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INJECTION OF SPECIES UNDER ELECTRICAL FIELD TO ENHANCE BIOREMEDIATION

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Civil and Environmental Engineering

Md. Fazle Rabbi
B.Sc., Bangladesh University of Engineering and Technology, 1988
M.S., Louisiana State University, 1995
December, 1997
ACKNOWLEDGEMENTS

In the name of all mighty God whose mercy and blessing is everywhere: My deepest appreciation is extended to the late Dr. Yalcin B. Acar, whom I met as a mentor/advisor and above all as a friend. He introduced me to the topic, gave me many resources to initiate and formulate the study and encouraged me every stage during his life time. It was a well rewarding experience to have been under his supervision.

I am immensely grateful to my advisors Dr. Roger K. Seals and Dr. John H. Pardue for their technical assistance to accomplish this study. Dr. Robert J. Gale provided invaluable suggestions towards the successful completion of this study and is also acknowledged with gratitude. I also owe a debt to the other committee members Dr. Donald Dean Adrian, Dr. Gary Breitenbeck and Dr. Caye M. Drapcho for their comments and suggestions which have aided in properly formulating and developing this work.

Thanks are due to all my fellow graduate students with whom I spent a pleasant time in LSU.

Finally I would like to thank all of my family members, especially my father, who have been continuous source of inspiration throughout my life.

This study was funded by Electrokinetics Inc., DOE, EPA and LEQSF.

This dissertation is dedicated to the late Dr. Yalcin B. Acar.
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ABSTRACT

Electrokinetics is one of the most viable alternatives for injecting/extracting water, organic and ionic species in low permeability soils as well as heterogeneous media because the transport processes are independent of the pore sizes. A better understanding of the principles offers the opportunity to employ multi-component species transport under electrical fields to inject electron acceptors, nutrients and other process additives for enhancement of in-situ bioremediation in low permeability and heterogeneous media. This study assesses the potential to employ and exploit the principles of multi-component species transport under electrical fields as mean to supplement, enhance and engineer in-situ bioremediation. It was determined that ammonium, sulfate, nitrate and phosphate ions can be injected in different types of soils and in a layered deposit with significantly different hydraulic and electrical conductivities. Ions transport rates of 8 to 20 cm/day occurred under current densities of 15 to 150 mA/cm² and voltage gradients less than 1 V/cm. A uniform distribution of the process additives could be achieved across the electrodes. These results are quite encouraging and demonstrate that the electrokinetics injection scheme has significant potential for in-situ bioremediation in low permeability soil as well as heterogeneous media.

The transportability of the injected ions also depend on the charge concentration of the other competing ions on the pore fluid. The
accumulation of these pore fluid ions in the system would decrease the transference number of the injected ions. The transportability of the injected ions could be increased by flushing intermittently or continuously the electrodes compartments to decrease the conductivity at the boundaries, which would increase the initial pore fluid ions to be flushