provided that soil's natural buffer capacity is sufficiently low. The transient and spatial variation of pH has further implications that aid in metal extraction. Soil surface properties such as cation exchange capacity and surface potential are highly pH dependent, especially at acidic pH levels. Furthermore, speciation (anions, cations, and their valance states) and solubility of contaminants are often pH dependent. The distribution of these contaminants would be transient and spatially varied with pH. In addition to the transient nature of pH, the soil redox potential would vary both spatially and in time during electrokinetic treatment. The pH-redox conditions at a point at any time during the treatment would determine the solubility and speciation of most heavy metal constituents. These conditions can limit or enhance the movement of the metals to an electrode site.

1.1.3 Application of Electrokinetics to Soil Decontamination

The first recorded use of electrokinetics applied to dewatering soils and sludges in the field was by Casagrande in 1949. Work and subsequent research in the electrokinetic decontamination of soils has accelerated in recent years following the detection of high concentrations of metals and organics in electroosmotically drained water of a dredged sludge by Segall and co-workers (1980). Other field work (Lageman (1989) and Banarjee and co-workers (1988)) has been conducted with reasonable success for heavy metal transport.

Hamnett (1980) performed laboratory studies on electrically induced movement of ions in sand. In evaluating the electrolytic migration of ions of different salts, it was found that smaller ions (e.g. Na) were more mobile than larger ions (e.g. K, Cu, Ni). Mitchell (1986) conducted work on the use of electrokinetics to create barriers around contaminated zones in soil. Acar et al. (1989, 1991) and Hamed et al. (1991) showed that the migration of an acid front from the anode toward the cathode region of soil is significant in the removal of heavy metals from clay soils. They also developed an analytical model for electrokinetics to predict the transient migration of acid front in soil which agreed well with their experimental data. Shapiro and co-workers (1989) also showed that analytical treatment and an associated model agreed well with their experimental results of acetic acid removal from soil, during which about 94% of the acetic acid was reported to remove with 1.2 pore volumes of flow through kaolinite soil. Pamukcu et al.(1991) presented the effects of speciation and precipitation on the efficiency of electrokinetic transport of zinc through soil. Bruell et al. (1992) demonstrated in the laboratory the effective removal of gasoline-range hydrocarbons and trichloroethylene from kaolinite soil with 3 to 5 pore volumes of electroosmotic water flow in the soil.

1.1.4 Development of Electrokinetic Concepts in Soil

The electrokinetic phenomenon was first discovered by Reuss in 1808. It was first treated analytically by Helmholtz in 1879, and later modified by Pellat in 1904, and Smoluchowski in 1921. This theory is widely known as the Helmholtz-Smoluchowski (H-S) theory which relates electroosmotic velocity, v_{eo} , of a fluid of certain viscosity ν, and dielectric constant θ, through a surface charged porous medium of zeta potential ζ, and length L , under an electric field E.

$$v_{eo} = \{\varepsilon_0 \theta \zeta / \nu\}\ E \,/\, L \qquad (1.1)$$

where, ε_0= permitivity in free space

The ζ in equation (1.1) varies with pH and ionic concentration of the pore fluid, and as such, is not a constant during electrokinetic treatment. Similarly, the potential gradient E/L is not constant in time and space. The theoretical computation of electroosmotic water transport, by this formula, does not agree well with experimental observations. Overbeek and Wijga (1946) showed that the generalized electroosmotic equation for a porous plug, as predicted by the H-S theory, does not apply when the plug has considerable surface conductance, as occurs in clays and colloids.

A notable approach to electrokinetic processes in porous medium was made by Spiegler (1958). He considered the interactions of the mobile components of soil (water molecules and ions) and the frictional interactions of these components with the pore walls. The 'true electroosmotic' flow was expressed as the difference between the measured water transport and the ion hydration in units of moles per Faraday. This quantity was suggested to be directly proportional to the concentration of free water in soil pores and indirectly proportional to the concentration of mobile counterions in this soil. This theory agrees with the phenomenon of water transport in the opposite direction by the electrolytic migration of anions. Therefore, at any time during electrokinetic treatment, if the concentration of anionic species in the free water exceeds the cationic species significantly, the opposite flow may retard the net flow toward the cathode.

Gray and Mitchell (1967) showed experimentally that though the electroosmotic flow increases with an increasing water content of most soils, the flow decreases with an increasing electrolyte concentration of the pore fluid. This electrolyte concentration effect is more evident in clays with high anion retention capacity such as kaolinite, as opposed to montmorillonite (Bohn, et al., 1985). Therefore higher electroosmotic flows are observed in kaolinite clays at the same concentration of dilute solutions of electrolytes. This observation is consistent with the prediction of electroosmotic transport according to the Donnan concept.

Khan (1991) and Khan and co-workers (1993) proposed a modified theory of electroosmotic velocity of water, v_{eo}, through soil. In this theory, the 'true electroosmotic' flow is directly proportional to the current carried by the charged solid surfaces in soil. In this approach, the zeta potential used in the Helmholtz-Smoluchowski theory is replaced by a constant surface potential, Ψ_d, which is invariable with ionic concentration and pH of the pore fluid. Therefore,

$$v_{eo} = \{\varepsilon_0 \theta \, \Psi_d / \nu \} \, I_s \, R_s / L \qquad (1.2)$$

where, R_s = surface resistance of soil
I_s = surface current of soil

Equation (1.2) further reduces to the following with $\Psi_d R_s$ shown to remain fairly constant for a wide range of electrolyte concentrations of the pore fluid:

$$v_{eo} = K \, I_s \qquad (1.3)$$

where, $K = \{\varepsilon_0 \theta \Psi_d / \nu \} \, R_s / L$ = constant

This theory agrees with Gray and Mitchell's (1967) observations and the much earlier observations of Napier (1846), who stated that "the measurable endosmose (electroosmosis) seems to be greater when the current has greatest difficulty to pass through, and when the decomposition (of water) was least". This follows that the *true electroosmotic flow* is large when the ratio of the surface current to the electrolytic current (carried by the ions in the pore fluid) is large, due to the reduced concentration of ions in the pore fluid. The modified theory basically emphasizes that the surface conductivity of the porous compact medium is the most essential precondition for electroosmotic flow.

1.2 Technology Programmatic Requirements

The technology being developed under the Department of Energy (DOE) project supports the DOE mission to find new and more efficient methods for the *in-situ* remediation of contaminated soils. The program, although tailored toward gathering of information on contaminants found at DOE sites, including surrogate radionuclides (non radioactive isotopes), heavy metals, plating wastes, and organics, are the same contaminants which are often found in the contaminated sites owned by the private sector.

Electrokinetics is a technique that can be thought of as an enhancement process for many applications of *in-situ* treatments. In order to be effective, as with other *in-situ* processes, a well-characterized site is desirable. Equipment, other than the specialized power equipment (electrodes), can be fabricated from readily available supplies. Water and utility distribution power is required. Since an aqueous solution may be produced at collection wells, post treatment of the aqueous solution will be required and disposal of by products will be necessary. In doing so, conventional and non conventional approaches may be considered.

The information developed in this research is expected to be useful in the integrated demonstration and/or site specific programs. The Integrated Demonstration Programs where the technology could easily be applied include plutonium and uranium in soils, VOCs in arid soils, and chromate at mixed waste landfills. The process is also applicable to the Integrated Programs, such as In-situ Remediation and Innovative Technologies. For example, the process is perceived to have high potential for application as an *in-situ* technology for use in removing strontium at Oak Ridge Laboratories, TN; containing contaminant transport at Lawrence Livermore Laboratories, Ca; and groundwater and soil cleanup at Rocky Flats, Co. The development of the new technology by the private and public sectors is well served by the DOE program which specifically addresses DOE needs, yet provides meaningful information for use in private sector. The Integrated Demonstrations provide a vehicle not readily available to the public sector under current EPA regulations.

2.0 METHODOLOGY AND APPROACH

Standard equipment was not available to conduct the electrokinetic tests on compacted soil specimens. A new apparatus was developed to simulate the electrokinetic phenomena in a homogeneous specimen of soil and measure the process parameters. In order to prepare replicate specimens of soil, a consolidation apparatus was also developed to compact well mixed soil slurries. The following sections present the description and operation of the test equipment and specifics of the testing program.

2.1 Facilities and Equipment

2.1.1 Electrokinetic Test Apparatus

The apparatus consisted of two parts: an electrokinetic (E-K) cell and a flow control panel. A schematic diagram of the electrokinetic apparatus assembly is given in Figure 2.1.1.1. (Detailed diagrams are given in Appendix A, Plates A1.1 and A1.2). The electrokinetic test apparatus used in this project was developed based on the following considerations:

i) electrode reactions will take place and hence electrodes should be isolated from the soil;
ii) electrode reactions will produce gas at the electrode surfaces and a convenient method for gas ventilation has to be provided to accurately measure the water transport;
iii) electrode surface has to be larger than the soil cross sectional area so that a low current density at the electrodes will produce a relatively large current density in the soil;
iv) ports for extracting inflow and outflow fluid samples have to be provided for the analysis and monitoring process.

Based on these considerations, the electrode surface area was selected to be six times larger than the soil sample cross-sectional area. Clear acrylic plastic was used for all cell parts to provide visibility and also detect gas generation at the electrode sites, the soil-water interface and possibly in the soil. The electrodes are made of high grade graphite rods to minimize electrode deterioration. The electrokinetic cell has the following components:

Sample tube: The sample tube has a ID of 3.55 cm and a length of 7.62 cm and is made of clear acrylic tube. The tube accommodates three auxiliary graphite electrodes (1 mm diameter), separated at equal distance along one side, through which voltage can be measured during experiments. The tube is assembled to the electrode chambers with O-rings placed inside the housings cut on the inner walls (facing the sample tube) of the chambers.

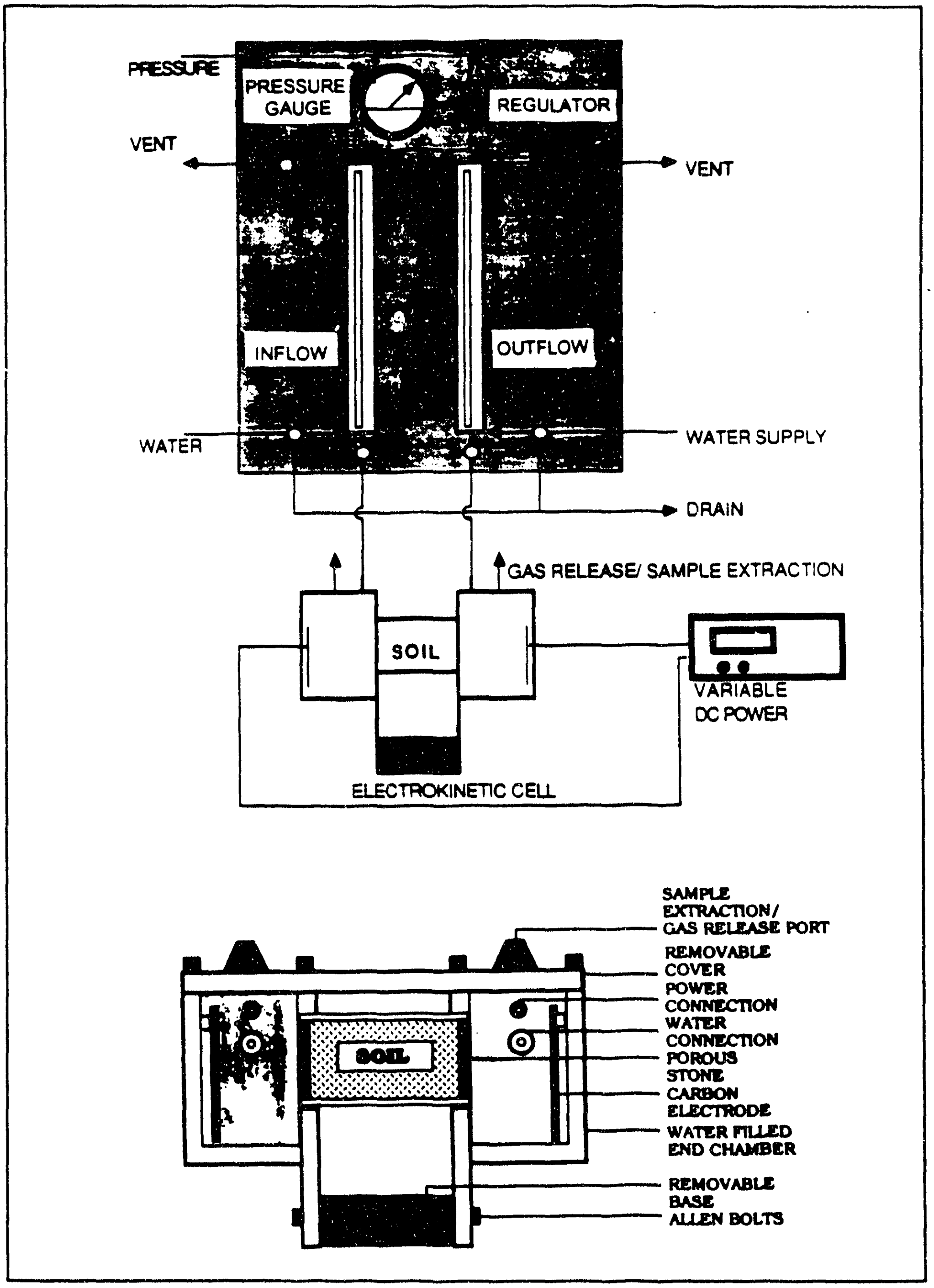

Figure 2.1.1.1 Schematic Diagram of the Electrokinetic Apparatus and Control Panel

Porous stones: Carborandum porous stones are placed at each end of the sample tube to hold the soil sample in place during the experiments. The porous stones have a permeability of 10^{-3} cm/sec, which is highly porous compared to the clay soils tested which have hydraulic permeabilities ranging from 10^{-6} to 10^{-8} cm/sec. Therefore, they do not influence the rate of flow through soil. The stones are washed with dilute nitric acid to ensure removal of metal impurities and particles which might clog the stone or influence the results of the chemical analyses. They are then boiled in distilled water before each usage.

Electrode chambers: These chambers are approximately 130 cm^3 in volume. They house the electrodes at each end of the soil sample tube. The end plates are removable for filling and emptying these chambers of fluid. This feature also facilitates cleaning of the chambers and the electrodes after each test run. Teflon membrane gaskets situated at these ends provide a water tight seal.
Electrodes: Electrode assemblies with a surface area of 22.6 cm^2 facing the soil specimen were constructed of graphite rods with a 0.635 cm diameter held together with conductive adhesive. The assembly's connecting rod is flush with the outer surface of the back wall. An electric socket is placed through the center of the exposed rod and fixed in place with carbon conductive epoxy glue. These connections are wired to a variable DC power source.
Fluid connections: Teflon or stainless steel quick-connections are provided on the bottom of the back wall of the electrode chambers. These outlet or inlets are then connected to volume measuring tubes and pumped via Teflon tubing. The advantage of the quick connections is that they close the connection upon detachment, which allows the electrokinetic (E-K) cell to be detached from the control panel while the electrode chambers are still charged with fluid.
Gas expulsion or sample extraction/injection ports: These ports are pressure valves provided on the cover plate over each electrode chamber. These valves have metal surfaces which are coated to control any deterioration by electrochemical reactions or metal ion deposition on them. Sample extractions or fluid injections are accomplished using a volumetric syringe which allows for accurate control of quantities of fluids.
Burettes: Glass burettes with a capacity of 25 cc are used to measure inflow, normally at the anode (positive electrode) chamber, and outflow, normally at the cathode (negative electrode) chamber to an accuracy of 0.1 cc.
Vent-pressure valves: Vented pressure valves exist at the top of each burette to provide gas expulsion.

Power Supply: Dedicated electrical units for each E-K cell consist of variable direct current (DC) power supply capable of applying either constant voltage (0 to 30 volt) , or constant current (0 to 1500 mA). These units also contain analog meters for measuring voltage and current. Detailed operating manuals of these units are provided in Appendix B2.1.

2.1.2 Consolidation Apparatus

A schematic diagram of the consolidation apparatus is shown in Appendix A, Plate A1.3. A detailed explanation of the operation of the unit are reported elsewhere (Khan, 1991, Wilkowe, 1992). The apparatus consists of a metal frame supporting a pneumatic cylinder into which pressurized air enters from the top, causing a piston and plate assembly to exert vertical pressure on the column of slurry. The slurry is contained within a 15 cm long cylindrical acrylic "guide tube" and "sample tube". The sample tube, 9 cm long, fits into the guide tube. This sample tube is mounted in the E-K cell, avoiding the disturbance effects of extrusion of the soil specimen. During consolidation, fluid is drained through the bottom of the sample via a porous stone resting on the base. The piston plate also contains a porous stone allowing drainage from the top. Air pressure is applied to the unit through an adjustable regulator (not shown in the schematic).

2.2 Reagents and Supplies

The soils and fluids used in the preparation of the clay slurries are given in Table 2.2.1.

The inorganic contaminants were prepared using soluble salts. The organic contaminants were obtained in liquid form. The solutions of the inorganic salts were prepared at a predetermined concentration, and mixed with a selected soil type. For the organic compounds, the slurry would be prepared at a known water concentration . It would then be transferred to a glass jar with an air-tight lid. A measured amount of the organic would be added directly to the slurry. The filled jar, allowing very little head space, would then be shaken rigorously to obtain a homogeneous mixing of the contaminant and the slurry. The following Tables 2.2.2 through 2.2.4 present the pertinent information on the inorganic salts and organic liquids used in this work.

Table 2.2.1 Materials used in preparation of soil slurries

Soil Type	Solid Components	Liquid Components	Liquid/Solid Ratio (by weight)	Comments **
I	Kaolinite**	Distilled Water	1	Georgia kaolinite
II	Kaolinite	Simulated Ground water**	1	Chemical Composition in Table 2.2.2
III	Kaolinite	Humic solution**	1	900 ppm solution of humic powder[1]
IV	Na-Montmorillonite**	Distilled water	5 - 6	Bentonite
V	Sand** and 10% Na-Montmorillonite	Distilled water	5 - 6	New Jersey beach sand ; - No 4; + No 200 sieve

[1] Humus Products of America

Table 2.2.2 Simulated Ground water Constituents

Property	Jefferson County , Idaho[1]	Laboratory Simulation
pH	7.69 ppm	7.90 ppm
Ca	46.75	47.06
Mg	13.9	14.00
Bicarbonate	212.5	90.51
Chloride	33.69	83.43
Sodium	31.88	32.04
Potassium	3.41	3.51
Sulfate	29.37	55.34
Fluoride	0.31	--
Silica	28.75	--
Nitrogen, Nitrite	0.01	--
Nitrogen, NO_2 +NO_3	2.54	--
Arsenic	1.87 ppb	2.01 ppb
Barium	55.38	54.95
Beryllium	0.5	--
Cadmium	1.0	0.98
Strontium	173.75	171.61
Zinc	45	173.66

[1] According to USGS Records of 1989

2.3 Experimental

A standard sample preparation and a standard electrokinetic test procedure were followed which are presented in the Appendices B2.2 and B2.3, respectively. The following is a general description of these experimental procedures.

2.3.1 Sample Preparation

Soil slurries are prepared by mixing a aqueous solution of the desired contaminant with the soil. The sample tube and guide tube are assembled on the base of the consolidation apparatus and filled about 3/4 of the way with slurry. After the removal of gas bubbles, the piston is lowered into the guide tube to the top of the slurry column and the apparatus assembled. A setting load of 2 psi is applied to overcome mechanical friction. Samples are consolidated to about 40 percent water content under a final pressure of 30 psi (200 kPa). Calibration of the instrument determined that, for a safety factor of two, consolidation be conducted for 24 hours at increments given in Appendix B3.

Table 2.2.3 Metal Salts Used in Preparation of Mix Water for Slurries

Metal	**Salt Formula**	**Concentration ***		**Source**
		High (ppm)	Low (ppm)	
As	$Na_2HAsO_4.7H_2O$	100	10	Fisher Scientific
Cd	$CdCl_2.H_2O$	1000	20	J.T. Baker Inc.
Co	$CoCl_2.6H_2O$	1000	--	Fisher Scientific
Cr	$K_2Cr_2O_7$	3000	--	Fisher Scientific
Cs	$CsNO_3$	1000	--	Sigma Chem. Co.
Hg	$Hg(NO_3)_2.H_2O$	130	5	Fisher Scientific
Ni	$Ni(NO_3)_2.6H_2O$	1000	--	Fisher Scientific
Pb	$Pb(NO_3)_2$	15,000	--	Fisher Scientific
Sr	$SrCl_2.6H_2O$	1000	--	Fisher Scientific
U	2% Nitric Acid Soln. 1000 ppm	100	10	SPEX Industries
Zn	$ZnCl_2$	22,500	1000	Fisher Scientific

* Metal concentrations were selected as representation of those found at various DOE sites

Table 2.2.4 Organic Liquids Used in Slurries

Organic Compound	**Concentration (ppm)**	**Source**	**Lot Number**
Acetic Acid	2000	Fisher Chemical	FL030589
Acetone	6800	Fisher Chemical	911166
Chlorobenzene	400	Fisher Chemical	870387
Hexachlorobenzene	1000	Aldrich Chemical	JY 07908LW
Phenol	100	Fisher Chemical	703309
Trichloroethylene	1000	Fisher Chemical	911623

After consolidation, the sample tube is removed from the consolidation apparatus and any soil extruding from the top end is trimmed. Porous stones and o-rings are attached to each end with silicone glue. After applying high vacuum grease to the inner circular openings of the chambers, the sample tube is mounted between the chambers, which is achieved by removing one chamber of the E-K unit, positioning the sample, and reassembling the cell. Three auxiliary secondary probes (10 probes in the modeling study) are then inserted through holes pre-drilled at equal lengths across the soil sample.

The end plates of the electrode chambers are coated with a silicon-based vacuum grease and attached. The chambers are then filled with the chosen fluid. The cell is connected to the panel by the fluid and power lines. With the drain valves closed, fluid is pumped into the burettes. Following this step all gas within the electrode chambers is to be removed through the gas expulsion ports which, will cause fluid to drain from the burettes into the chambers, completely filling the electrode chambers. After the gas removal, fluid levels in the burettes are adjusted. The cell is now ready for an experiment.

2.3.2 Electrokinetic Testing

In all the E-K experiments, a constant 30 volts DC potential was applied across the electrodes. The actual voltage gradient in soil varied in time and space and also with type of soil-contaminant pair. The following is a record of data collected before, during, and after the E-K test:

During consolidation: Water content, pH, and quantitative chemical analysis sampling is done on the slurry. The volumes of the top and bottom waters extracted during consolidation are measured and analyzed for chemical concentration.
During sample preparation: A portion of the trimmings from the consolidated sample is analyzed for water and chemical content. This measurement provides an "initial" concentration of contaminant in the sample and allows for normalization of concentrations obtained after the E-K test.

During the E-K test: Volumetric electroosmotic inflow and outflow readings are taken from the burettes. The system is checked to ensure that it is delivering 30 volts, and the resulting current is recorded. Voltage readings through the anode and cathode chambers are taken via the power connections, and voltage drops across the soils are taken via the secondary electrodes. Readings were generally taken at zero, 15, and 30 minutes and one and two hours at the start of the test. For the shorter tests, readings were taken at two to three-hour intervals. For the longer-term tests, readings were taken about every 12 hours.

After the E-K test: During cell disassembly, the pH of the anode and cathode fluid is recorded and a sample is taken for chemical analysis. Because the cathode fluid is generally basic which may cause certain metals to precipitate, it is acidified with HCl before chemical analysis to provide a more accurate chemical content. The colors of the water and soil are recorded. The soil is then extruded from the tube and measured at the center of the soil cross-section at 5 to 10 evenly spaced points along its length for pH, water content, and reduction-oxidation (redox) potential in millivolts.

2.3.3 Measurements and Analysis

Water content samples were dried for at least 24 hours in an oven at about 100°C, according to ASTM D4959. The pH of water was measured using a Beckman digital pH meter and standard bulb probe. A flat probe, Orion #913600, was used for the soil pH readings. The redox potential of the soil was measured with a millivolt meter and flat platinum redox probe, Orion #967800.

Quantitative inorganic chemical analyses were performed according to Standard Methods for the Examination of Water and Waste Water (SMEWW) (1989). The SMEWW methods for specific elements are listed in Table 2.3.1. The quantitative chemical analysis for the organics was performed by a Hewlett Packard 5880A Series Gas Chromatography equipped with a Restek Crossbonded 100% dimethyl polysiloxane capillary column and a FID detector.

2.4 Data Reduction and Interpretation

All the data was collected in separate worksheet files using the QUATRO-PRO spread sheet program. These worksheet files were categorized as the FLOW data file, CHEMICAL data file and INDEX PROPERTY data file for each contaminant used.

Table 2.3.1. Inorganic Analysis Methods

SMEWW No.	Standard Method	Instrument	Element(s)
3111	Atomic Abs. (AA) Flame	AA Spectrophotometer Perkin Elmer	Cd, Co, Cr*, Cs, Ni, Pb, Sr*, Zn
3113	Atomic Abs. Graphite Furnace	AA Spectrophotometer Perkin Elmer	As
3120	Atomic Emission	Inductively Coupled Plasma Amer. Research Labs	Cr, Sr, U
3500 - Hg - C	Dithizone Method	UV-Vis Spec. Bausch & Lomb Spectronic 70	Hg

* The most recently analyzed samples for these elements were performed on the AA

2.5 Quality Assurance

A Quality Assurance Project Plan was developed for the program following EPA guidelines. This plan was closely adhered to for sample preparation and electrokinetic testing procedures, as well as sample storage, sample custody, and document control. The consolidation apparatus was calibrated as discussed previously and detailed in Appendix B3.

A standard coding procedure was used for specimen identification. The specimens were identified by the following qualifiers:

a) soil type: K, M, S;
b) pore water type: S, G, H;
c) contaminant type: element name, or abbreviated name, e.g. As, TCE;
d) concentration of contaminant: H, L;
e) specimen identification number; 1,2, 3, etc.;
f) operator: first initial of the person conducting the test.

The abbreviations designate the following:

1) K - kaolinite, M - montmorillonite, S - sand plus montmorillonite;
2) S - distilled water, G - simulated ground water, H -humic solution
3) H - high concentration, L - low concentration

The chemical analysis for the inorganic contaminants were performed following the APHA-AWWA-WPCF standard methods as given in the QA project plan and Table 2.3.2 above. Uranium contaminated samples were sent to a certified laboratory (General Laboratories, NC) for analysis. A number of randomly selected soil and water samples were sent to two different certified laboratories (Wayne Analytical & Environmental Services, Pa and General Laboratories, NC) to check the repeatability. The results are shown in Appendix B1.1 in Table B1.1.1. Table B1.1.2 include a comparison of chemical analysis results with targeted concentrations for the EPA Matrix Samples. Chemical analyses were repeated for those samples that showed inconsistencies with replicate results. When larger quantities of soil samples were used (5 g instead of 1g specified in standard methods) the reproducibility improved. This is attributed to possible inhomogeneous distribution of the contaminant in the soil specimens. Using the US EPA Contract Laboratory Program as a reference, the following QA/QC procedures were integrated into the inorganic chemical analysis in addition to the methods already given in the QA project plan: Initial Calibration Verification (ICV), Continuing Calibration Verification (CCV), Spiked Sample Analysis, and Duplicate Sample Analysis. Sigma brand or ESC prepared solutions were used for ICV and CCV's, while Fisher brand solutions were used to calibrate the instrument.

The chemical analysis for the organics was performed using a Hewlett Packard 5880A Series Gas Chromatography (G.C.), equipped with a 5880A Series G.C. Terminal (level four), with a Restek (Restek Corporation, Bellefonte, Pa.) Rtx - 1 Cross Bonded 100% Dimethyl Polysiloxane Column (30 m. length; 0.053 mm. ID; 5 μm. df) with a FID detector.

The extracted samples were evaluated at Lehigh University's Seeley G. Mudd facility. The chemical analysis for the organic contaminants were performed following the APHA - AWWA - WPCF standard methods as given in the QA project plan. The extraction methods were evaluated experimentally to determine the procedures effectiveness. Organic compound/extraction solvents solubilities, as referenced in the CRC Handbook of Chemistry and Physics, were evaluated for maximum soil desorption. Soil slurries containing individual organic compounds were prepared and then extracted following the modified APHA-AWWA-WPCF methods. For acetic acid and acetone, greater than 96% extraction efficiency was achieved in the solvent/soil mixture. For the remaining organic compounds (chlorobenzene, hexachlorobenzene, phenol and trichloroethylene) extraction efficiencies in the solvent/soil mixtures approaches 100%. One soil sample, a chlorobenzene contaminated kaolinite soil, was sent to an independent, certified laboratory for analysis (Wayne Analytical and Environmental Services, Wayne, Pa). This outside evaluation was performed to verify the efficiency of the soil extraction procedure being used for these analyses. The laboratory thermally extracted the previously extracted soil and analyzed for residual chlorobenzene. Chlorobenzene was not detected in the soil sample. The results indicated that the modified extraction method fully removed the contaminant from the soil/fluid matrix.

During the analyses, randomly chosen samples were repeated and the results checked for reproducibility and accuracy. Chemical extraction and analyses were repeated for those samples that showed inconsistencies with replicate results. As with the inorganic analyses, when larger quantities of soil samples were used (2 gram rather than 1 gram samples), the repeatability improved.

The following extraction methods were used based on the information provided in the referenced documents. For the extraction of the target organics from soils, 1 or 2 gram(s) of soil was combined with 15 ml of the appropriate solvent. The mixture was sonicated and the subsequent suspension was allowed to settle. The resultant supernatant was then analyzed for the target organic compound. The extraction parameters are listed in Appendix B1.1 in Table B1.1.3

3.0 RESULTS AND DISCUSSION

The results of this project are presented in the following 6 subsections:

3.1 Electrokinetic treatment of soils containing metal contaminants
3.2 Electrokinetic treatment of soils containing organic contaminants
3.3 Analytical and empirical modeling of electrokinetic contaminant transport
3.4 Chemical enhancement of electrokinetic contaminant transport
3.5 Physical enhancement of electrokinetic contaminant transport
3.6 Electrokinetic treatment of a reference soil matrix with mixed contaminants

The first two sections, 3.1 and 3.2, will be treated as the background feasibility analysis of electrokinetics for a wide variety of soils-contaminant combinations. The remaining four sections are special cases in which limited number of tests are conducted to assess the validity of analytical or semi-empirical predictions, enhancement of techniques that can be used in conjunction with E-K, and viability of the technology in a real situation of soil contamination with mixed wastes. The overall conclusive results of this work which are supported by a statistically significant number of repeated tests can be itemized as follows:

1. Ions transport in compact soils by electrokinetic migration was observed for all metals in all soil materials. Therefore clean-up of soils may be achieved either by clean water displacement as in pumping well extraction, or simply by the effective movement of ionic species in solution, even when the liquid phase may be stationary.

2. Electroosmotic flow was achieved in all soil types. The current efficiency of the electroosmotic transport (volume of liquid transported toward cathode per quantity (amp.hr) of electricity) is high in soil-contaminant combinations for which electroosmotic flux is the dominant mechanism of contaminant transport. This appears to be the case when cation concentration is low, or the contaminant remains undissociated and poorly adsorbed onto clay surfaces. This agrees well with the Donnan principle and earlier observations by Gray and Mitchell (1967) and Probstein and Renaud (1986).

3. Current efficiency may be indirectly related to removal efficiency for some ionic species. An increase in current efficiency may signal the removal of current carriers from within the pore space by precipitation into insoluble salts or by adsorption onto clay surfaces. Anion retention capacity of clay, as well as it's cation retention, appears to play an important role in current efficiency determination of soil-contaminant systems.

4. Ionizable organic compounds behave similarly to ionic inorganics. If the organic compounds are undissociated and poorly adsorbed by the clay, their transport to an electrode site is governed by the electroosmotic flow. This transport is close to a plug flow phenomenon, the removal efficiency may be predicted reasonably using a simple semi-empirical model. This was demonstrated using o-nitrophenol which has a low soil/water partition coefficient. Short term tests conducted with organics of high partition coefficients did not show appreciable migration for the duration of treatment.

5. Long term tests, with strontium in kaolinite soil exhibited migration patterns which were dependent on time and spatial variation of the voltage gradients in the soil. The transport mechanism of strontium deviated significantly from the plug flow prediction of the existing convection, diffusion and adsorption models of contaminant transport. The experimental and theoretical results coincided well after 4 pore volumes of through flow with the modified approach of time and spatial variation of voltage gradients. The transient and spatial variation of the oxidation and reduction state of the soil appeared to be one of the controlling factors in the transport mechanism.

6. The chemical enhancement of electrokinetic treatment through injection of complexing agents and reverse pH control at the electrode chambers proved to be effective in contaminant removal. In all cases of chemical enhancement, the current efficiency increased significantly over that of the unenhanced runs under identical conditions. The increased current efficiency was due to the increase of flow as well as decrease of current. The short term experiments run in this phase of the work demonstrated the beneficial effects of fine tuning the engineered process with respect to the needs of a particular application.

7. The physical enhancement of electrokinetic treatment through the application of heat proved to increase the fluid flow and current efficiency. The resultant analytical data suggest that the contaminant was completely removed from the soil. Experiments applying short term shear waves to the soil, did not indicate appreciable enhancement of current efficiency and fluid flow under the wave frequencies and durations investigated. Further investigation is suggested, including long term evaluations, to fully understand more of the process parameters.

8. Tests conducted with synthetic reference matrix soil contaminated with mixed wastes showed consistent and uniform reduction of the 4 metals and 2 organics investigated in the high concentration series. The low concentration samples showed little removal of the contaminants after the contaminant concentration in soil was reduced to a uniform constant level by electrokinetic treatment. This level was interpreted as the strongly adsorbed quantity of the contaminant to soil. The soil's high buffering capacity appeared to effect these results in both the high and the low concentration cases. In the high concentration case, a uniform, neutral pH was achieved throughout the soil, which appeared to promote the removal of the metals. In the low concentration case, high pH across the soil promoted metal retention and formation of insoluble metal salts thereby retarding their removal. These test results highlighted the importance of issues such as natural soil buffering capacity and preferential exchange and retention of metals by soil (Sposito, 1984), in mixed waste situations.

3.1 Electrokinetic Treatment of Soils Containing Metal Contaminants

3.1.1 Electrokinetic Flow of Water

The flow from the anode chamber into the soil is designated as INFLOW, whereas the flow from the soil into the cathode chamber is designated as OUTFLOW. In saturated soils, these two quantities measured over time should be equal to each other under steady state flow conditions, that is with no change in the volume and saturation state of the soil medium. Deviation of the outflow from inflow signals the following possible occurrences during testing:

1. Consolidation or volume densification of the soil,
2. Decrease or increase in the saturation state of soil, either by replacing water volume by air or gas, or replacing air/gas volume by water.
3. Leakage of liquid from the confined compartments and compressibility of gases generated by electrolysis of soil water.

The effects of these occurrences will cause the measured quantities of INFLOW and OUTFLOW to deviate. However, in all the cases, INFLOW is the best indication of 'potential' flow through soil since it would be least biased by the volume change processes that may occur in soil during electrokinetic treatment.

The INFLOW, OUTFLOW and CURRENT variation with duration of electrokinetic treatment with constant 30 volts applied across the electrodes are presented in the Appendices (A2.1). An example for kaolinite clay with strontium is shown in Figure 3.1.1.1. The majority of the measured flows exhibited steady state behavior with close matching of the inflow and outflow curves. The current densities, measured in current per unit cross sectional area of the specimen (A = 9.89 cm^2), varied considerably from one soil type to another as well as from one metal to another, largest being for the montmorillonite soils. As current densities increased, the deviation from steady state flow increased, due to the volume change and gas generation in the soil pores. Soil types with low current efficiencies were those with high current densities and non-steady state flows. In a few cases for which the ionic concentrations were fairly large, such as zinc, the net flow to the cathode site ceased and at times reversed toward the anode. This is consistent with Donnan principle that the electroosmotic flux toward cathode is directly proportional to the ratio of concentration of water to concentration of cations, $[H_2O] / [+]$. Therefore at high concentration of the cation, the ratio becomes small and so does the electroosmotic flow toward cathode.

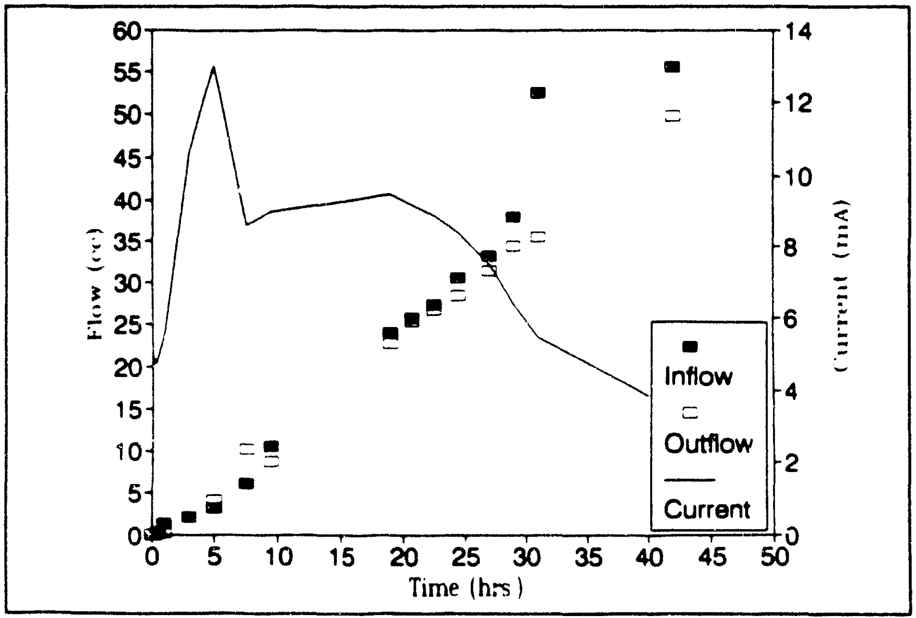

Figure 3.1.1.1. Electroosmotic Flow and Current Variation With Time in Kaolinite Clay With Distilled Water and Strontium

The plates found in Appendices A2.2 show the current efficiency graphs for each metal type categorized with respect to soil types. Kaolinite soils showed constant current efficiencies with little dependence on the pore fluid composition (distilled water, simulated ground water, humic solution). The volume of inflow (normalized by the soil water volume) per moles of electrons transferred varied from 4 to 250 moles^{-1} for all of the metals and all the pore fluid types. The current efficiencies for montmorillonite soils appeared to be more dependent on the metal ion type, as these value ranged from 4 to 30 moles^{-1}. For all of the soil specimens, the current efficiency remained constant with moles of electrons transferred, in general. This observation indicated a steady state transport of liquid with no major changes in the hydraulic and electrical resistivity of the soil system during the period of electrokinetic treatment. The consistency of data also confirmed the intended functioning of the equipment with minimum volume change and electrolytic reactions in the soil. Therefore, in a field situation if water is supplied at the anode end, the transport is expected to continue at a steady state for extended periods of time with no major changes in the physical state of the soil. This was demonstrated by long term tests with strontium, up to 18 pore volumes of water transport through kaolinite soil for which the long term current density remained around 0.14 mA/cm^2 . These results are discussed in section 3.3 under modeling efforts.

3.1.2 Electrokinetic Migration of Metal Ions

All the metal ions migrated in the soil under the influence of the applied electric field. The rate and direction of migration, and the actual percent removal of the metal from the soil varied significantly with the metal type. The metal concentration measured at three points in the soil samples, normalized by the original measured concentrations are presented for each soil-contaminant pair in the Appendices A2.3. An example with strontium in kaolinite clay is shown in Figure 3.1.2.1. Each graph shows the results obtained for three replicate specimens. In some of the soil-contaminant pairs treatment time was staggered to observe the transient behavior of the transport. Since the minimum time span for the treatment was 24 hours, earlier concentration profiles that may have been more characteristic of the general transport type (e.g. transport with advection and dispersion, or transport with adsorption and diffusion) may have been missed. In addition, since only three points were sampled along the soil length, the actual concentration profile may not be well represented by the linear distribution assumed between the consecutive points.

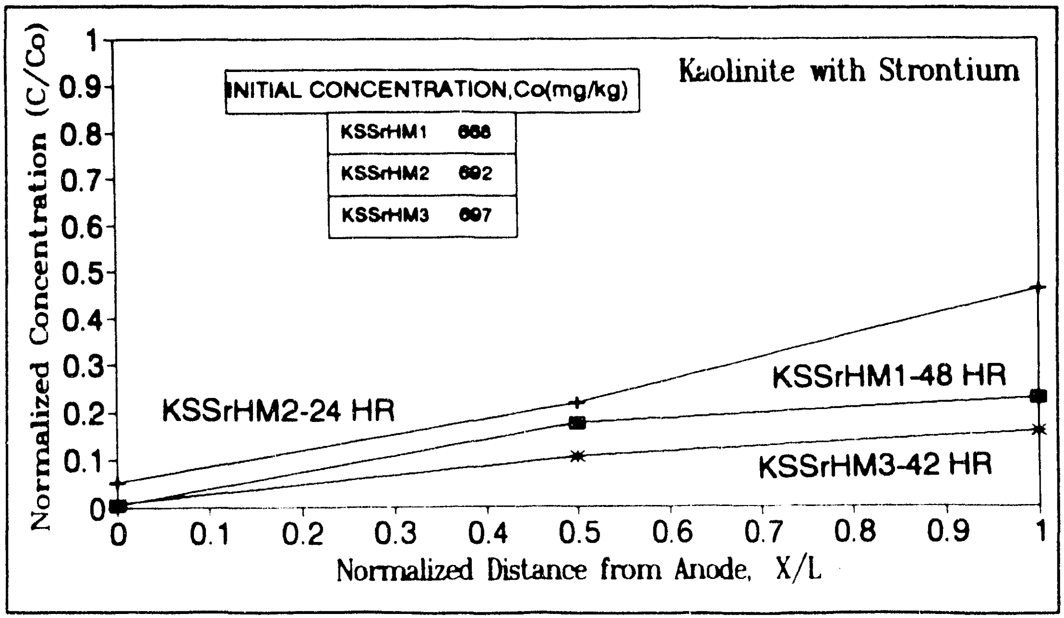

Figure 3.1.2.1. Concentration Profiles of **Strontium** in Three Replicate Kaolinite/Distilled Water Soil Specimens After E-K Treatment

Observing the concentration profiles, it becomes clear that none of the metals are transported via a plug flow mechanism. In this case, the plug flow mechanism would best be characterized by a "step function" shaped profile of contaminant concentration that marches in time from the anode toward the cathode end. In the majority of the profiles there is significant reduction in concentration of the metals in the first half (anode to center) of the soil specimen and an increase in concentration at the cathode end of the soil. This concentration is probably due to the formation of hydroxide salts and also the increased cation retention capacity of the soil resulting from an increased pH at the cathode end of the soil at the soil-water interface. The pH profile of soil after an E-K test is typically given in Figure 3.1.2.2, (kaolinite with strontium). High pH favors formation of hydroxide salts, however, when the metal tends to remain in solution for a wide range of pH, such as strontium, the increase in concentration at the cathode end diminishes in time as more of the metal is released into the cathode chamber, as observed in Figure 3.1.2.1.

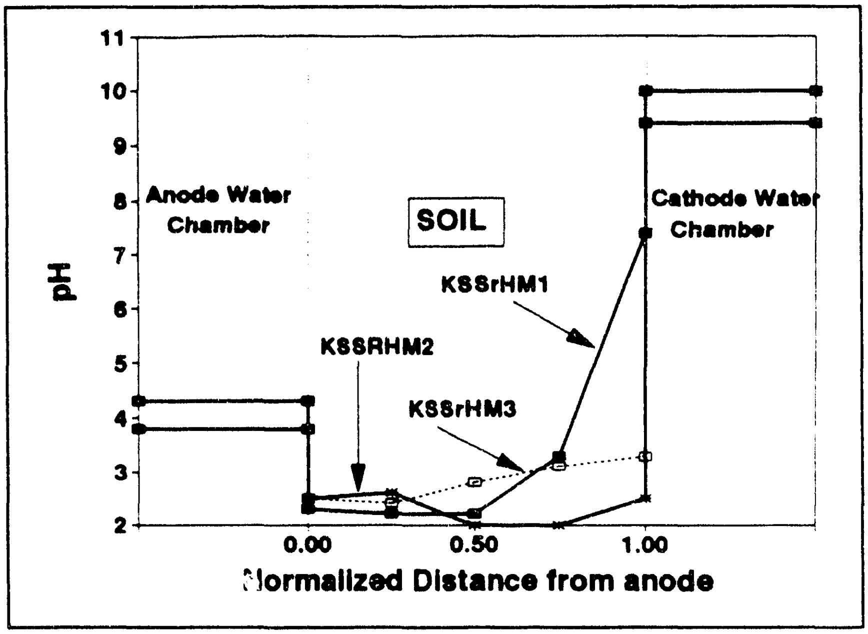

Figure 3.1.2.2. pH Distribution From Anode to Cathode Chambers in 3 Duplicate Specimens of Kaolinite Clay With Distilled Water and **Strontium** After E-K Treatment

The rate of migration and ultimate decontamination appear to be highly dependent on the type of soil-metal combination. Judging from the speciation distribution of metals with pH and the oxidation/reduction state, the metals that have complex chemistry exhibited removal and migration trends that could not be predicted analytically. The following trends were observed for each of the metals tested:

A. **Arsenic**: Arsenic was in anionic ($HAsO_4^{=}$) form in the initial mixing state into the slurry. Figure 3.1.2.3 shows the fraction of arsenic found at three different locations in the soil and the electrode chamber waters after the 24 to 48 hours of electrokinetic treatment of high As concentration soil specimens. Arsenic showed substantial reduction from its initial concentration at both the cathode and anode regions of the soil specimens. Very little removal was achieved into the electrode water chambers. Most of the product appeared to have accumulated at the center of the soil specimens by the end of the short term treatment. Arsenic speciation and solubility is greatly affected by the pH and redox potential of the soil. The availability of arsenic , in the form of arsenite (As(III)) increase at low redox potential and alkaline conditions. The average pH of the center section was 2.9 ranging from 1.8 to 3.0. Subsequent analysis of redox potential variation of kaolinite clay during electrokinetics showed that, in general, the anode end of the soil remains in oxidizing state, while the cathode end is in reducing state. At high redox levels (oxidizing state) the majority of As is found in arsenate form (As(IV)) which is not as soluble as As(III), and tend to be retained on the oxide surfaces of the clay minerals (Masscheleyn et al., 1991). Accumulation of arsenic at the center of the soil specimens can be explained by the low pH and the oxidizing state of the soil at that location. Accumulation was evident at the center of the soil samples for most of the specimens except for the low concentration case in which the metal appeared not to migrate substantially.

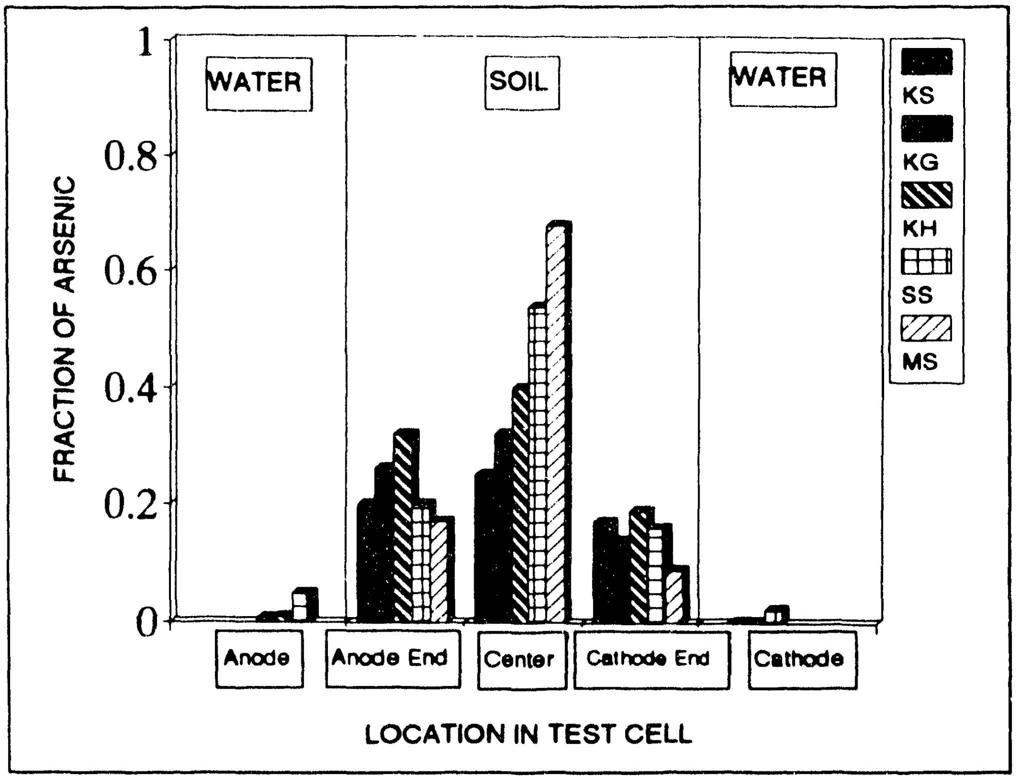

Figure 3.1.2.3. Average Distribution of **Arsenic** in Soil and Electrode Chambers Waters After E-K

B. **Cadmium:** Figure 3.1.2.4 shows the fraction of cadmium found at three different locations in the soil and the electrode chamber waters after the 24 to 48 hours of electrokinetic treatment of high Cd concentration soil specimens. Cadmium is a divalent cation which showed a migration path toward the cathode. Cadmium exhibited a maximum concentration at the cathode end of the soil sample. This is attributed to the increase in the hydrolysis with an increase in pH at the cathode end. The average pHs measured at the cathode ends were 5.3, 8.1 and 9.0 for the distilled water, groundwater and the humic solution specimens of kaolinite clay, respectively. Until around pH 8, Cd remains in its divalent cationic form. Beyond this value it starts forming complex species which are either charged positively or negatively or neutral. The tendency and the abundance of these products control the removal rate until the acid front reaches the cathode region of the soil. However, with the high pH prevailing at the soil-water interface of the cathode end of the soil, a thin layer of precipitate would form at the interface making it difficult for cadmium to be removed into the water chamber. There is also an increase in soil adsorption capacity with increasing pH which would contribute to the accumulation of the metal at this region (Sposito, 1984; Basta and Tabatabai, 1992).

C. **Chromium**: Chromium was introduced to the soil in anionic form, ($Cr_2O_7^{=}$) chromate. Chromate (chromium in the hexavalent oxidation state) is an anion which carries a negative two charge. Figure 3.1.2.5 shows that approximately 30% of the Cr was extracted into the anode chamber by the end of 24 to 48 hours of treatments. In this case, the electromigration of the ion took place in the opposite direction of the electroosmotic water flow. There was accumulation of the metal at the discharge end (anode end of the soil) owing to the increased anion retention of the soil at low pH and also to the deceleration of ionic migration due to electrophoretic and relaxation effects (Kortum and Bockris, 1951).

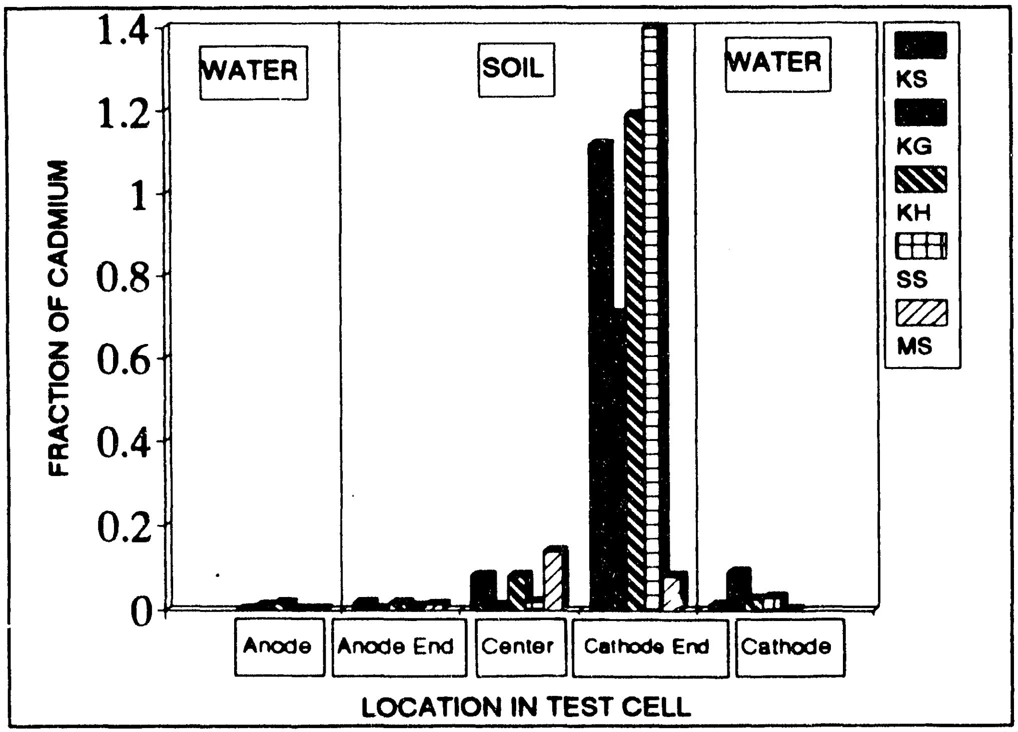

Figure 3.1.2.4. Average Distribution of Fraction of **Cadmium** in Soil and Electrode Chamber Waters After E-K

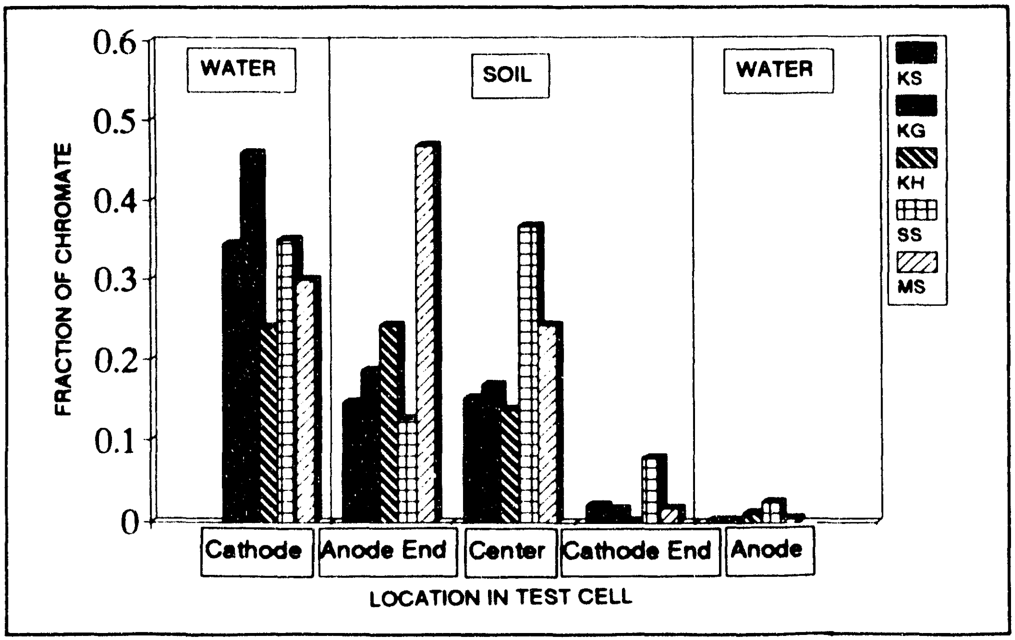

Figure 3.1.2.5. Average Distribution of Fraction of **Chromium** (anionic form) in Soil and Electrode Chamber Waters After E-K

D. **Cesium**: Cesium is a monovalent cation which strongly exchanges with most clays. During the short term tests (24 to 48 hrs), more than 40% of the cesium metal was transported into the cathode water chamber of the kaolinite soils. This trend is shown in Figure 3.1.2.6. Similar results were observed with cesium as those observed with strontium. In the Cs case, the migration rate of the metal appeared to be slower, perhaps due to the larger ionic atmosphere of Cs which would promote lover electromigration velocity. Also, the affinity of the clay to Cs may have contributed to the delayed response. A significant fraction of the cesium was removed to the cathode water chamber in the kaolinite and humic solution specimen for which the electroosmotically permeated water was also humic solution. This result demonstrates the high affinity of the humic solution to cesium and its potential as an effective chealating agent to mobilize cesium from clay soils.

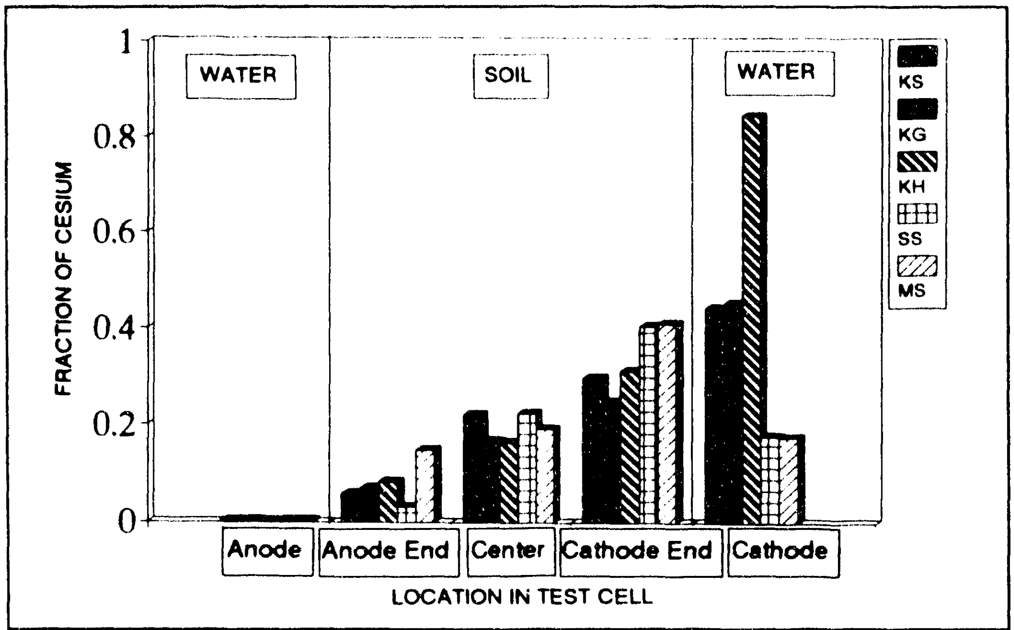

Figure 3.1.2.6. Average Distribution of Fraction of **Cesium** in Soil and Electrode Chamber Waters After E-K

E. **Cobalt**: Cobalt is a divalent cation which is its only oxidation state under normal conditions. It is fairly insensitive to hydrate below a pH of 9. The neutral species of $Co(OH)_2$ dominates above pH 9, and anionic species ($Co(OH)_3^-$, $Co(OH)_4^=$) appear after pH 11. As result of these trends significant removals (average of 94%) were achieved for all soil specimens in the anode half of the soil, while there were heavy concentration accumulations up to 10 times the original at the cathode regions.

F. **Mercury**: Mercury was found to be the metal with the lowest removal rate of any metal investigated. Mercury is conventionally thought of as having two oxidation states; mercurous, +1 state and mercuric, +2 state. Generally, above pH 4, the Hg^{+2} forms a stable complex such as $Hg(OH)_2^0$ which may be transported through the soil by electroosmotic advection. Better removals were achieved with sand specimens (60 to 80 % in the anode half of the specimen) than the clay specimens, perhaps owing to the larger pore space of the sand matrix that would allow better the transport of any precipitated material by water advection.

G. **Nickel**: Nickel, which was tested as a divalent ion, is found to exist above pH 8 as $Ni(OH)^+$ and Ni^{+2} both of which are cationic and move by ion mobility. At pH levels higher than 9, anionic ($Ni(OH)_3^-$, $Ni(OH)_4^=$) and aqueous neutral ($Ni(OH)_2$) species of Ni(II) appear. At high concentrations of Ni(II), $Ni(OH)_2$ precipitates. The removal trend of nickel was similar to that of cobalt. An average removal of 94% was achieved in the anode half of the soil specimens while there were heavy accumulations of the metal at the cathode regions.

H. **Lead**: Lead is one of the preferentially adsorbed metals by clay minerals (Basta and Tabatabai, 1992). It is mostly in the form of a divalent cation below pH of 9. Above pH 9 the PbO is the stable species (Dragun, 1988). At sufficiently high pH (>11) it forms an anionic species of hydrolysis product, $Pb(OH)_6^{-2}$, which is expected to migrate in the opposite direction of electroosmotic flow. Other hydrolysis products of lead which occur at pH levels greater than 6 are: $Pb_2(OH)^{+3}$, $Pb_4(OH)_4^{+4}$ and $Pb_6(OH)_8^{+4}$. These species would exhibit increased ionic velocities due to their higher valances. The effect of high pH on the clay adsorption of metal becomes more significant at high concentrations of the metal, as shown by Basta and Tabatabai (1992). The accumulation of lead at the cathode end of the soil specimens is shown in Figure 3.1.2 7. This accumulation is attributed to: (i) precipitation and anion species formation, (ii) increased concentration of lead at the discharge end (cathode region of soil), (iii) increased adsorption and retention of lead on clay due to high pH and increased concentration at the cathode region of the soil.

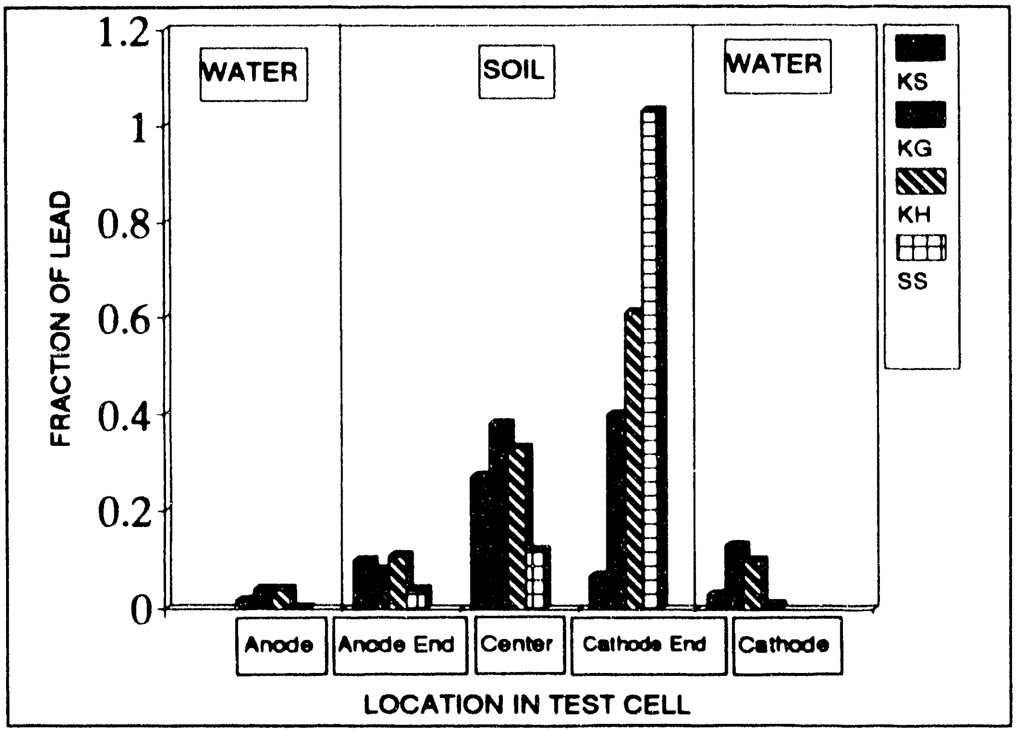

Figure 3.1.2.7. Average Distribution of Fraction of **Lead** in Soil and Electrode Chamber Waters After E-K

I. **Strontium**: Strontium remains a divalent ion for a large range of pH values and is stable to hydrolysis throughout the pH range (2 to 10) of the electrokinetic tests. Figure 3.1.2.8 shows fraction of the metal in the soil and electrode chamber waters after the short duration of electrokinetic treatments. The accumulation of the metal at the cathode end is due to retardation effects of electrophoresis and relaxation as the concentration of the cation increases at the cathode region (Kortum and Bockris, 1951) The mechanism which triggers the accumulation is probably the increased cation retention capacity of the clay at high pH levels. As the pore volume fraction of water transported through the soil increases, the concentration profiles shift down as illustrated in Figure 3.1.2.1. In that particular Figure, the pore volume fraction of water transported through soil for the specimen labeled as KSSrHM2 was 0.48, whereas it was 0.92 and 1.26 for the specimens labeled KSSrHM1 and KSSrHM3, respectively. Subsequent long term tests on strontium contaminated kaolinite clay with distilled water showed nearly complete removal of the metal after about 4 pore volumes of water transport (Wilkowe, 1992). Figure 3.1.2.9 shows the variation of strontium concentration remaining at the three locations of soil specimen with pore volume of water transported for 4 specimens of kaolinite clay with distilled water and similar initial concentration of Strontium (average 718± 50 mg/kg). As observed, at about constant rate of electroosmotic water flow (1.25 ± 0.5 cc/hr), which corresponded to an average electroosmotic hydraulic conductivity of 3.5 x 10^{-5} cm/sec, The variation of strontium concentration in soil with pore volume of water flow is nonlinear. The data indicated that after about one pore volume of water flow, the concentration reduction of the metal at each location became steady with pore volume of water flow. Analysis of this data shows the relative contributions of electromigratory transport (at the beginning of the treatment) and the electroosmotic transport of strontium (after 1 pore volume of water flow) to the overall decontamination process when most of the metal constituent is expected to be present in the pore water.

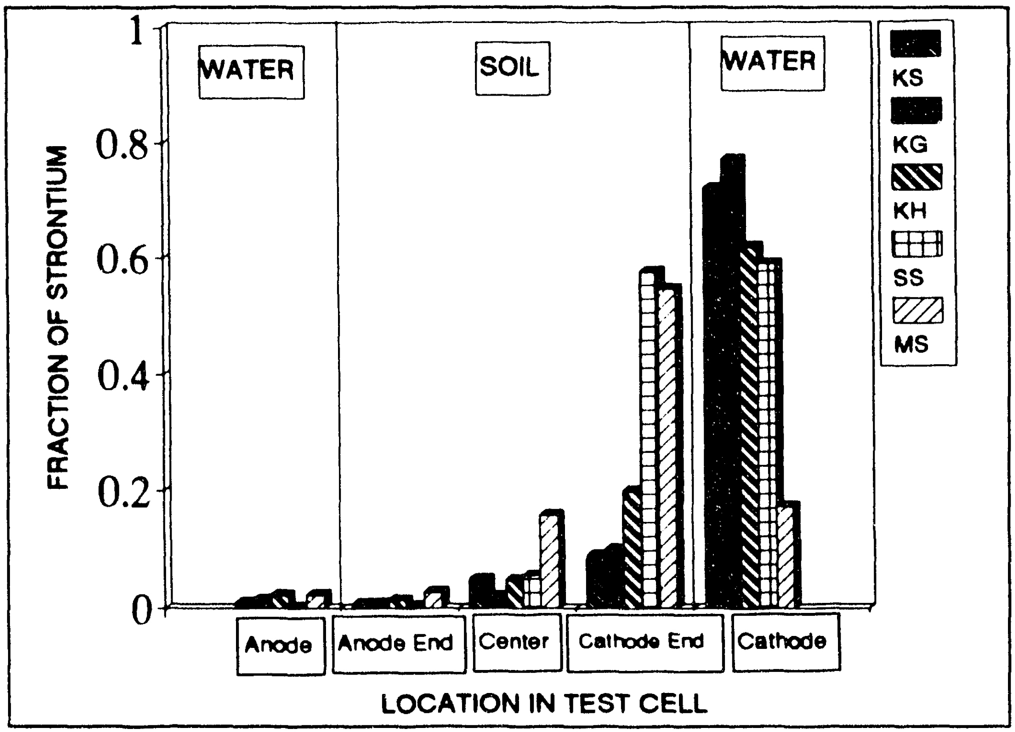

Figure 3.1.2.8. Average Distribution of Fraction of **Strontium** in Soil and Electrode Chamber Waters After E-K

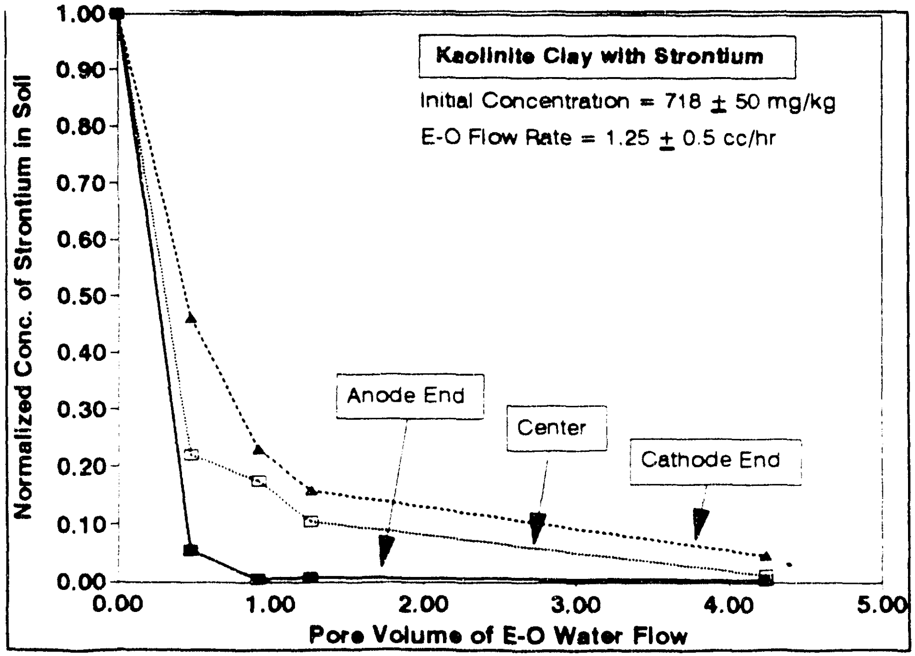

Figure 3.1.2.9. Variation of **Strontium** Concentration With Pore Volume of Flow in Kaolinite Clay Specimen

J. **Uranium**: Uranium was introduced in the soil as the uranyl salt from a series of hydroxide complexes. Below the pH of 6, they are cationic in nature. At approximately pH 6, the $UO_2(OH)_2.H_2O$ precipitate (Borovec, 1981). At higher pHs, the anion hydroxide species such as $UO_2(OH)_3^-$ and $UO_2(OH)_4^=$ occur which would then migrate in the opposite direction of flow. These species may never be able to travel back to the anode chamber since they would encounter low pH environment on the way and tend to change form and sign. However, as long as the high pH gradient prevail at the soil-water interface at the cathode end, uranium would be difficult to transport into the cathode water chamber. As observed in Figure 3.1.2.10, little uranium was transported to the cathode chamber, while most of it accumulated at the cathode region of the soil specimens. There was as much uranium measured in the anode water chamber as in the cathode chamber, probably due to the diffusion of the metal.

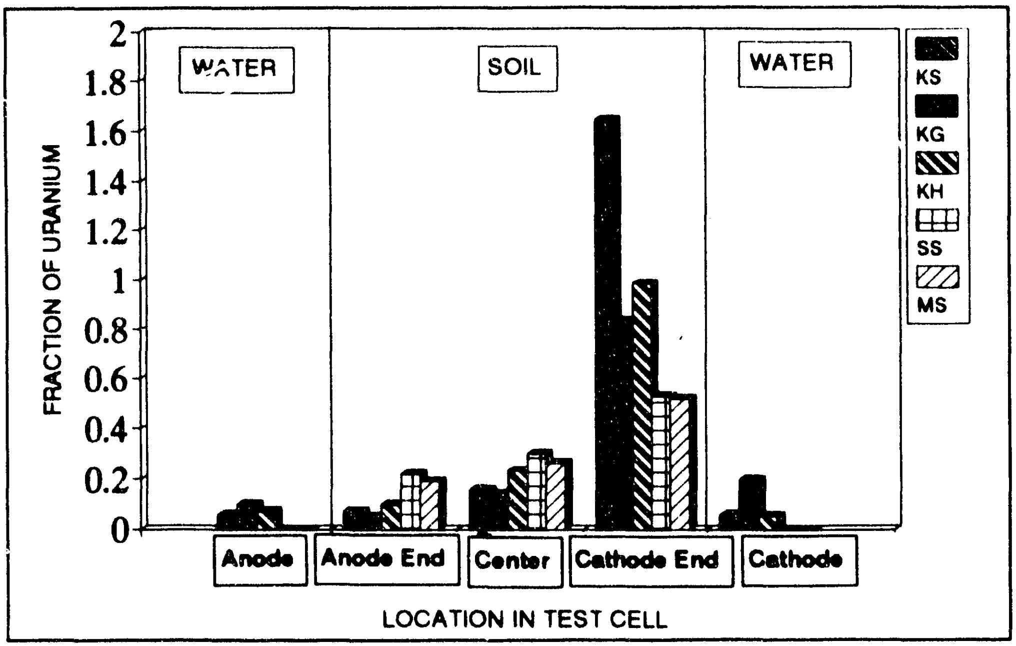

Figure 3.1.2.10. Average Distribution of Fraction of **Uranium** in Soil and Electrode Chamber Waters After E-K

K. **Zinc**: Zinc is amphoteric for which the divalent cation is stable below pH 7.7. The neutral species ($Zn(OH)_2$) predominates above pH 9.1. The anionic species, $Zn(OH)_3^-$, $Zn(OH)_4^=$ become significant after about pH 11. Due to the amphoteric nature of zinc and its tendency to form polynuclear hydrolysis species, similar removal fractions were achieved at the anode and cathode waters. Accumulation was mostly observed at the center of the specimens except for Na-montmorillonite soil as shown in Figure 3.1.2.11.

In an overall analysis of the data, the best removals from about 85 to 95% was achieved over 24 to 48 hour period for Cd, Cr, Co, Sr and Ni in all the soil types. During this time period, the average potential gradient in the soil remained constant at 3 volts/cm . In these experiments, the soil types ranged from pure clays (kaolinite, montmorillonite) mixed with either distilled water, simulated ground water or humic substance solution; to a sand-clay mixture. Among the three soil types (kaolinite, montmorillonite and sand-montmorillonite) tested, kaolinite showed the highest efficiency of electroosmotic water flow, followed by the clayey sand. Kaolinite exhibited constant flow efficiency regardless of the nature of the metal ion in the mixture, whereas, flow through montmorillonite and clayey sand was influenced by the type of metal ion present. Figure 3.1.2.12 illustrates these findings, where the variation of normalized cumulative flow versus the number of moles of electrons transmitted in the distilled water specimens of the three types of soils contaminated with Cd, Co, Ni and Sr. As observed, the kaolinite soil results are close together, whereas the

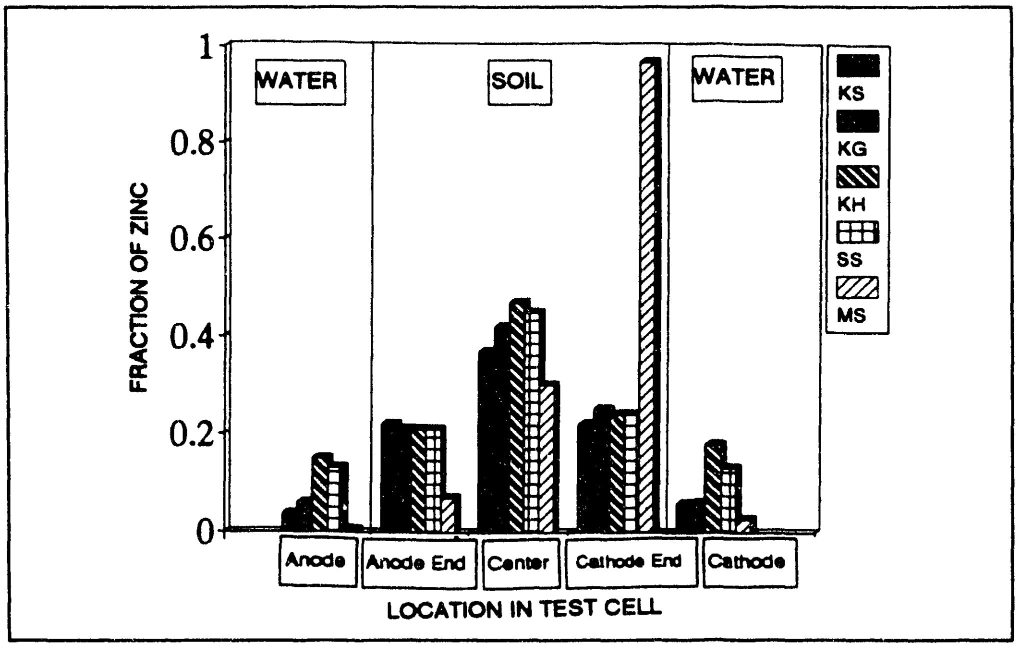

Figure 3.1.2.11. Average Distribution of Fraction of Zinc in Soil and Electrode Chamber Waters After E-K

montmorillonite and sand -montmorillonite results have significantly larger spans of variation. At the top of the montmorillonite span resides the flow data for Sr clay mixture, then for Co mixtures and towards the bottom is the flow for Ni mixtures. This behavior is consistent with findings of Gray and Mitchell (1967) in their fundamental treatment of electroosmosis. The differences between the flows in the three soil mediums can also be explained by the anion retention tendency of the clay. This tendency is higher in kaolinite, therefore is probably least affected by anion migration.

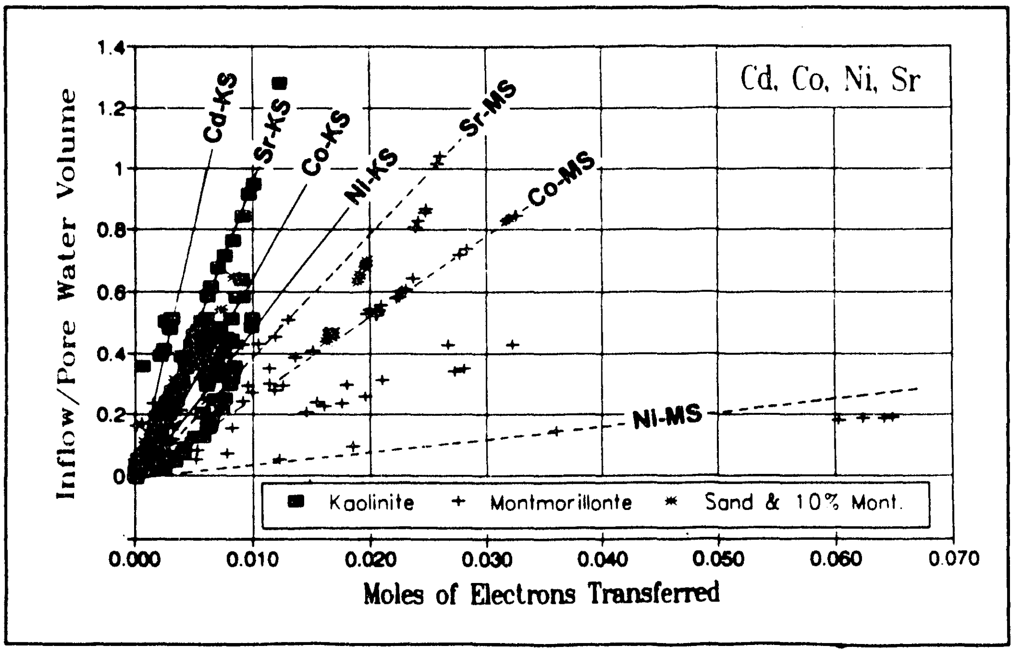

Figure 3.1.2.12. Current Efficiency Variation in Distilled Water Specimens of Three Types of Soils with Cadmium, Strontium, Cobalt and Nickel

The water flow toward the cathode was lower in mixtures containing higher concentrations of the metal for the same quantity of electricity as illustrated in Figure 3.1.2.13, where the number of moles of water flowing toward cathode is correlated with the number of moles of electrons transferred in kaolinite clay for two initial concentrations of cadmium. Although more water per electron was transmitted towards the cathode for the low concentration Cd case, it didn't necessarily result in higher removal of the metal. Assuming a linear distribution of the metal concentration between the anode and the center of the soil, the percent removals were computed as 84% for the high concentration case, and 16.5% for the low concentration case. At lower concentrations, the current carried by the clay surface may constitute a larger portion of the total current and result in a larger net flow of water in the cathode direction, or electroosmosis, as observed by Napier in 1846. At higher concentrations, the current is easier to pass through the soil, because the bulk of it would be carried through the pore space. The quantity of true electroosmotic flow to the cathode may remain the same, however the flow would probably be counteracted by the movement of a larger concentration of anions that drag water molecules along. The anion retention of the clay then plays an important role in the development of a net water flow to the cathode. That is, the higher the anion retention capacity of the soil the higher the net flow toward the cathode. This is best illustrated by the pore volume of water transport to cathode and percent removal or concentration reduction of metal calculations for 4 different metals presented in Table 3.1.1. As observed, the variations in concentration reduction percentages for Cr, Cs, Sr and U appear to depend on the soil matrix, and the metal and pore fluid type, with little or no correlation to the volume of water flow during the short term treatment. For the cationic species (Sr^{++}, Cs^{+}, UO_2^{++}) the volume of water, represented as the fraction of the pore volume, ranged between 0.25 and near 1.00. The flow for the anionic form of Cr, ($Cr_2O_7^{=}$), was consistently lower than that of the cationic species. This demonstrated the effect of water dragging action of the migrating ions on the net flow towards the cathode. In the case of the anionic species $Cr_2O_7^{=}$, as the anion migrates towards the anode, it drags along sufficient amount of water to measurably reduce the net flow towards the cathode. Obviously, both the anion and cation retention capacity of the soil, which subsequently effect the ratio of the cations to anions that are free to migrate, influence the quantity of water movement towards the cathode.

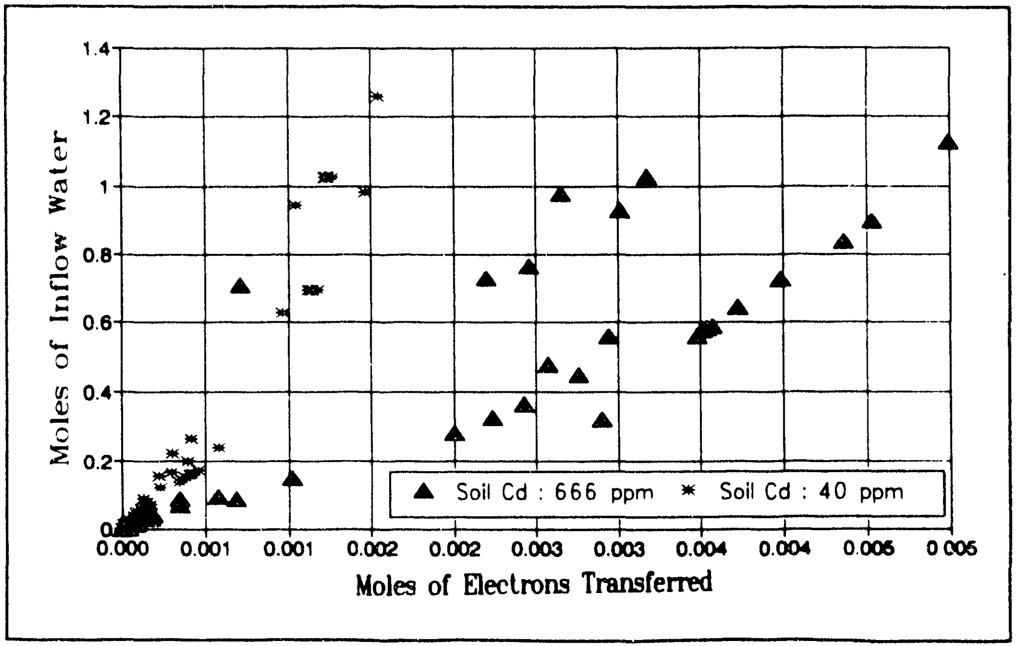

Figure 3.1.2.13. Current Efficiency Variation in Kaolinite With Distilled Water and High and Low Concentrations of **Cadmium**

Table 3.1.1. Average Percent Reduction of Metal Concentration (at the lowest concentration location) and Pore Volume Fraction of Water Transported Toward Cathode Chamber

Metal	KS✧		KH		KG		MS		SS	
	% Rem①	PV②	% Rem	PV	% Rem	PV	% Rem	PV	% Rem	PV
Cr	93	0.18	97	0.15	95	0.23	95	0.12	97	0.12
Cs	72	0.65	74	0.30	77	0.64	55	0.96	89	0.30
Sr	98	0.41	96	0.88	99	0.44	92	0.53	99	0.63
U	79	0.35	70	0.69	85	0.25	44	0.77	33	0.64

✧ KS: Kaolinite/Distilled Water; MS: Na-montmorillonite/Distilled Water;
SS: Sand/10% Na-mont.\Distilled Water; KG: Kaolinite/Ground Water; KH: Kaolinite/Humic Soln.

① % Rem : percent removal at the location of lowest concentration achieved

② PV: Pore volume of water transported to the cathode chamber during treatment

The pH and redox potential, E_h, dependence of the solubility of metal complexes are important parameters to consider in the electrokinetic transport of metallic contaminants. The transient acid-base distribution during electrokinetic process predict that the acid front would propagate toward the cathode, desorbing and solubilizing metal complexes and eventually flushing them out of the soil (Acar et.al, 1989, 1990, 1991 and Hamed et al. 1991). However, natural soils or ground water may possess high buffering capacities which may not allow acid front movement. In such cases, high pH (alkaline) environments may favor precipitation of the metal or result in a distribution of a complex species of the metal, either cationic or anionic. The more complex the speciation of the metal, the more difficult it is to predict its extraction from soil by electrokinetics. Electrokinetic extraction of metals which remain in solution in a single state for a wide range of pHs are easier to predict as will be demonstrated by the results of strontium mixed clay soils. For other metals, such as zinc and mercury, whose solubility is affected by its oxidation state which is influenced by soil pH and the redox potential, the concentration profiles do not appear to have trends consistent with the predicted electrokinetic processes. Finally Table 3.1.2 shows a summary of the percent removal of each metal as calculated using the minimum concentration reached in the soil.

Table 3.1.2. Percentage of Metals Removed At The Lowest Concentration Location★

METAL⊙	Metal Removal (%)				
	SOIL TYPE✧				
	KS	KG	KH	MS	SS
As	54.7① 53.7 - 56.3② 17.5 (L) 7.7 - 25	56.8 50.7 - 66.3	27.2 0 - 47.4	64.3 43.6 - 75.3 40.9 (L) 11.9 - 59.5	54.7 32.9 - 72.8
Cd	94.6 91.7 - 96.3 37.0 (L) 33.3 - 44.4	98.2 97.4 - 98.6	92.7 87.6 - 95.7	86.6 76.8 - 96.4 91.3 (L) 87.5 - 94.1	98.0 97.9 - 98.2
Co	92.2 91.1 - 93.2	93.9 79.7 - 100	95.9 94.8 - 96.7	89.4 75.9 - 98.6	97.5 96.0 - 98.2
Cr	93.1 92.3 - 93.6	94.8 92.4 - 96.5	97.6 95.4 - 99.7	93.5 86.7 - 98.0	96.8 95.9 - 97.5
Cs	71.9 67.0 - 78.3	80.1 77.5 - 81.8	74.7 74.1 - 75.6	54.7 31.2 - 74.0	90.5 89.1 - 93.1
Hg	26.5 4.3 - 41.7 24.5 (L) 0 - 48.9	13.1 5.5 - 25.0	42.5 7.1 - 75.4	-- 31.1 (L) 13.3 - 43.6	78.3 61.3 - 95.8 60.6 (L) 37.3 - 97.0
Ni	88.4 77.2 - 98.4	95.4 94.7 - 96	93.9 93.5 - 94.1	93.6 92.5 - 94.5	95.9 93.6 - 98.0
Pb	69.0 64.2 - 74.2	75.2 62.6 - 82.1	66.9 57.4 - 78.9	--	83.0 72.2 - 90.1
Sr	97.8 94.7 - 99.6	99.5 99.4 - 99.6	96.0 88.8 - 100	92.3 89.8 - 94.0	99.0 98.7 - 99.2
U	79.3 68.0 - 91.2 38.2 (L) 26.4 - 47.7	84.3 82.9 - 85.9	67.4 22.1 - 96.4	39.8 20.7 - 52.3 65.4 (L) 22.1 - 96.4	33.0 17.9 - 47.1
Zn	54.6 42.1 - 74.6 36.2 (L) 7.6 - 72.0	43.3 42.8 - 43.8	36.3 31.3 - 43.5	64.4 24.4 - 90.7 71.0 (L) 48.1 - 93.8	54.5 41.1 - 67.9 79.4 (L) 53.0 - 93.8

★ Percent Removals Calculated Using the Minimum Chemical Concentration

⊙ All Concentrations High Unless Otherwise Noted (L: Low, H:High)

✧ KS: Kaolinite/Distilled Water; MS: Na-montmorillonite/Distilled Water;
SS: Sand/10% Na-mont./Distilled Water; KG: Kaolinite/Ground Water; KH: Kaolinite/Humic Soln.

① Average Percent Removal for 3 Replicate Specimens

② Range of Percent Removals for 3 Replicate Specimens

3.2 Electrokinetic Treatment of Soils Containing Organic Contaminants

3.2.1 Electrokinetic Flow of Water

The INFLOW, OUTFLOW and CURRENT data, with respect to time of the electrokinetic treatment, with a constant 30 volts applied across the electrodes, are presented in the Appendices A2.4 for all the tests conducted with organic contaminants. The duration of the treatments were 24 hours in all of the cases. During this time, the current flow in the soil varied from 1.5 to 5.0 mA, with an average of approximately 3.5 mA. The corresponding current efficiency variations with different soil specimens are presented in the Appendices A2.5. A typical example of current efficiency variation with soil type for hexachlorobenzene is given in Figure 3.2.1.1. In general, the current efficiency, represented as the volume of inflow (normalized by the soil water volume) per moles of electrons transferred, remained constant with moles of electrons transferred during each test. It did not vary with the organic compound in the soil but with the pore fluid type. Lower efficiencies were achieved when the pore fluid contained higher concentration of electrolytes, similar to the case of inorganics. In general, the current efficiency varied from 25 to 800 moles^{-1} for all of the organics and all the pore fluid types. Sand and montmorillonite soils showed low current efficiencies ranging from 25 to 100 moles^{-1}. The current efficiencies for kaolinite soils appeared to be more dependent on the pore fluid, as these value ranged from 250 to 800 moles^{-1}. The absence of major differences between the current efficiencies measured for identical soil types containing different organic compounds indicated absence of transport of these organic compounds by electromigration. Therefore, any transport of the compound should mainly be governed by electroosmotic advection.

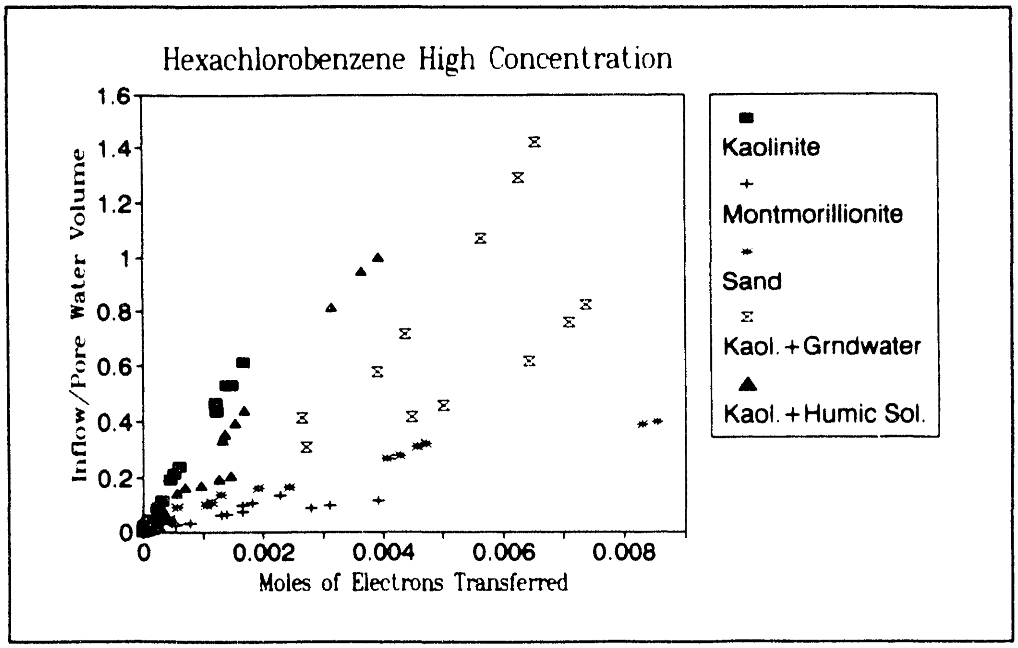

Figure 3.2.1.1. Current Efficiency Variation in Five Soil Specimens with **Hexachlorobenzene**

3.2.2 Electrokinetic Migration of Organics

All the organic compounds migrated in the soil under the influence of an applied electric field. The rate, predominant direction of migration, and the actual percent removal of the organic compound from the soil varied significantly with the nature of the organic compound and soil type. Removal appeared to be dependent upon the amount of indigenous organic material present, the steric effect of the organic molecule with respect to the soil matrix, and the surface chemistry which occurs between the organic compound and the soil (bonding type, strength of bond, adsorption vs. absorption). The organic concentrations measured at three points in the soil samples normalized by the original measured concentrations are presented for each soil-contaminant pair in the Appendices A2.6. An example of the resulting concentration profiles after 24 hour treatment of 3 replicate kaolinite and distilled water specimens containing acetone is presented in Figure 3.2.2.1. As in the case of inorganics, since only three points were sampled along the soil length, the actual concentration profile may not be represented by the linear distribution which is assumed to exist between the points.

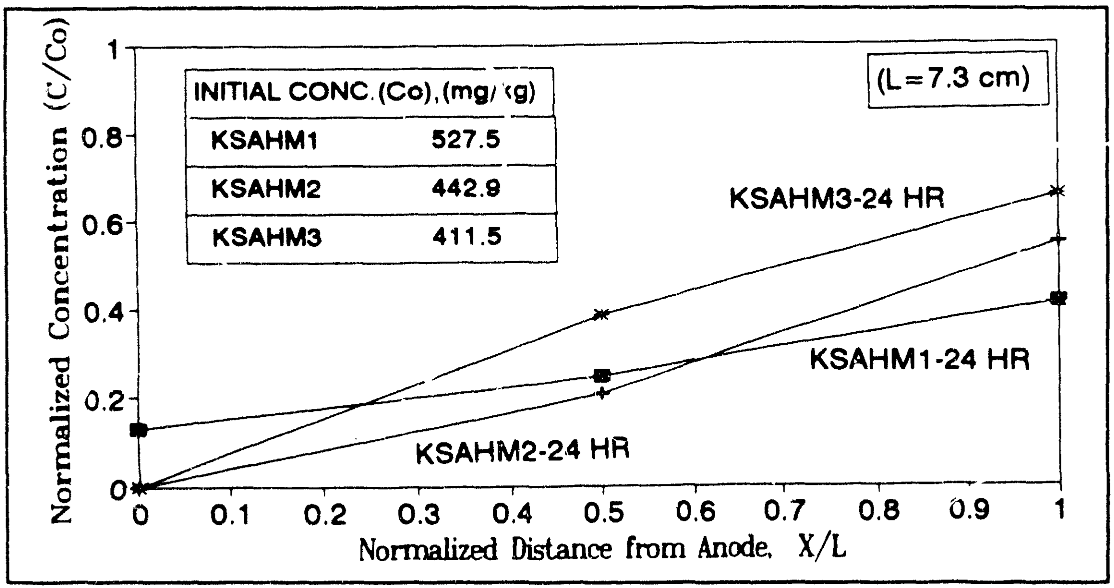

Figure 3.2.2.1. Concentration Profiles of **Acetone** in Three Replicate Kaolinite/Distilled Water Soil Samples After E-K Treatment

Observing the organic concentration profiles, it was again postulated that plug flow was not the predominant transport mechanism. These profiles showed either concentration accumulation at the cathode region or fairly uniform concentration distribution throughout the soil specimens. A few of the specimens contaminated with hexachlorobenzene, chlorobenzene or trichloroethylene showed variations from these general trends or variations from the behavior of their replicates. All of these specimens, whose post treatment organic compound concentration profiles were different, contained significantly lower concentrations of the compounds in each case. Therefore the variations were attributed to either quantitative measurement difficulties of the compounds at the concentration levels near the instrument's detection limits (nonlinearities) or adsorption of most of the compound on the soil at these low concentrations. However, in the majority of profiles, there is significant reduction of the organic concentration in the first half (anode to center) of the soil specimen with the organics accumulated at the center or cathode regions of the soil. Results of percent removal of the organic compounds, measured at the location of lowest concentration, are presented in Table 3.2.1.

The following trends were observed for each of the organics tested:

A. Acetic Acid: Acetic acid in kaolinite soils generally demonstrated movement towards the cathode. Overall, accumulation of the compound was away from the center of the soil. Acetic acid in montmorillonite soils also migrated towards the cathode region, however resulted in more uniform concentration distribution throughout the soil specimens at the completion of the 24 hour treatments. Similar trends were observed in sand specimens as those of the montmorillonite specimens, but the percent reduction of the compound was higher in these specimens.

B. Acetone: Acetone in kaolinite soils demonstrated movement towards the cathode and substantial reduction in the soil at the completion of 24 hour treatments. The post electrokinetic treatment measurements of acetone concentration in soil for the kaolinite and ground water specimens were found to be below the instrument's detection limits. Acetone in montmorillonite soils migrated towards the cathode. Acetone in sand soils migrated towards the cathode portion of the soil cell, with one specimen showing greatest concentration at the center of the soil cell. In all of the cases, substantial reduction of the compound was achieved at the completion of the short term treatments.

C. Chlororobenzene: Chlorobenzene was not detected in any of the soil specimens both pre- and post electrokinetic treatments. This occurrence indicated that the chlorobenzene was perhaps present at concentrations below the instrumentation detection limits. Probable causes of undetection of the compound in the soil specimens prior to the treatment may be inhomogeneous mixing of the chemical into the soil-water slurry and volatilization of the compound during the preparation of the specimens.

D. Hexachlorobenzene: Hexachlorobenzene in kaolinite soils with distilled water demonstrated contaminant migration towards the center portion of the soil. The specimens with higher initial concentrations of the compound (60 - 170 ppm) showed uniform reduction of the compound throughout the soil specimens. At low initial concentrations (19 - 40 ppm) the post electrokinetic concentration distributions showed large variations throughout the soil specimens indicating little or no removal of the compound. Hexachlorobenzene in montmorillonite and sand soils showed organic migration towards the cathode region of the soil, with substantial reduction of concentration throughout the soil specimen, even at the low concentration ranges.

E. Phenol: Phenol in kaolinite soils with distilled water and humic solution demonstrated organic contaminant migration from the anode towards the cathode producing concentration profiles more characteristic of plug flow than concentration accumulation at a region. That is, the normalized concentration in the cathode side half of the soil was approximately a constant one, while measurable reductions were observed at the anode side half of the soil. Phenol in montmorillonite showed migration towards the cathode at high initial concentration (330 ppm), while the normalized concentration data fluctuated at around one for lower initial concentration specimens (150 - 200 ppm). Phenol in sand consistently demonstrated organic contaminant migration from the anode toward the cathode, with the greatest accumulation of the compound in the cathode portion of the soil. Again, percent removal improved with increasing initial concentration of the compound in the soil specimen.

F. Trichloroethylene (TCE): TCE in kaolinite soils with distilled water and simulated ground water did not indicate organic movement towards a particular direction within the soil cell. The soil concentration measurements showed much variation between replicate specimens of similar initial concentrations. Similar to the results obtained with other organic compounds, more repeatable results were obtained with specimens containing higher initial concentrations of the compound (> 1000 ppm). Overall, the concentration profiles of TCE in most soil specimens showed uniform reduction of the compound ranging from 20 to 70 % throughout the soil at the completion of 24 hour electrokinetic treatment periods. The quantitative measurements of TCE in montmorillonite soil were inconclusive; since all the measurements were below the detection limits of the instrument. Best reduction of TCE was achieved in sand soil specimens in which the contaminant migrated away from the anode towards the center/cathode portion of the soil.

In an overall analysis of the data, the greatest organic compound movement, from anode to cathode appeared to have occurred in the soil specimens containing acetic acid, acetone, and phenol. Observing the data presented in Table 3.2.1 the best removals were achieved with acetone, hexachlorobenzene and trichloroethylene.

Table 3.2.1. Percentage of Organics Removed At the Lowest Concentration Location★

ORGANIC COMPOUND	Organic Compound Removal (%)				
	SOIL TYPE✧				
	KS	KG	KH	MS	SS
Acetic Acid	39.5① 11.2 - 53.7②	84.5 53.4 - 100	76.6 29.8 - 100	39.3 23.4 - 52.1	67.3 62.9 - 72.1
Acetone	95.7 87.0 - 100	100 100	98.3 94.9 - 100	58.2 42.6 - 73.5	93.5 80.6 - 100
Chlorobenzene	BDL③	BDL	BDL	BDL	BDL
Hexachlorobenzene	26.8 0 - 80.3	76.0 52.0 - 100	36.8 0 - 91.9	97.3 96.5 - 98.0	81.7 77.7 - 85.6
Phenol	33.7 30.3 - 36.9	6.3 0 - 18.8	48.1 27.4 - 69.4	19.1 0 - 57.4	25.5 0 - 56.0
Trichloroethylene	57.6 23.8 - 77.1	47.0 0 - 73.0	100 100	BDL	84.6 35.4 - 100

★ Percent Removals Calculated Using the Minimum Chemical Concentration

✧ KS: Kaolinite/Distilled Water; MS: Na-montmorillonite/Distilled Water;
SS: Sand/10% Na-mont./Distilled Water; KG: Kaolinite/Ground Water; KH: Kaolinite/Humic Soln.

① Average Percent Removal for 3 Replicate Specimens

② Range of Percent Removals for 3 Replicate Specimens

③ BDL: Below Detection Limit (Initial Concentration Measured BDL)

3.3 Analytical and Empirical Modeling of Electrokinetic Contaminant Transport

The removal of chemical species from porous media using electrokinetics relies on the convection of the pore liquid containing the chemical toward one of the electrodes, where the fluid is collected. In addition to convection, charged molecules and particles will migrate in the electric field, they will be transported by diffusion, or become adsorbed onto the soil. The model used in this study includes the combined transient effects of convection due to electroosmosis, diffusion, adsorption, and electromigration in a one-dimensional system. A finite-difference solution was used to develop a software code in Pascal to predict transient contaminant concentrations along the soil column. The model was used in a semi-empirical manner since the actual electrokinetic test data (i.e. time dependent voltage gradients in soil, electroosmotic flow velocity) were used to generate the theoretical concentration profiles. This solution was then compared to the actual concentration profiles obtained in these laboratory tests. The software code which was used, is available from the Fritz Engineering Laboratory, Lehigh University, Bethlehem, Pennsylvania.

3.3.1 Model Development

A general model of electroosmosis was developed by Acar and co-workers (1989, 1990, 1991) which presents a model of H^+ migration and pH gradient development under electroosmotic flow and electromigration of hydronium and hydroxide ions. Their finite element solution, when compared to experimental data, shows an excellent correlation. Shapiro and co-workers (1989, 1993) developed a similar model that predicted well the transient behavior of concentration fields for acetic acid in solution which was transported by convection, diffusion, and migration in an electric field. Both of these models employ the second-order differential advection-dispersion equation as the governing equation. With certain modifications to be discussed later in this chapter, contributions from each of these models served as the basis for the development of the model in this study.

The second-order one-dimensional advection-dispersion equation for reactive constituents in saturated, homogeneous porous media is given below:

$$\partial C/\partial t = D_x\,(\partial^2 C/\partial x^2) - v_x(\partial C/\partial x) + R + \rho_b/\eta(\partial S/\partial t) \qquad (3.1)$$

where;

C = contaminant concentration, mg/L
t = time
x = coordinate direction taken along the flow path
D_x = hydrodynamic dispersion in the direction of the flow path, m^2/hr
v_x = velocity of the species in the pore fluid, m/hr
R = chemical reaction term
ρ_b= bulk dry density of the medium, g/cm^3
η= porosity of the medium
S = mass of chemical adsorbed onto the soil per unit mass of soil

Modification of this basic equation to include the actual electrokinetic parameters required a detailed investigation of these parameters and material constants. Numerical values for all parameters and constants discussed in this section are found in Appendix C3, Table C3.1. The values were determined experimentally using kaolinite soil samples laden with strontium.

In past studies, both Shapiro and co-workers and Acar and co-workers made the simplifying assumption that the electrical gradient is constant in time across the specimen. In this study, ten electrodes were inserted through the specimen for the purpose of measuring the voltage gradient as a function of time. The data showed that the electric gradient was not constant, and when fitted to a fourth-order regression curve in time, exhibited oscillatory behavior. Graphs of the voltage variation, δV as a function of time, $(\partial V/\partial t)$ for six parallel tests of varying durations may be found in Appendix A3.1.

The electromigration velocity, v_m, of an ion can be represented as:

$$v_m = (zF/RT)D^*(\partial V(x)/\partial x) \qquad (3.2a)$$

Taking V(x) constant over the finite length of $\delta x = L/9$ (distance between the 10 auxiliary electrodes along the length, L, of soil specimen), the regression curves describing the variation of potential in time $(\partial V/\partial t)$ were incorporated into the finite difference code. Then, using the appropriate values of the constant terms in the above equation, the electromigration velocity of strontium between two consecutive electrodes was represented as:

$$v_m = (1.75 \times 10^{-3})\partial V/\partial t \qquad (3.2b)$$

for:

z = valance ⇒ +2 (for strontium)
T = ambient temperature (°K) ⇒ 62°F = 290°K
R = ideal gas constant ⇒ 287 Joules/kg/°K
D^* = coefficient of molecular diffusion
~ coefficient of hydrodynamic dispersion ⇒ 7.2×10^{-7} m^2/hr
δx = distance between auxiliary electrodes = L/9 ⇒ 0.00956 m
F = Faraday constant ⇒ 95,480 Coulombs/mole

The convection velocity, v_c, due to electroosmotic flow of water is determined from laboratory data as a function of the slope of the flow curve, soil porosity and cross-sectional area of flow:

$$v_c = 1/\eta(s/A) \qquad (3.3)$$

where,

η = soil porosity
s = slope of flow curve, m^3/hr
A = cross-sectional area of flow, 0.000958 m^2

The flow curves generated in this study may be found in Appendices A3. The electroosmotic flow rate remained fairly constant with an average value of 1.25 ± 0.5 cm^3/hr for all six strontium laden kaolinite specimens tested.

The reactions taking place in the pore fluid of an electrokinetic system are assumed to be the fast dissociation-association reactions of water. Therefore, for chemical equilibrium conditions, in which the forward and reverse rate balance may be assumed, the chemical reaction term, R, in Equation 3.1 takes on a value of zero. Obviously this assumption can not hold true for reactions which yield precipitates, as would be in the case of most metals. However, for the problem at hand, the time scales associated with convection, diffusion, and electromigration are generally much larger than the reaction times of water, and the metal ion involved, that is, strontium remains a divalent ion for the operating pH ranges (2 to 10) of electrokinetic treatment. Therefore, the chemical reaction term, R, was taken to be zero.

In the adsorption term of Equation 3.1, $\delta S/\delta t$ represents the rate at which the chemical constituent in the pore water is adsorbed onto the soil, and $(\rho_b/\eta)(\delta S/\delta t)$ represents the change in concentration in the fluid caused by adsorption. The amount of contaminant adsorbed by the soil is commonly represented as a function of the concentration in solution, S = f(C) (Freeze and Cherry, 1979). Buchter and co-workers (1989) studied the retention of 15 heavy metals by 11 soils. He found, for solute species at low or moderate concentrations, straight-line relations on logarithmic plots such that:

$$S = k_d C^n \qquad (3.4)$$

Equation 3.4, where k_d and n are coefficients dependent upon the solute species, is known as the *Freundlich isotherm*. Buchter and co-workers (1989) presents *linear* isotherms, where n = 1, and k_d is the *distribution coefficient*. It is a valid representation of adsorption only if the isotherm is linear. This is assumed for strontium in this study. This assumption may be substantiated by the trend of linear isotherms found for heavy metals by Buchter and co-workers (1989). Furthermore, he found pH to be the most important factor affecting k_d, with low pH soils retaining less than high pH soils. The soil pH gradients in this study remained consistently low (2 to 5) for long periods of time (and wide ranges of concentration). Thus, the low k_d value found in this study during background tests of 2.5 ml/g is reasonable. It should be noted that both the pH values and the k_d value found in this study were among the lowest found by Buchter and co-workers (1989). Now Equation 3.1 may be rewritten as

$$(1 + (\rho_b/\eta)k_d)\ \partial C/\partial t = D^*(\partial^2 C/\partial x^2) - v_x(\partial C/\partial x) \qquad (3.5)$$

where, $v_x = v_c + v_m$

The coefficient on the left hand side of Equation 3.5 is called the *retardation coefficient*, r_c. Because of adsorption, the effects of diffusion will be lowered and there will exist a retardation of the chemical front relative to the bulk mass of water.

3.3.2 The Revised Equation

The advection-dispersion equation can now be simplified and tailored for the uses of this study:

$$\partial C/\partial t = D^*_{eff}\,(\partial^2 C/\partial x^2) - \{v_{c,eff} + (1.75 \times 10^{-3})(\partial V/\partial t)/r_c\}\,\partial C/\partial x \qquad (3.6)$$

where;

r_c = retardation coefficient
$D^*_{eff} = D^*/r_c$ = effective diffusion coefficient, m^2/hr
$v_{c,eff} = v_c/r_c$ = effective convection velocity, m/hr

Before the electrokinetic test, each sample is assumed to have a uniform concentration profile of chemical. The boundary conditions are assumed such that, the chemical concentrations at the soil-water interfaces (just outside the soil) is zero at the anode, and it is equal to that of the soil concentration at the cathode. The boundary condition at the anode fails to take into account the effect of diffusion, however, it is considered valid since distilled water is supplied at the anode. The boundary condition at the cathode end may not be valid entirely for t=0, because initially both of the electrode chambers are filled with distilled water. However, the condition becomes true almost immediately as solute is diffused and pumped electrokinetically through the system. This model can be applied to predict transport of an anionic species towards the anode by simply reversing the sign of the diffusion and the electromigration term in equation 3.6.

3.3.3 Advantages and Limitations of the Model

In previous models of electrokinetic flow, the electric gradient across the soil sample was assumed to be linear and constant in time. This study provides an in-depth experimental determination of voltage gradient variation throughout an electrokinetic test and incorporates this variation into a revised model. This model accounts for diffusion, convection, electroosmosis with a varying voltage gradient and adsorption at constant pH. Consolidation effects, solute chemical reactions, precipitation, neutralization, ion exchange reactions, pH dependent speciation and their behavior are not included in the analysis.

3.3.4 Discussion of Results of Strontium Removal Tests

3.3.4.1 Contaminant Transport

In comparing the numerical analysis and the experimental results, two topics emerged as relevant; the mechanism of contaminant removal (i.e. plug flow or diffused flow) and the extent of removal. The determination of the mechanism of removal involves a comparison of the concentration profiles predicted by the model with the observed profiles in the laboratory. The concentration profiles found experimentally at the termination of each electrokinetic test are given in Appendices A3.3 along with the theoretical values. Figure 3.3.4.1 shows the theoretical and the experimental concentration profiles of strontium in soil after 24 hour, 48 hour and 4 day long electrokinetic treatments. The concentrations measured by the atomic adsorption (AA) spectroscopy may be found in Appendix C3, Table C3.2. A chemical mass balance for Sample 1 (24-hour treatment) is given in Table C3.3, in which about 13% of the chemical remains unaccounted for.

As observed in Figure 3.3.4.1, although the actual concentration values fluctuate along the soil column, these profiles do not appear to exhibit the plug flow behavior predicted by the analytical solution until after 4 days of treatment, which correspond to over 4 pore volumes of electroosmotic water flow through the kaolinite specimens. The actual concentration distribution of strontium decreases fairly uniformly across the length of the soil. Figure 3.3.4.2 shows the variation of experimental and predicted removal of strontium from kaolinite with pore volume of water flow. Prior to the four-day test, which corresponds to a pore water volume removal of about 4.4, the model highly underestimates the electrokinetic removal. For example, at 48 hours or about 1.5 pore water volumes, the model predicts only about 22 percent contaminant removal, while the laboratory results show nearly 90 percent removal. The model and experimental results agree on about 99 percent removal by the fourth day (4.4 pore volumes of flow) and complete removal thereafter. Several possibilities exist for the failure of the advection-dispersion equation to adequately predict electrokinetic flow in this study. Electrochemical processes, such as redox potential and transient pH gradient development, may play a crucial role in contaminant transport and thus may need to be incorporated into the model. Use of the retardation coefficient, r_c may not be relevant since the soil is contaminated prior to electrokinetic treatment and it is expected to have adsorbed its capacity of the chemical at the beginning of the treatment. The retardation coefficient used in the model serves to reduce the convection as well as the electromigration velocity of the transported contaminant, which may explain the delayed concentration profiles produced by the model.

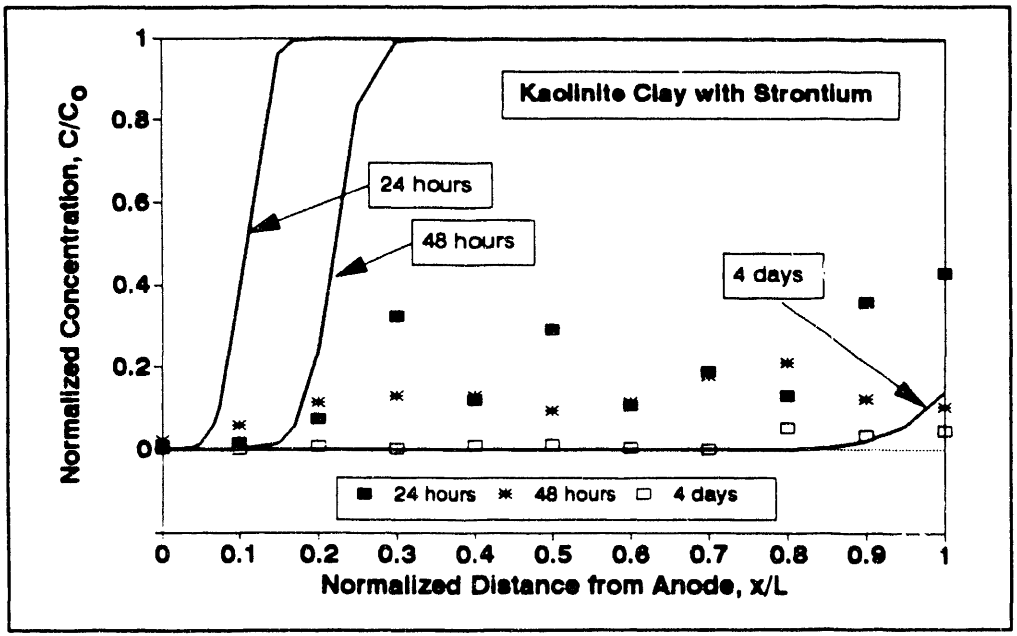

Figure 3.3.4.1. The Theoretical and Experimental Concentration Profiles of **Strontium** in Kaolinite Clay in Extended E-K Treatment Tests

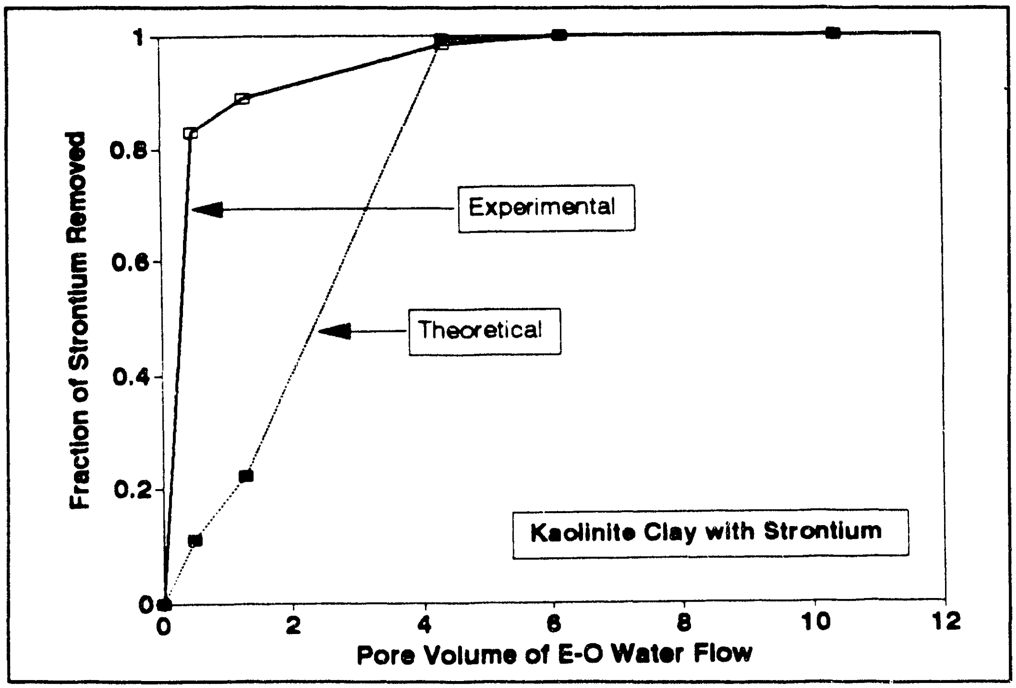

Figure 3.3.4.2. Predicted and the Experimental Percent Removal of **Strontium** From Kaolinite With Pore Volumes of Flow

3.3.4.2 System Parameters and Measurements

The monitoring of electroosmotic flow, current, voltage, and redox potential during laboratory testing was imperative in order to determine model input parameters and to project future modifications to improve the model. Cumulative electroosmotic flow for all the tests are given in Appendices, A3.2. The inflow and outflow curves were linear, and coincided with each other, which signaled steady state flow through out the six parallel tests. Figure 3.3.4.3 shows the variation of flow and current with time and pore volume of flow. The average rate of flow was measured 1.25 ± 0.5 cm^3/hr. Measurements of the current showed an initial peak which leveled off to a constant value after about 5 pore volumes of flow. The current density during that phase was a constant at 0.14 mA/cm^2. This corresponded closely to the time that, experimentally, all of the strontium was flushed out of the soil. At this stage, the current efficiency was computed on the order of 3.0 ml/mA.hr. This value falls within the range of electroosmotic transport as a functions of concentration and water content given by Mitchell (1976).

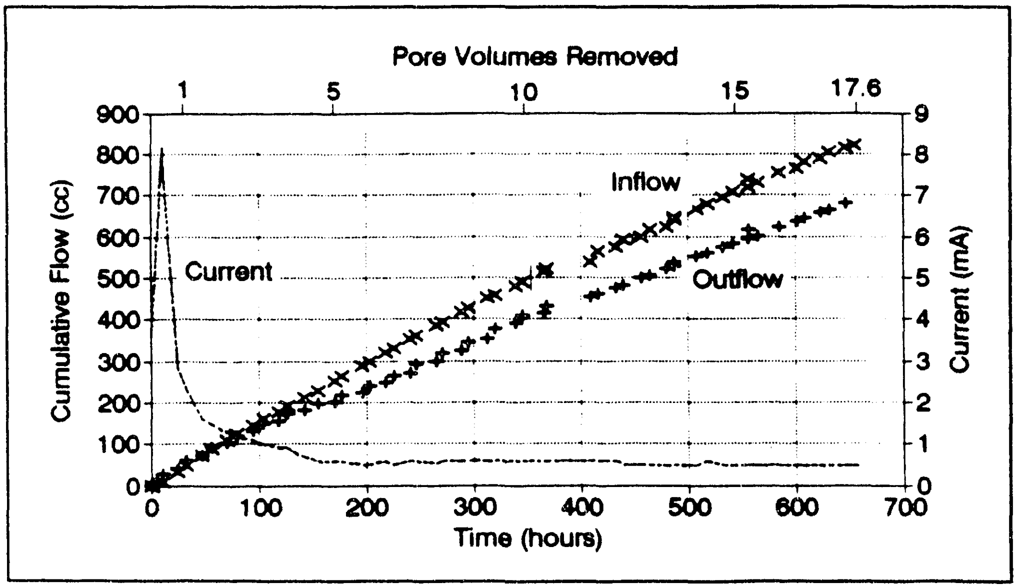

Figure 3.3.4.3. Electroosmotic Flow and Current Variation with Time for Extended E-K Testing of Strontium Contaminated Kaolinite and Distilled Water Soil Sample

The voltage gradients along the soil specimen, as measured by the auxiliary electrodes at the termination time, and the redox potentials measured right after the termination time for each of the six laboratory tests, are shown in Appendices A3.5. The voltage gradient has already been shown to vary greatly with time. In Figure 3.3.4.4 demonstrating the 24 hour test, the voltage gradients across the soil sample is large, but the steep curve flattens in time and becomes relatively flat by the end of four weeks (see A3.5.6). This transient behavior further illustrates the importance of incorporating a varying voltage gradient into an electrokinetic model, particularly for short-term studies. Redox potential (E_h), the presence or absence of electrons in the soil, may be an important electrochemical parameter affecting electrokinetic decontamination. Typically, as observed in Figure 3.3.4.4, the redox curve follows the same pattern as the voltage gradient curve, becoming roughly flat by 28 days. The importance of redox to the electrokinetic process stems from its ability to alter the oxidation state of an element in an aqueous system (Patrick et al., 1972). Although Dragun (1988) shows that strontium remains as Sr^{+2} for wide ranges of E_h, it may be difficult to predict the removal of such metals as arsenic, mercury, and zinc, which show a large variation in speciation for different redox-pH couples. The incorporation of redox potential into the electrokinetic model may improve its ability to predict decontamination.

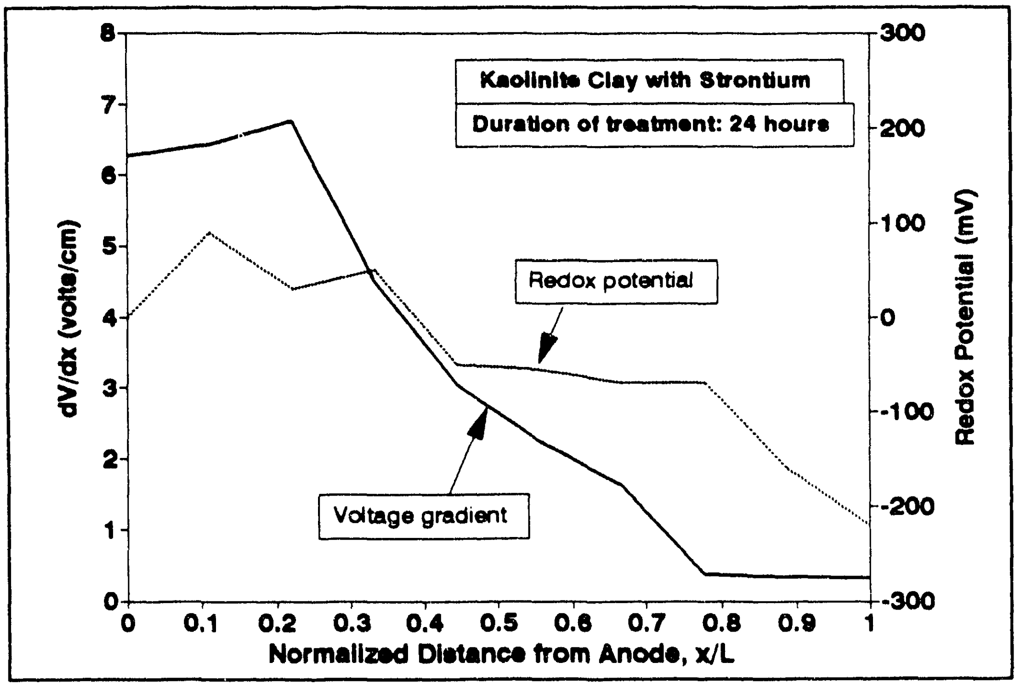

Figure 3.3.4.4. Voltage Gradient and Redox Potential Variation in Kaolinite with **Strontium** After 24 Hours of E-K Treatment

As observed from Figure 3.3.4.4 the voltage gradient and redox potential vary significantly across the soil as strontium moves from the anode to the cathode region, measured after 24 hours of constant voltage across electrodes (30 volts).The voltage difference measured between consecutive probes, separated at equal distances, vary by as much as 6 volts at the anode end to 0.5 volts at the cathode end. The redox potential changed from positive (+100 mV) at the anode, to negative values (-200 mV) at the cathode region of the soil. The redox potential varied in time as well as space indicating transient formation of oxidized or reduced layers of soil during the treatment. After four weeks of treatment, the variation in voltage gradients are significantly smaller (voltage difference change from 1.6V to about 1V between consecutive probes) and the redox potential is approximately constant across the soil at 50 mV, indicating an oxidized state of soil generally, except the very end of the cathode side of the soil which displayed negative potential.

3.3.4.3 Comparison of Constant and Varied Voltage Gradient Models

As previously stated, the contribution of the modeling portion of this study has been to improve the predictions of electrokinetic flow by introducing into the analysis the time dependent voltage gradients measured across the soil sample. To determine the extent of improvement, the finite-difference computer model was run for the four day test with a constant voltage gradient of 3.5 V/cm. The results of this run are shown in Figure 3.3.4.5. From the graph, the addition of a varying voltage gradient is an obvious improvement for the long term prediction of contaminant removal. The variable voltage gradient approach affects the prediction by accelerating the flow of chemical through the system, which agrees better with the experimental data.

3.3.5 Discussion of Results of Acetic Acid Removal Tests

The semi-empirical model was tested against experimental results using kaolinite as soil medium and acetic acid as the contaminant. The electrokinetic tests were conducted for 24 hours and 48 hours on specimens containing 244 and 1817 mg of acetic acid per kg of kaolinite clay, respectively. The flow and

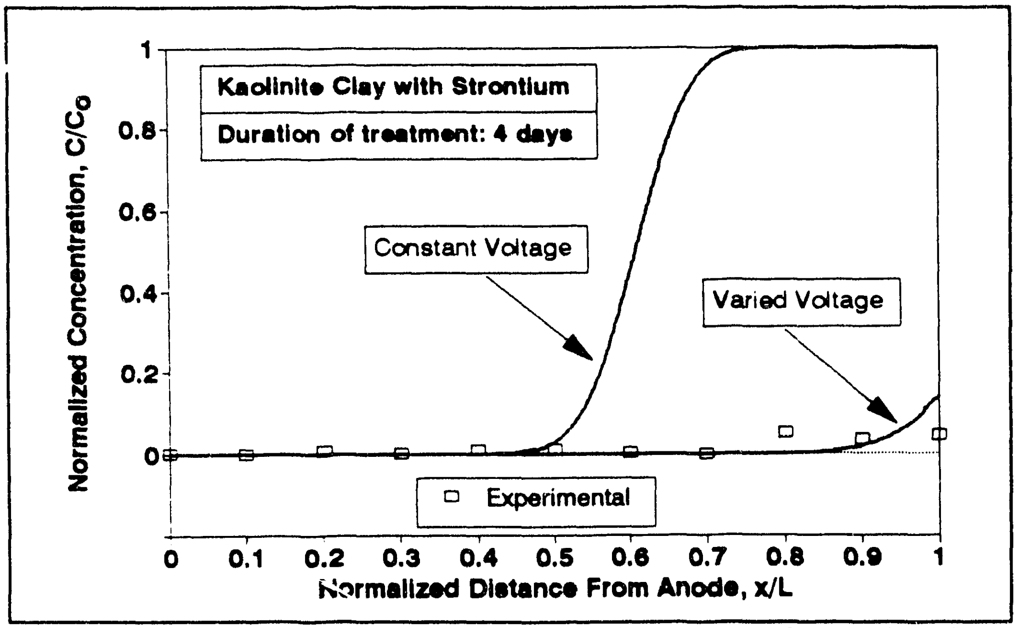

Figure 3.3.4.5. Comparison of Theoretical Concentration Profiles of **Strontium** in Kaolinite with Constant and Variable Voltage Gradient Application in E-K Treatment

current variation graphs for these tests are given in Appendices, A3.8. The voltage gradients and the redox potential measurements for the acetic acid specimens showed significantly less variation in space and time when compared to those with strontium. The voltage gradient was fairly constant at around 0.25 - 1.57 V/cm, while the redox potential changed from 80 mV at anode end to -25 mV at cathode region for the 24-hour treated specimen. Similarly, the voltage gradient was around 0.52 - 1.42 V/cm, and the redox potential changed from 100 mV at the anode to -150 mV at the cathode for the 48-hour treated specimen.

The pH profiles for these samples were uniform across soil at around 3.7. At this pH value the acetic acid would remain undissociated and therefore the electromigration velocity of the molecule can be assumed to be negligible. The relatively small variation of soil voltage redox potential in time also indicates that the acetic acid molecule is probably inactive in the process. The model was run for 24 hours and 48 hours with the following assumptions:

1. No adsorption of acetic acid onto soil; retardation coefficient, r_c=1.
2. Electromigration velocity, v_m=0.
3. Convection velocity, v_c, estimated as a function of the slope of the flow curve (equation 3.3).

The predicted removal and the experimental removal of the acetic acid are plotted against pore volumes of water flow in Figure 3.3.5.1. As observed, the model predicts complete removal of the acid after about 1.5 pore volumes of water flow. In the model, the migration is due to the convection velocity of electroosmotic water flow only. The experimental data, on the other hand, shows more removal than predicted in the high concentration case, and half as much removal than predicted in the low concentration case. The model when used with the assumptions listed above appears to agree better with the high concentration acetic acid case. In the low concentration case, factors such as back diffusion of the molecules from a concentration front may play an important role in the absence of its electromigration velocity in the direction of flow. The concentration profiles of acetic acid in Figure 3.3.5.2 do not indicate a plug flow phenomena, but rather a dispersed flow. This is probably more evident in the lower initial concentration case of acetic acid. In the higher concentration case, some dissociation may take place which accelerate the removal by electromigration. Superimposed on the concentration profiles are concentration data from replicate tests with acetic acid in Figure 3.3.5.2. These replicate data are in good agreement with each other.

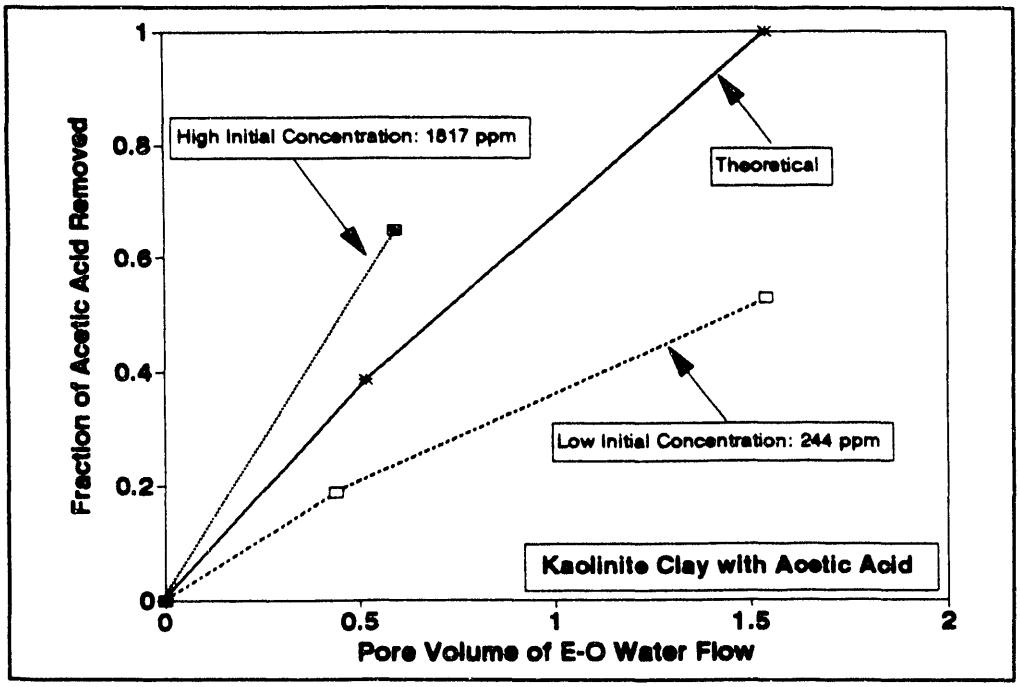

Figure 3.3.5.1. Predicted and Experimental Percent Removal of Acetic Acid with Pore Volume of Flow

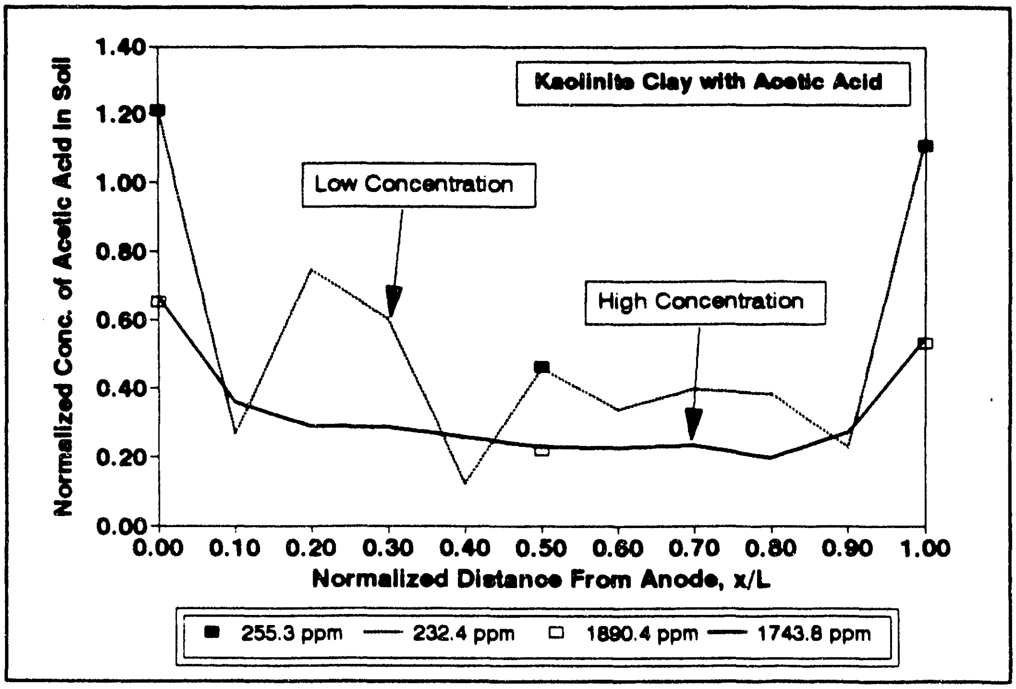

Figure 3.3.5.2. The Concentration Profiles of Acetic Acid in Kaolinite Clay After E-K Treatment

3.3.6 Empirical Model of Electrokinetic Decontamination

An empirical model of electrokinetic soil decontamination was developed by Khan (1991) based on the electroosmotic water flow velocity. The model tested fairly well for low concentrations of cations and for organic compounds when they are not strongly adsorbed by soil. A modified theory of electroosmotic velocity of water through soil was proposed (Khan, 1991; Khan et al., 1993). In this theory, the 'true electroosmotic flow' is directly proportional to the current carried by the charged solid surfaces in soil. In this approach, the zeta potential used in Helmholtz Smoluchowski theory is replaced by a constant surface potential, Ψ_d, which is invariable with ionic concentration and pH of the pore fluid. Then the electroosmotic velocity, v_{eo}, is expressed as a function of soil surface current, I_s, only (see equation 1.3). The model uses the electroosmotic velocity determined from surface current of the soil matrix, and the mean residence time of the solute in soil measured from a tracer test to develop a dimensionless parameter. Figure 3.3.6.1 shows the experimental and the predicted results for o-nitrophenol in kaolinite clay. O-nitrophenol represents a poorly adsorbed organic compound, the adsorption of which was measured as 0.015 mg of o-nitrophenol per gram of kaolinite clay. O-nitrophenol will also remain nonionic at the operating pH range (2 to 4) of the majority portion of the soil during electrokinetic treatment. Under these conditions, the dominant contaminant transport mechanism by electrokinetics can be modeled as convection by electroosmosis and diffusion. The good agreement of the experimental and predicted curves for o-nitrophenol removal shown in Figure 3.3.6.1 support this conclusion.

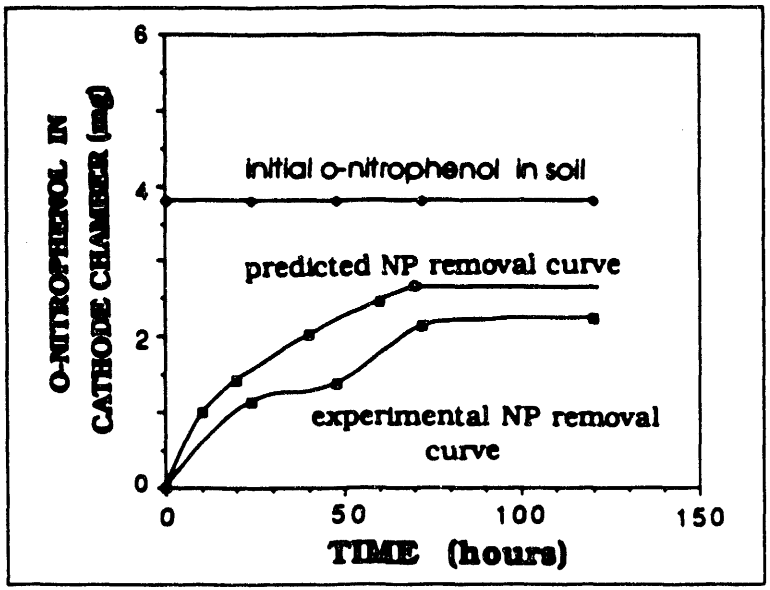

Figure 3.3.6.1. Predicted and Experimental Removal of O-nitrophenol from Soil by E-K Treatment

Figure 3.3.6.2, which shows the variation of the measured electroosmotic flow toward cathode and the mass of o-nitrophenol removed into the cathode chamber with time, is presented to further illustrate the role of electroosmotic advection in the transport of organic compounds in soil by electrokinetics. As observed, the curves are fairly parallel and linear with no abrupt changes. The average time rate of electroosmotic flow is 0.87 cm^3/hr, and the average time rate of o-nitrophenol accumulation in the cathode chamber is 0.017 mg/hr. Using these values, it can be computed that about 0.02 mg of o-nitrophenol per 1 cm^3 of electroosmotic water flows into the cathode chamber, assuming that electroosmosis is the single dominant mechanism of transport. Observing from Figure 3.3.6.2, in 120 hours of treatment, approximately 110 cm^3 of water has discharged into the cathode chamber , which follows that about 2.20 mg of o-nitrophenol should have accumulated in this chamber. The actual measured mass of o-nitrophenol in the cathode chamber at the end of 120 hours of treatment was 2.28 mg (see Figure 3.3.6.1). The closeness of the predicted and measured masses of the compound in the cathode chamber validate the initial assumption that electroosmotic advection is the dominant mechanism of transport for o-nitrophenol in kaolinite clay.

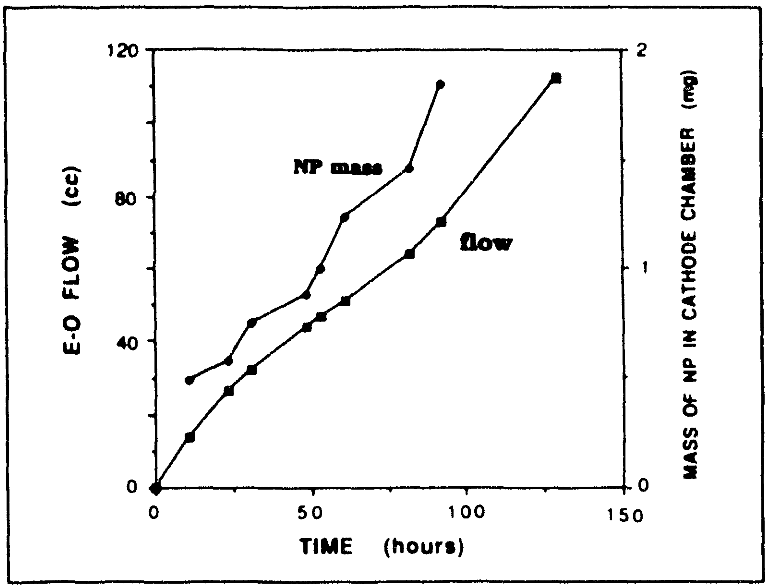

Figure 3.3.6.2. Accumulation of O-nitrophenol and Electroosmotic Water Flow in the Cathode Chamber

The mass of o-nitrophenol accumulated in the cathode chamber corresponded to approximately 60% of the original mass of the compound injected into the kaolinite specimen. Using this information the adsorbed mass of the compound can be estimated as 1.52 mg. Then, using the approximate dry clay mass of 76 g, and the maximum adsorption value of 0.015 mg o-nitrophenol per gram of clay, the total mass of substance adsorbed onto the clay can be computed as 1.14 mg. The closeness of these values also confirms the previously drawn conclusion that in the presence of nonionized, poorly adsorbed organic compounds the primary mechanism of transport is electroosmosis. Subsequently, the electroosmotic velocity of water through a given soil can be used to predict the rate of removal of organic compounds which are: (i) poorly adsorbed by soil, (ii) nonionized, (iii) with known aqueous concentrations in soil.

The empirical model developed by Khan (1991) was also tested to predict transport of zinc occurring at a low concentration in soil. The zinc concentration selected for the electrokinetic tests was 325 mg/kg of soil, which is slightly above the maximum concentration of naturally occurring zinc in soils (10 - 300 mg/kg). Using the empirical model, the predicted removal agreed well with the actual removal data in this case also.

3.4 Chemical Enhancement of Electrokinetic Contaminant Transport

In background testing, considerably large pH gradients developed between electrodes. These pH variations in the soil samples are available in Appendix C1, from the Index Property Tables. The pH at the anode end had been observed to drop from approximately 6.0 down to 2.0. The pH at the cathode end had increased from roughly 6.0 to 11.0. It is believed that this increase in pH at the cathode causes the metals to precipitate out of solution as they approach a sharp boundary of high pH at the interface of soil and electrode chamber water. As precipitation occurs, the metals are no longer mobile, and they remain in the soil pores as their concentration increases at that location. A secondary effect of increased pH at the interface is that, soil at these high values of pH develop a larger capacity to adsorb and retain metal ions that remain in solution (Sposito, 1984).

To enhance removal, two control mechanisms were tested to increase solubility and desorption of the metal ions in the soil pores. One method is the reverse pH control, whereby the pH was brought down to

2.0 in the cathode chamber, and up to 11.0 in the anode chamber manually at time intervals. The other method involved injection of a complexing agent to chelate the metal into a stable form. The complexing agent was expected to bond with the contaminant and prevent the ions from being adsorbed onto the surface of the soil particles, thereby yielding a higher removal of the contaminant. The form of the complex is often very stable and the metal ion is firmly combined with the molecule by multiple bonds making it unavailable to form insoluble salts or other hydrolysis products. In doing so, the ionic migration may be sacrificed either by the size and type of the new formation. However, removal may be ensured by a plug flow type transport, as expected in the transport of aqueous neutral complexes by electroosmotic water flow.

A surfactant was applied at the anode to enhance dissolution and transport of some of the organic contaminants. Four organic compounds, chlorobenzene, hexachlorobenzene, phenol and trichloroethylene, were studied in the surfactant enhanced electrokinetic tests. The surfactant was an anionic complex, sodium dodecylbenzene sulfonate. In one series of tests, the surfactant was added only to the anode chamber and burette. In a second series, surfactant was added only to the cathode chamber and burette and in a third series, the surfactant was added to both the anode and cathode chambers and both burettes.

3.4.1 Chemical Enhancement Methods for Metals

Detailed description of the methodology and discussion of the results of the chemical enhancement of electrokinetic treatment of metal containing soils are given by Apatoczky (1992).

Complexing Agent: A complexing or chelating agent is a compound (usually organic) which firmly binds metal cations. The metal ion is held in a stable structure so that it is not free to form insoluble salts or be adsorbed onto the soil particles. Ethylenediamine (EDA) was selected as a chelating agent in this project. Each ethylenediamine molecule ($H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$) provides two N donor atoms which readily forms complexes with a wide variety of metal ions. The EDA forms a cathodic molecule, and therefore it migrates in the direction of the cathode.

Reverse pH Control: Unenhanced base tests have revealed that large pH gradients develop between the anode and cathode sites. A low pH is observed at the anode and a high pH at the cathode. Three problems can occur as a result of this gradient. First, at a relatively high pH, metals have a tendency to form precipitates. If this occurs, the metals lose their ionic mobility and they will remain in the soil pores where they have precipitated. Secondly, at differing pHs, metal ions will form various species. If the species formed is negatively charged then it will migrate towards the anode site until it reaches a section in the soil where the pH becomes acidic. Once the acidic pH is encountered, the metal will form a new species again. If this new species is positively charged, the molecule will once again migrate towards the cathode. This back and forth process can continue to occur thereby rendering the electrokinetic process ineffectual. For example, the distribution of hydrolysis products for lead shows that at pH values greater than approximately 6.0, lead begins to form various undesirable species (Baes, 1976). Cobalt begins to form precipitates at a pH value of approximately 9.0 and mercury exhibits the same trend at roughly pH value 7.0. Some of these species are anionic and others exist in a solid phase.

Another factor to be considered is the tendency for metal ions to become adsorbed onto the soil particles as a result of an increase in exchange capacity for the soil with increasing pH. This pH effect on single-metal adsorption has been discussed in detail by Basta and Tabatabai (1992). Therefore, if a suitable pH can be maintained throughout the soil, so that metals remain in the aqueous phase as soluble cations, their E-K removal efficiency should increase. One way of doing this is to maintain controlled solutions at the electrode sites. But since it takes only a few minutes (usually 15 to 30 minutes) for the electrode sites to obtain their final pH values during an E-K treatment, it is necessary to automate the process. A practical way that was experimented with was to control the pH by adding acid or base to the anode and cathode chambers.

3.4.1.1 Methodology

The first set of samples that utilized a complexing agent were set up in the manner that was described in Section 2.0, except that before the initiation of the test, the EDA was injected directly into the anode chamber of the cell in two of the samples. In the third sample the complexing agent was mixed into the slurry before consolidation. These samples are designated as KSEDA(metal)HM(#). The amount of chemical present in the soil sample was calculated and the complexing agent was added according to a 10 to 1 molar ratio of EDA to contaminant.

The same procedure was followed for the tests that were pH controlled. However, at the beginning of the test, the pH was measured by removing a small amount of water through the gas ports. The pH at the anode was raised to approximately 11.0 by adding concentrated sodium hydroxide (NaOH), and the pH at the cathode was lowered to approximately 2.0 by adding concentrated hydrochloric acid (HCl). pH readings were taken periodically throughout the tests. When the actual pH readings deviated from the desired pHs by more than 2 units, acid and base additions were repeated accordingly to bring the pHs back to the desired values.

3.4.1.2 Discussion of Results

The electrokinetic experiments were divided into three categories according to the contaminants, Co, Pb, and Hg. The tests were then subdivided into two categories - those which utilized the complexing agent EDA, and those which were pH controlled. The results from these experiments were compared with the results obtained in base experiments without enhancement. All the data in these groups of tests can be found in the Appendices A4.2 through A4.5. The index property and chemical concentration data are provided in Appendix C4. Typical soil pH distributions in the background and enhanced tests of mercury contaminated kaolinite specimens are shown in Figure 3.4.1.1.

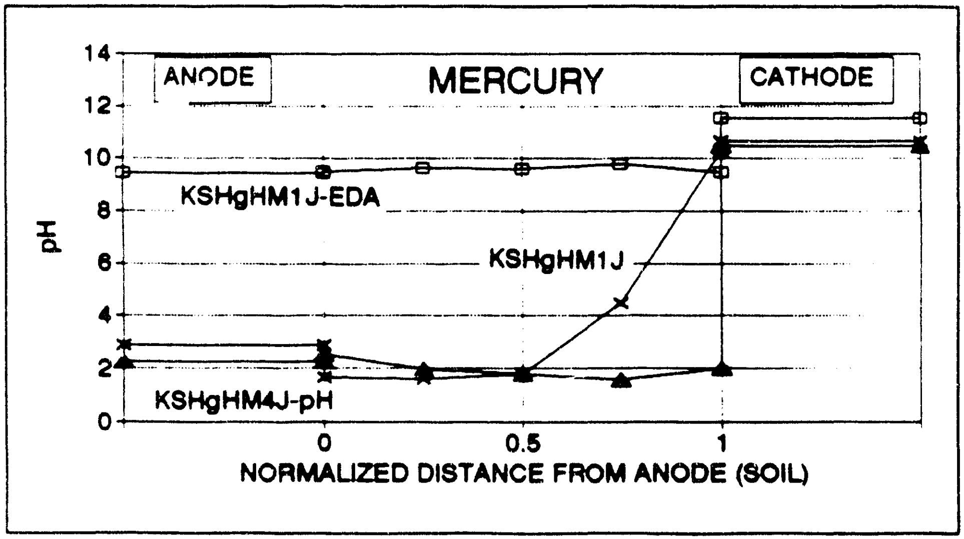

Figure 3.4.1.1. Post Enhanced and Unenhanced E-K Treatment pH Profiles of **Mercury** Contaminated Kaolinite Clay Soil Samples

I. COBALT SERIES:

In the cobalt series, the highest amount of flow was obtained from the tests which were conducted with the addition of EDA. The highest cumulative flow per moles of electrons transferred was also achieved in this series. The amount of contaminant removed was also slightly increased by the addition of EDA, as shown in Figure 3.4.1.2. The removal at the anode of the EDA specimens was close to the results obtained in the unenhanced base tests. However, the EDA series exhibited less of an accumulation of cobalt at the cathode end This indicated an overall improvement in the removal process.

While the pH controlled samples did not exhibit an increase in electroosmotic flow, they did demonstrate the highest amount of removal. Apparently, maintaining lower pH throughout the soil sample prevented the cobalt ions from precipitating out of the aqueous phase. The EDA injection, on the other hand, caused a high pH in the soil, which apparently arrested the H^+ ions and acted as a buffer against acid propagation.

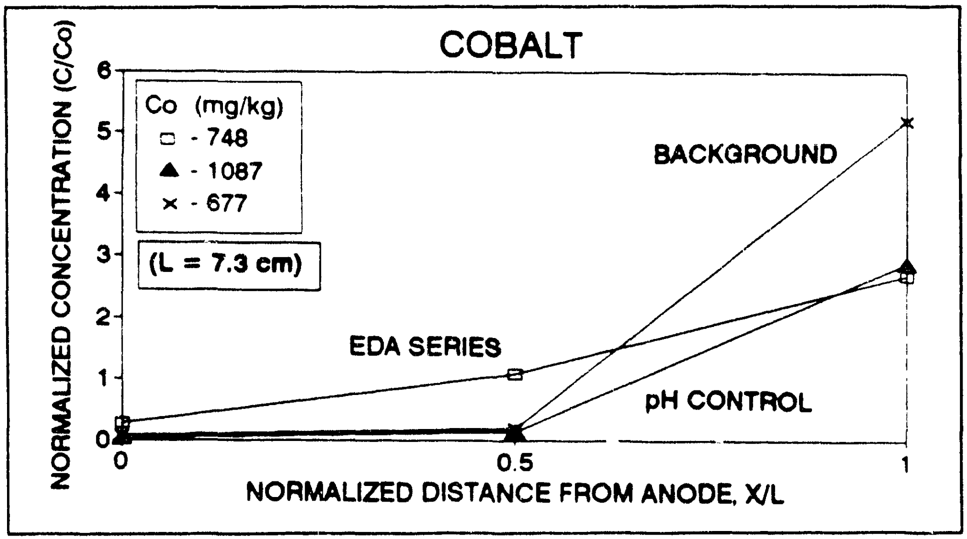

Figure 3.4.1.2. Post E-K Treatment **Cobalt** Concentration Profiles for Enhanced and Unenhanced Test Specimens of Kaolinite Clay Soil

II. MERCURY SERIES

In the soils which were contaminated with mercury, a notable improvement in electroosmotic flow was achieved in the EDA series. The removal process was also improved. The removal was better at the anode and cathode when compared to that of the background tests, as observed in Figure 3.4.1.3. The pH control tests produced good removal of mercury throughout the soil. In these tests the pH throughout the soil remained at approximately 2.0, which is well below the threshold at which Hg complexes precipitate.

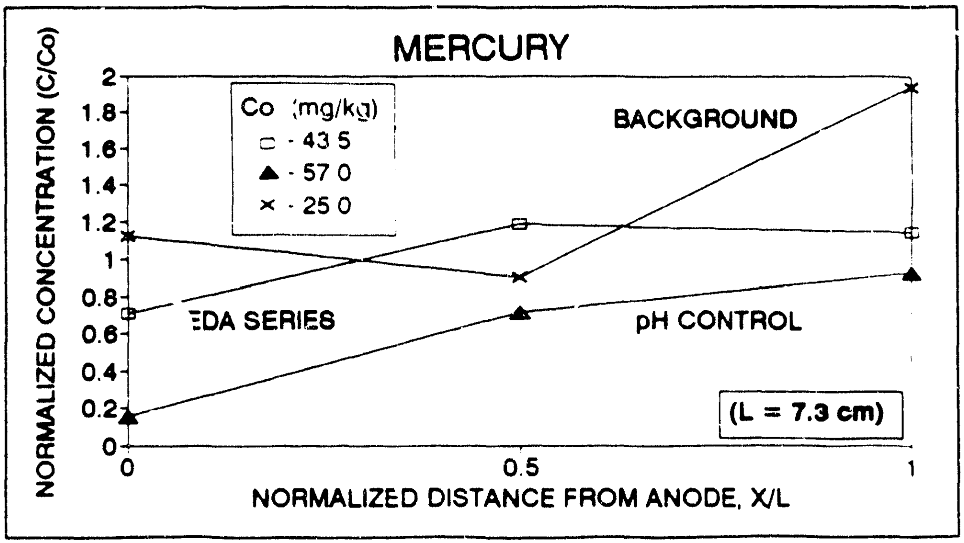

Figure 3.4.1.3. Post E-K Treatment **Mercury** Concentration Profiles for Enhanced and Unenhanced Test Specimens of Kaolinite Clay Soil

III. LEAD SERIES

As observed previously, the EDA series exhibited a higher amount of water flow per moles of electrons transferred than did the unenhanced background tests in the lead series. The EDA enhanced tests exhibited significant improvement in lead removal at the cathode region. While the concentrations in the anode and center remained slightly higher in the enhanced specimens than in the background tests, the enhanced method prevented the large accumulation of lead at the cathode region of the soil. The final concentration profiles for the 24 hour tests indicated possible plug flow type migration of the metal, as observed in Figure 3.4.1.4.

The lead samples which were pH controlled exhibited a higher flow rate than the background tests. The amount of removal was also significantly increased throughout the soil. The amount of removal was greatest (75%) when the pH control was extended to 48 hours of testing. The pH profiles of the enhanced test compared to that of the background, clearly showed a uniform low pH throughout the soil at the end of 24 hours.

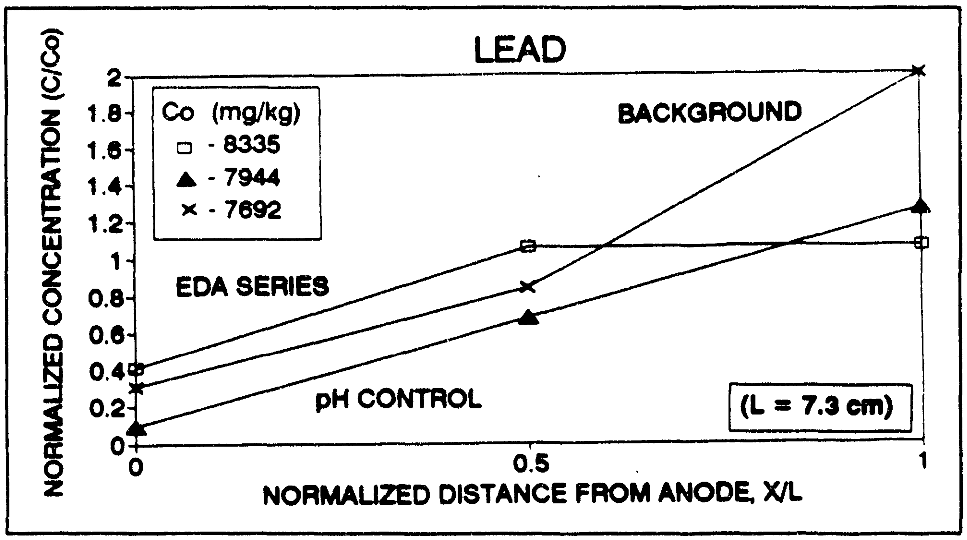

Figure 3.4.1.4. Post E-K Treatment Lead Concentration Profiles for Enhanced and Unenhanced Test Specimens of Kaolinite Clay Soil

Overall, the addition of EDA dramatically increased the current efficiency of the process. In all of the tests, including the zero contamination (pure kaolinite) samples, the pH throughout the soil specimen remained between 8 and 10 when EDA was injected into the anode chamber. Regarding these relatively high pH values observed, it is the result of acid-base equilibrium:

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2 + 2H^+ \leftrightarrow [H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3]^{+2}$$

H^+ will compete with metal ions with EDA for the lone electron pairs present on the nitrogen. If the proponated complex is thermodynamically more favorable than metal chelation, then the protonated complex will be formed, resulting in an increase in pH. When EDA is present in abundance, as was the case in this investigation (10/1 molar ratio of EDA/contaminant), sufficient metal chelation should take place also. EDA injection slowed, or probably completely arrested the electromigration of metal ions, however, enhanced the removal by making the metal unavailable for clay retention or precipitation. The metal concentration profiles of EDA injected specimens appear to be produced by a plug flow phenomenon which is dominated by electroosmotic advection. This mechanism is also evidenced by the significant increase in the measured current efficiency in these specimens.

The specimens, prepared by premixing EDA, showed the typical behavior of swelling clays, which is attributed to probable intrusion of the organic molecule into the lattice space of the clay mineral causing it to expand. The flow rates for these specimens were low, similar to Na-montmorillonite clays which are swelling type clay. The organic modification of soils/clays may prove to be beneficial if they become organophillic and preferentially select organic molecules over metal ions, therefore releasing them into the pore space. This aspect of the process was not looked into, although it may have implications as an alternate enhancement for metals removal.

pH control amplified the flow of water in some samples, but more importantly, it yielded the most significant improvement in chemical (organic and inorganic) removal. For all the metals investigated, pH control generated higher percentages of removal than the unenhanced background tests. The acidic pH forced the chemicals to remain in solution thereby preventing precipitation and adsorption onto soil.

3.4.2 Chemical Enhancement Methods for Organic Compounds

The current efficiency increased slightly and the 24 hour pH gradients appeared to be unaffected with the surfactant treatment. Each compound, however, responded slightly different to the surfactant treatment.

Chlorobenzene: When surfactant was injected at the anode side, contaminant mobility increased towards the cathode with approximately 80% reduction of the compound at the anode region and 50% increase at the cathode region.

Hexachlorobenzene: When surfactant was added at the anode side, substantial reduction of the compound occurred at the anode and center of the soil. When it was added at the cathode side reduction of the compound took place at the cathode and center of the soil. When the surfactant was injected into both of the chambers, no measurable quantity of hexachlorobenzene was detected in the post treated specimen. In all of the cases contaminant removal appeared to increase sharply over the unenhanced soil system.

Phenol: Contaminant reduction was most significant when the surfactant was added to the anode chamber of the soil system. The reduction of the compound was fairly uniform with the addition of the surfactant into both of the electrode chambers. The mobility of phenol was unaffected when the surfactant was added to the cathode chamber.

Trichloroethylene: TCE responded to surfactant treatment with largest reduction at the center and slight accumulation at either end of the soil when the surfactant was injected into the cathode chamber. No measurable reduction was observed when the surfactant was added into the anode chamber.

Table 3.4.1 summarizes the percent removal of the contaminant investigated after the chemically enhanced and unenhanced E-K treatment of kaolinite clay. These percentages are calculated using the minimum concentration of the compound achieved in each test.

Table 3.4.1 Percentage of Contaminants Removed From Kaolinite with Chemical Enhancement

Compound★	Compound Removal (%)			
	E-K Test Type			
	Unenhanced Tests	pH Control	Ligand Enhancement	Surfactant Enhancement (Max. Removal)
Cobalt	92.2① 91.1 - 93.2②	98.2 96.9 - 99.9	85.2 83.4 - 87.0	–
Mercury	26.5 4.3 - 41.7	83.8 65.9 - 100	27.8 25.6 - 29.9	–
Lead	69.0 64.2 - 74.2	90.5 85.1 - 97.2	43.7 20.3 - 67.0	–
Chlorobenzene	BDL③	–	–	82.2
Hexachlorobenzene	26.8 0 - 80.3	–	–	100
Phenol	33.7 30.3 - 36.9	–	–	81.0
Trichloroethylene	57.6 23.8 - 77.1	–	–	80.1

★ Percent Removals Calculated Using the Minimum Chemical Concentration
① Average Percent Removal for 3 Replicate Specimens
② Range of Percent Removals for 3 Replicate Specimens
③ BDL: Below Detection Limit (Initial Concentration Measured BDL)

3.5 Physical Enhancement of Electrokinetic Contaminant Transport

The experimental work to investigate procedures which may be applicable to physically enhance the removal of contaminants and to increase the efficiency of the electrokinetic decontamination process involved major modification of the existing laboratory set up. It was attempted to increase the migration potential of contaminants by either of following two ways:

i. Thermal enhancement: increasing the temperature of the pore fluid,
ii. Shear Wave enhancement: applying low amplitude-high frequency shear waves through the soil sample.

3.5.1 Thermal Enhancement

3. 5.1.1 Methodology

The cylindrical soil chamber was wrapped with heating tapes that are controlled by a temperature controlling unit. The cell was also insulated circumferentially to lessen heat loss to the environment once the desired temperature is reached. Temperature control and monitoring were performed with three thermocouples mounted into the soil sample through the acrylic soil chamber. The two end thermocouples were used for monitoring, while the center thermocouple maintained the desired constant temperature with a rheostat and a temperature controller. A schematic diagram of the test set-up is given in Figure 3.5.1.1.

Following a number of trials, the applied temperature of 115°F was selected. The soil samples were heated gradually in order to prevent overheating of the tape. The desired soil temperature was reached within one hour. Higher temperatures were avoided in order to prevent the excessive contraction-extraction of the acrylic test set-up. Temperature throughout the soil sample was monitored via a Model L1124S Speed Servo II Multipoint recorder which records temperature data at two-minute intervals. The voltage applied to the soil sample was 30 volts DC.

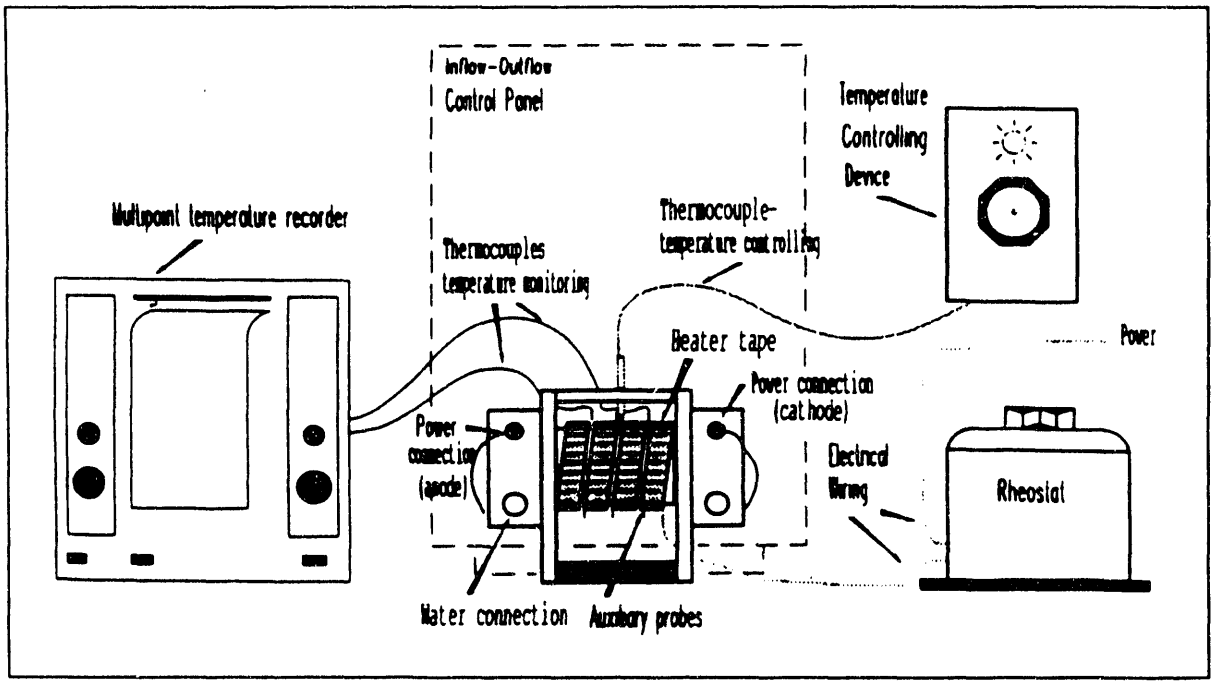

Figure 3.5.1.1. A Schematic Diagram of the Thermal Enhancement E-K Test Set-up

3.5.1.2 Results and Discussion

Thermally enhanced electrokinetic tests were run on blank and TCE-contaminated samples. The enhanced electrokinetic flow data was plotted and curve fit. The best fit was a straight line fit to the data. These plots are given in Figures 3.5.1.2 and 3.5.1.3. Figure 3.5.1.2 shows the comparison of thermally enhanced electrokinetic test results of kaolinite/distilled water to the unenhanced samples. Figure 3.5.1.3 gives the comparison of thermally enhanced electrokinetic test results of kaolinite/distilled water-TCE contaminated samples to the unenhanced samples. In all cases of thermal enhancement, the current efficiency increased significantly over that of the tests without enhancement, all other conditions being the same. The electroosmotic flow with thermal enhancement was observed to increase by a factor of five in some cases compared to flow with no enhancement. The chemical analysis data showed no TCE contaminant left in the soil samples at the end of thermally enhanced electrokinetic runs.

Campanella and Mitchell (1968) have presented some analyses for the interpretation of volume changes due to the thermal expansion of the soil, compressibility of the soil, and physico-chemical effects. When the temperature of a normally consolidated specimen was increased rapidly, a significant pore pressure would develop, even though the sample was maintained under fully drained conditions. The increased flow results presented here also agree with their findings. Therefore, the increased transport of TCE is attributed to thermal effects which probably promoted the migration of the contaminant into the pore fluid environment away from the clay surfaces by way of: 1) dissolution and 2) increased flow rate due to the increased water pressures.

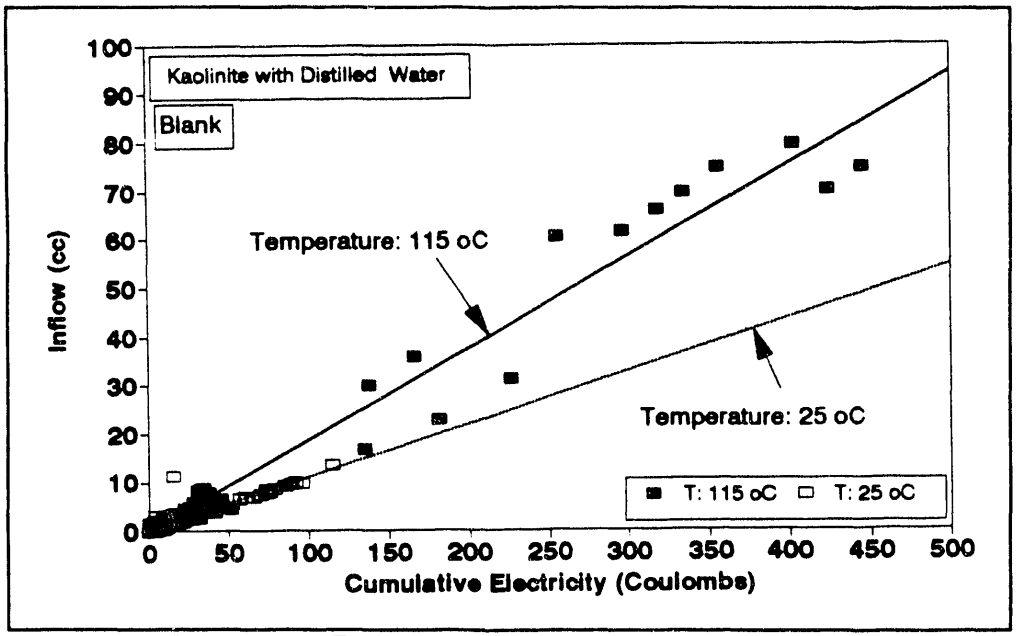

Figure 3.5.1.2. Current Efficiency of Thermally Enhanced and Unenhanced Kaolinite Clay with Distilled Water

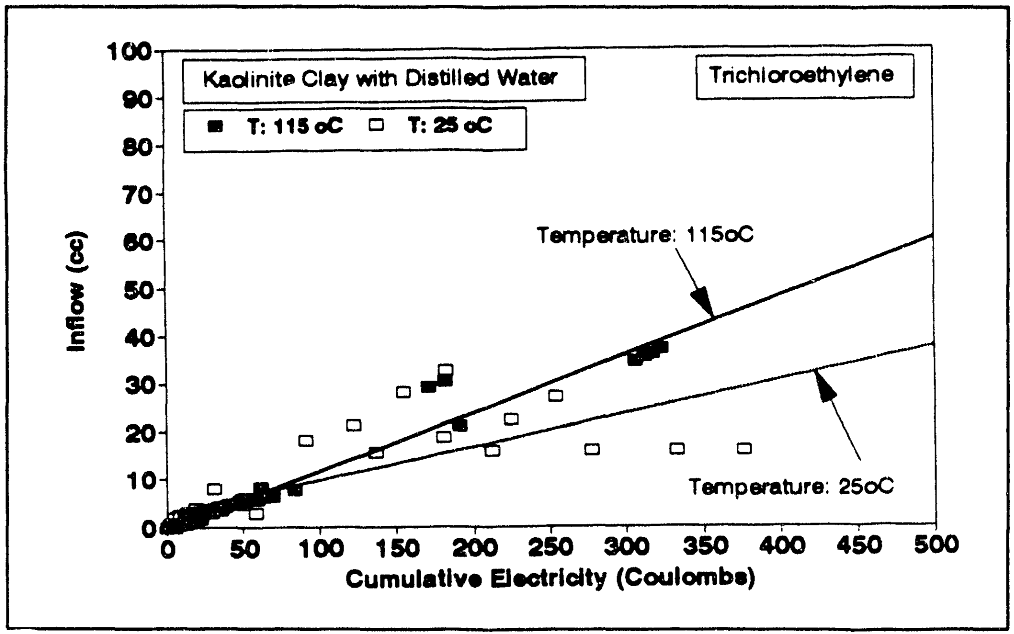

Figure 3.5.1.3. Current Efficiency of Thermally Enhanced and Unenhanced Kaolinite Clay with Distilled Water and **Trichloroethylene**

3.5.2 Shear Wave Enhancement

3.5.2.1 Methodology

In these series of experiments the approach was based on the phenomenon of seismic waves causing temporary instability condition in the ground by increasing pore water pressures progressively through the soil. Shear waves vibrate the particles perpendicular to the direction of the wave propagation.

Since the soil is confined with no deformation allowed, the vibratory or cyclic strains cause a progressive increase in the pore water pressure in the soil. This progressive increase (the level of which is dependent on frequency, amplitude, duration of vibration, and soil physical properties) should cause an increased tendency for the water to flow out of the soil pores. Thus, simultaneous application of the electrical potential and shear waves should cause an enhanced flow rate, and therefore increase the flushing of contaminants. Another anticipated result of shear wave propagation is the physical loosening of the contaminants that may be in the form of colloids or micelles, away from the clay surfaces by the particle velocity imparted. Similar work has been conducted by Muralidhara and co-workers (1990) in which the mechanical energy transmitted in an acoustic field coupled with electrokinetics was demonstrated to enhance mobilization of some organic compounds and metals.

The E-K cells were modified to facilitate the application of shear waves. Inflow and outflow were monitored via a control panel. An automated acquisition system for voltage, current, and pressure data were used. The following units were mounted on the electrokinetic cells to apply the shear waves: 0.240"x 0.240"x 0.023" piezoceramic bender elements were soldered to electrical wiring in series and mounted normal to the surface of each porous stone with proper casing so that they would be embedded into the soil when assembled (Dyvik and Masdhus, 1986). One bender element was used to generate a shear wave pulse which propagates along the length of the specimen and the other element was used to monitor the arrival of the shear wave at the other end. Due to the very short travel time of the shear wave from one end of the specimen to the other, the use of an oscilloscope of high resolution and accuracy was needed. The use of a function generator allowed for the application of different wave forms with a range of amplitudes and frequencies. A pore water pressure transducer was used to monitor the pressure variations within the specimen during the application of shear wave. Figure 3.5.2.1 shows a schematic diagram of the experimental set-up.

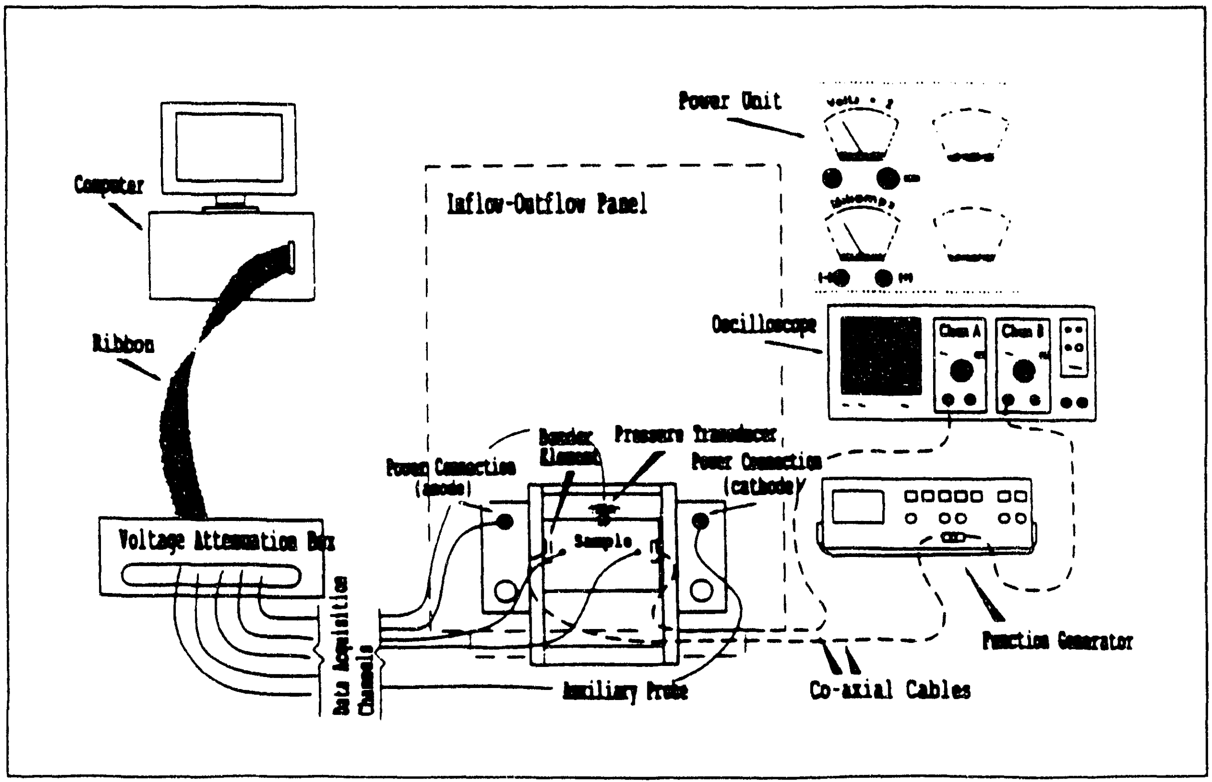

Figure 3.5.2.1. A Schematic Diagram of Shear Wave Enhancement E-K Test Set-up

3.5.2.2 Discussion and Results

The piezoelectric bender elements were placed in an approximate area of 0.25" x 0.50" at the center of the porous stones. Therefore, the flow area of the porous stone was decreased by about 15 percent. This difference was evidenced by a slight decrease in water inflow during the electrokinetic runs with the bender element mounted-porous stones at the ends of the soil sample, but without application of shear waves. The blank and contaminated (TCE) kaolinite soil samples were subjected to E-K treatment with shear wave enhancement at two different frequencies, 1500 Hz and 4000 Hz. The duration of these tests were again 24 hours.

The results of these tests showed no appreciable improvement in current efficiency or contaminant removal over the duration and frequencies of shear wave enhancement investigated. Since the level of increased pore water pressures is dependent on frequency, amplitude, and duration of vibration, it may be necessary to run more electrokinetic tests with shear wave enhancement for longer terms to find the most effective shear wave frequency and amplitude.

3.6 Electrokinetic Treatment of Reference Soil Matrix With Mixed Contaminants

In response to the Resource Conservation and Recovery Act (RCRA) Hazardous and Soil Waste Amendments of 1984 prohibiting the continued land disposal of untreated hazardous wastes, the EPA has instituted a research and regulatory development program for establishing Best Demonstrated and Available Technologies (BDAT) for RCRA and Superfund wastes. Under Phase I of this program, a surrogate soil containing a wide range of chemical contaminants typically occurring at Superfund sites was prepared for use in bench - scale or pilot - scale performance evaluations of available treatment technologies. This soil is referred to as SARM, an acronym for Synthetic Analytical Reference Matrix. Ten electrokinetic tests (three on "clean" soil and seven on "contaminated" soil) were run to evaluate the feasibility of this technology in removing contaminants at a "typical" hazardous waste site.

3.6.1 Composition of SARM

The clean and the contaminated SARM samples were prepared and provided by US EPA. The "clean" SARM consisted of 30% by volume clay (a mixture of montmorillonite and kaolinite), 25% silt, 20% sand, 20% topsoil, and 5% gravel. The components were first air-dried, then mixed together in a standard truck-mounted cement/concrete mixer. A prescribed list of the most frequently occurring chemicals found at Superfund sites were then added to the clean SARM in a series of smaller-scale mixing operations utilizing a 15 ft^3 mortar mixer. These chemicals include metal contaminants (arsenic, cadmium, chromium, copper, lead, nickel, zinc) and organic contaminants (acetone, chlorobenzene, 1,2 dichloroethane, ethylbenzene, styrene, tetrachloroethylene, xylene, anthracene, bis(2-ethylhexyl)phthalate, and pentachlorophenol.

3.6.2 Methodology

For this project, four tests on Category II SARM (low organic and low metal concentrations) and three tests on Category IV SARM (high organic and high metal concentrations) were conducted. These tests were run in a manner similar to that described in Section 2.0, with the exception that no consolidation was performed in the preparation of the contaminated soil specimens. Plastic tubes were used to extract the soil from their jars as it was originally packed at the EPA laboratory. The retrieved specimens were subsequently inserted into the cylindrical soil chambers of the electrokinetic apparatus. After the electrokinetic test, the soil samples were analyzed for four metals (cadmium, nickel, lead, and zinc) and two organics (acetone and chlorobenzene). The "clean" reference soil specimens were prepared by slurrying the dry soil (as received from EPA) and consolidating it to 200 kPa normal pressure. All the flow results, pH profiles, and concentration profile results for these tests can be found in Appendices A6. The index property and chemical concentration data are given in Appendix C6. The low concentration SARM specimens are designated as RSIIL(#), and the high concentration specimens are designated as RSIVH(#).

3.6.3 Discussion of Results

3.6.3.1 Electroosmotic Water Flow

The duration of E-K treatment was staggered for the replicate samples to detect any improvement in decontamination with time. One of the low concentration sample runs (RSIIL4B) was terminated after 168 hours (7 days). The data of electroosmotic water flow through clean SARM specimens were similar to those of the artificial specimens prepared by mixing sand and 10% Na-montmorillonite. The flow rates were relatively high, but not steady state. High current densities (0.7 - 1 mA/cm^2) developed with flow which indicated possible dissolution of the clay constituents. Similar trends were also observed in the sand and clay mixed specimens. The current efficiency graph for the low and the high contaminant concentration sample tests is given in Figure 3.6.3.1. The variation of normalized flow with moles of electrons transferred is fairly linear and the low concentration specimens exhibit higher current efficiency than the high concentration specimens. These observations are consistent with the earlier findings with specimens containing single metal contaminants. Therefore, the electrokinetic flow of water appears to be unaffected by the presence of mixed wastes in the soil.

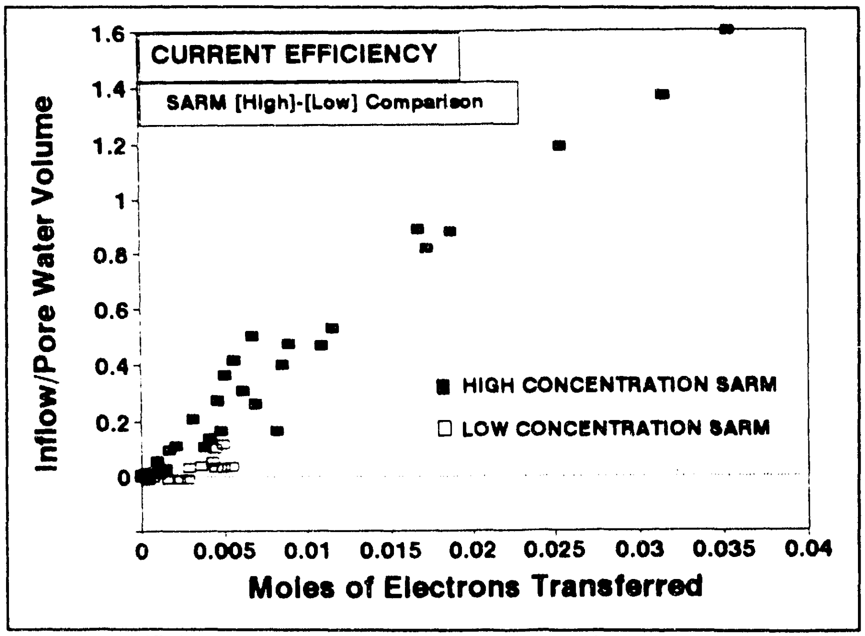

Figure 3.6.3.1. Current Efficiency of Synthetic Reference Soil Matrices **(SARM)** with High and Low Concentration of Contamination

3.6.3.2 Contaminant Transport

The metal and the organic compound concentration profiles for the low concentration SARM specimens are given in Fig 3.6.3.2. The samples designated as **RSIIL1B**, **RSIIL2B** were retrieved from the top half of the jar containing the original mixture of SARM, while the samples designated as **RSIIL3B**, **RSIIL4B** were obtained from the bottom half of the jar. Subsequent analysis of initial concentration of the four metals (Cd, Ni, Pb, Zn) in the top and bottom halves of the SARM soil revealed different results. A replicate low concentration (Category II) SARM soil was again sampled at the top of the container to confirm the initial findings. These results are presented in Table 3.6.1. As observed, there is a factor of three difference in concentration between top and bottom in 4 of the metals analyzed. This concentration increase may be attributed to segregation of the soil specimen whereby the heavier soil particles settle down increasing the dry density (Table C6.1). The slight variation in the water content at the top and the bottom

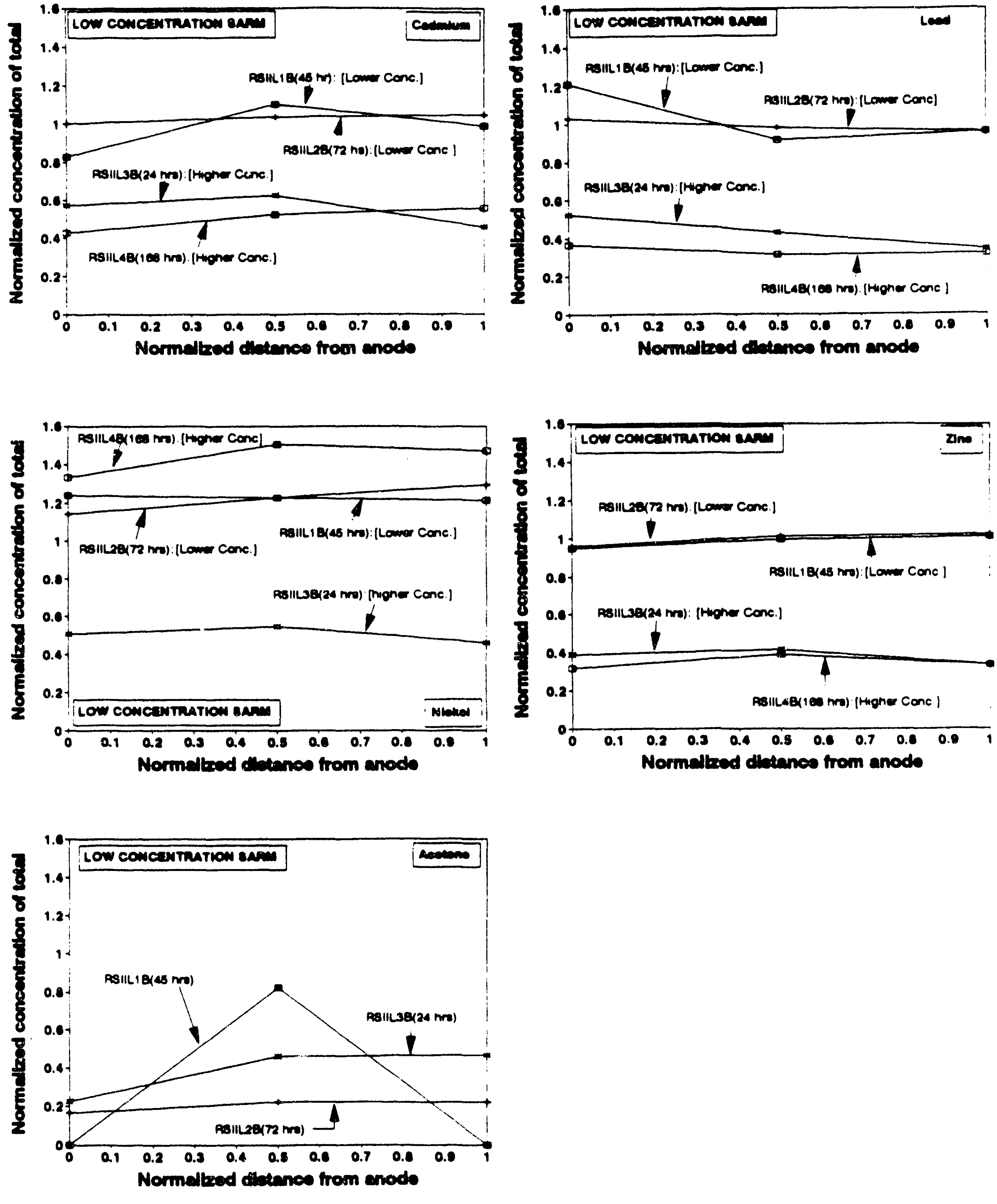

Figure 3.6.3.2. Concentration Profiles of Selected Contaminants in **Low Concentration SARM** Soil Specimens

may also be a factor in these results. The concentration profiles were prepared with this variation taken into consideration.

The four metal concentration profiles for RSIIL1B (45 hours) and RSIIL2B (72 hours) are consistent and are fairly uniform across the soil specimens. The normalized concentrations of all four metals remain at around one throughout the soil which indicate little or no removal of the metal for the duration of treatments. There may be several reasons for this occurrence:

(i) The four metals analyzed are strongly adsorbed onto soil, and other metals, which are present in the mixture are preferentially moved by electrokinetics.
(ii) These metals are not in ionic state, and thus migration in the aqueous phase does not occur.
(iii) The soil-contaminant mixture has a high buffering capacity which does not allow the acid front to propagate as fast as it does in pure systems.

Table 3.6.1 SARM (II) Metal Concentration Analysis (RSIIL Series) - Initial Concentration

Metal	EPA Target Concentration (mg/kg)	Lehigh Analysis of Concentration★, (mg/kg)			
		SARM Jar #1 Top	SARM Jar #2 Top	Average of Jars 1&2 / Top	SARM Jar #1 Bottom
Cd	20	21.1	22.6	21.9	49
Ni	20	58.3	36.6	47.5	70
Pb	280	256.0	298.6	277.3	901
Zn	450	491.5	524.4	508.0	1536

Water Content (%)	-	17.9	18.0	-	19.7

★ Jar #1 and #2 contain replicate samples or contaminated SARM provided by EPA

The last conclusion may be supported by the measured pH distribution in the soil and the electrode chambers at the completion of each test (A6.4). The average pH variation from anode to cathode region for the low concentration series was 4 to 12, and for the high concentration series it was 4 to 6. The soil pH gradient remained fairly constant through the 7 days of treatment for the low concentration specimens, with a linear distribution of pH from about 4 at the anode region to 12 at the cathode region . Soils exhibit significantly higher retention capacities at high pH values. Furthermore, all four metals analyzed will form insoluble salts in these pH ranges observed. The pH profiles of the high concentration specimens at the completion of the 24 to 72 hours of treatments show that the pH remains fairly constant at around 6, except for the first quarter of the samples at the anode end. It appears that these soil-contaminant mixtures also maintain a level of buffering capacity; however, not as high as the low concentration sample series. This is probably due to the initial pH resulting from the higher concentration of the metals present in these mixtures.

The samples designated RSIIL3B (24 hours) and RSIIL4B (168 hours) have higher initial concentrations of the metals since they were retrieved from the bottom portion of the sample jar, as indicated in Table 3.6.2. At these concentrations, they are probably present in excess of the exchange capacity of the soil. Therefore, the metals in the aqueous phase are expected to migrate. Except for nickel, the 24 hour and the 168 hour concentration profiles of the metals in these samples are sufficiently close. This observation may indicate that once the metals in excess of the soil exchange capacity are removed, prolonged treatment may have little effect unless enhanced by a secondary (chemical or physical) method. Since there is little difference between the 24 hour and 168 hour treatment profiles, it may be viable to assume that by 168 hours most of the excess metal is removed from the soil. Therefore the remaining metal in the soil should be strongly adsorbed. If this assumption is valid, then the ratio between the average concentration distributions of RSIIL1B, RSIIL2B (all metal exchanged and strongly adsorbed) and the RSIIL4B (some metal available in excess of soil exchange capacity) should roughly be the same as the ratios between the corresponding initial metal concentrations in these soil samples. These ratios are computed as: 0.45 for Cd; 0.67 for Ni; 0.31 for

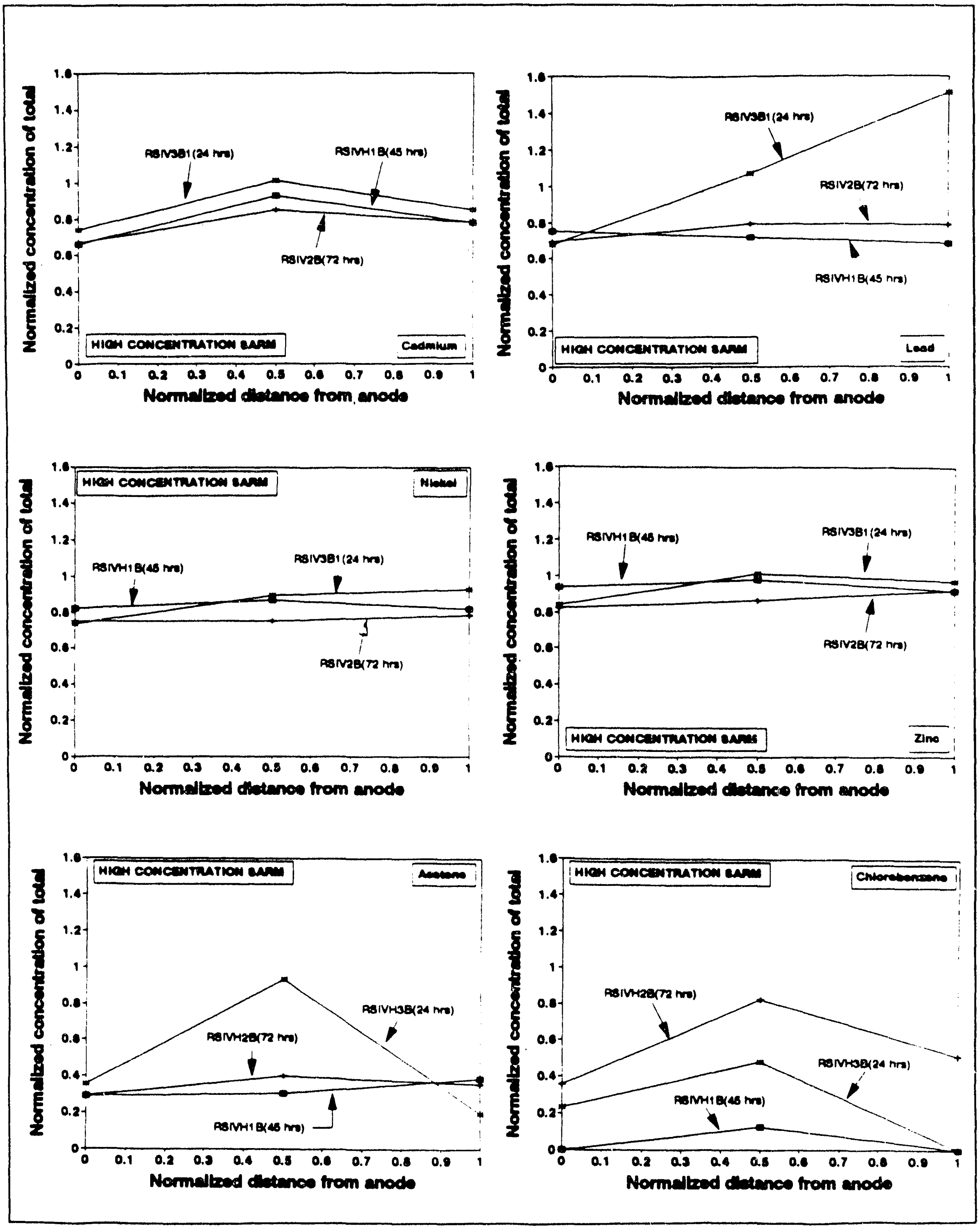

Figure 3.6.3.3. Concentration Profiles of Selected Contaminants in **High Concentration SARM** Soil Specimens

Pb, and 0.33 for Zn. Observing the metal distributions for Cd, Pb and Zn, these ratios hold true between the two sets of specimens. Also presented in Figure 3.6.3.2 is the distribution of acetone for 3 replicate samples of SARM (II). The acetone is reduced by approximately 80% throughout the soil at the completion of 72 hours of treatment. These samples were also analyzed for chlorobenzene. The measured concentrations of chlorobenzene were below the detection limits of the equipment, and therefore are not presented here.

The concentration profiles of the four metals and acetone after the E-K treatment of SARM (IV) (high contaminant concentration soil) are presented in Figure 3.6.3.3. All of the metals were reduced consistently with increasing time of treatment, the greatest being lead by about 25% at the end of 72 hours. Acetone shows a similar trend to that of the low concentration case. It appears to have reduced by about 60% across the soil after 72 hours. The chlorobenzene results showed inconsistencies with respect to the duration of treatment. These results may be biased by the volatilization of the material during preparation and handling of the samples and E-K testing. The reduction of chlorobenzene in the overall soil specimen was evident with all the normalized profiles falling below one with treatment (A6.5).

In the overall analysis of the results pertaining to SARM soil, the following observations were made:

1. Soil's natural buffering capacity may be an important factor in the prediction of metal extraction from soil by electrokinetics.
2. In mixed waste cases, preferential migration of metals may be caused by electrokinetics. This migration may further be governed by the soil exchange capacity and preferential retention of the metals by the soil.
3. In natural soils, it may be necessary to use secondary treatment or enhancement methods in conjunction with electrokinetics to extract metals into the aqueous phase due to the buffering of the soil/mixture and the high pH maintained throughout the treatment.
4. Unlike the general trends observed in pure systems of clay and single contaminant, the SARM soils did not exhibit a sharp concentration increase of metals at the cathode end of soil. In contrast, the reduction appeared to be more uniform throughout the soil specimens, for the metals and organics analyzed. This trend was more evident in the high concentration series and may be attributed to the development of a relatively uniform and neutral pH distribution throughout the soil.
5. Electrokinetic flow of water was observed in both the high and the low concentration series of samples with relatively higher current efficiency in the low concentration case. The inflow versus moles of electrons relation was a straight line, indicating consistency of the behavior observed for SARM samples with that of the pure soil samples.

4.0 TECHNOLOGY STATUS

Electrokinetics is a technology which will have an impact on the future *in-situ* remediation of DOE sites. The process in the laboratory has demonstrated the potential to move contaminants of both ionic and nonionic nature through various types of soil. Two mechanisms have been inferred by the laboratory studies and validation of the model used in the program. These mechanisms are electroosmosis which is the primary movement of water, and ion mobilization which moves ions toward the anode or cathode, depending upon their residual charge. Anions, such as chromate and arsenate, moved toward the anode while cations such as cesium and strontium moved toward the cathode.

The electrokinetics treatment is an integrated system which has the potential to solve soil remediation problems under a broad range of real site conditions. The process can work in parallel with a surfactant flush, pump and treat scheme. The electrokinetic process has been demonstrated in the field for other activities such as site dewatering, water collection and oil recovery. It is one of the few processes, which can treat contaminated soils without excavation, and without requirement of a large area for operation of equipment.

4.1 Technology Development Evaluation

Progress has been made in electrokinetic technology development, as related to the following:

Cost / Benefit: A cost evaluation, based on laboratory results and previous in-field investigations (Bell and Titus, 1974; Bell et. al, 1983; and Titus et. al, 1985) provided our basis for estimating the treatment costs. For a 10,000 cubic yard site including equipment, power, and post-waste treatment, the cost is on the order of $37.5/cubic yard. This estimation compares favorably with estimations calculated by other researchers in this development field.

Assuming a 10,000 cubic yard site of 150' x 60' and 30' deep for treatment by electrokinetic process, the following itemized cost estimates are made:

Item		Cost
• Equipment		
Depreciation (6 months use)		
Electrical Equipment	$ 20,000	
Surface Equipment	$ 15,000	
		$ 35,000
Disposable		$ 50,000
• Manpower		
Supervision	$ 38,000	
3 Workmen @ $ 50,000/year each	$ 75,000	
		$113,000
• Liquid treatment on surface		$ 50,000
• Laboratory work; indirect cost and profit		$100,000
• Contingency		$ 27,000
TOTAL		**$ 375,000**

This estimation results in a net cost of $ 37.5/cubic yard of soil.

If alternatively, the contaminated soil is excavated, part incinerated and part moved to a hazardous landfill, and the hole backfilled with clean fill material, the estimated cost is on the order of $ 500/cubic yard. For 10,000 cubic yards of contaminated soil, the total cost is then $ 5,000,000. Assuming there are 50 such sites, the overall cost would be $ 250,000,000. Application of electrokinetic treatment to these sites, at a cost of $ 37.5/cubic yard should then produce savings of over $ 230,000,000. Based on the waste volumes estimated in the June 1990 DOE/S-0078P Environmental Restoration and Waste Management Five-Year Plan our estimates are conservative but attainable. In the Five-Year Plan, clearly defined contaminated soils totaling more than 9 million cubic yards are identified.

Risk Reduction: The benefit of electrokinetics to reduce acute health risks is its projected ability to direct contaminants toward a collection system. This feature of the process can prevent uncontrolled migration through the vadose zone and ground water. Because excavation is not involved in this process, the risk of human exposure to the contaminated soil is greatly reduced. Although a secondary aqueous phase is produced, the collected material can be treated by conventional means in a closed system treatment process.

Required Performance Specifications: Performance specifications have not been identified for most *in-situ* treatment process. Although reductions of up to 99.9% have been demonstrated in the laboratory, field demonstration guidelines need to be developed through field testing and treatability studies on site specific soil samples using electrokinetic process.

Regulatory Requirements: It is anticipated that the regulatory requirement issues relating to public health, safety, and risk can be met. It is anticipated that the contaminants will be removed to a level where (theoretically) material will not be adsorbed to the soil, so there will be no adverse impacts to the health or safety of humans through air release or transport to groundwater.

Schedule Advantages: Electrokinetics is not a long "lead time" process. The necessary hardware to construct an electrokinetic treatment is readily available. The start-up time for this remedial scheme is dependent upon the availability of the necessary site data and operating permits. A field demonstration could realistically be established within 9 to 12 months.

4.2 Technology Integration Evaluation

Approach to regulatory compliance: The pertinent regulatory issues may include the following:

1. Minimum excavation requirement;
2. *In-situ*-Process;
3. Minimum or no noise during operation;
4. No adverse visual impact.

Acceptability to the public: The process should be acceptable to the public, since there is minimal impact on the environment during and following remediation.

Unique contribution to the contaminant remediation technology: E-K remediation is a unique process, being one of the few available technologies which can effectively function *in-situ*. In low permeability soils, this technology has promise for high removal efficiencies. The process can work with both inorganic and organic contaminants.

Need for ancillary technologies: Technology may be required for the treatment of produced fluids containing organic and inorganic contaminants. Both innovative and conventional techniques may be used, including chemical treatment ion exchange and carbon adsorption.

Opportunities for technology transfer: Opportunities for technology transfer may be appropriate. The electrokinetic treatment process holds promise as a break through technology for the remediation of large areas of DOE contaminated sites without the need for excavation and removal.

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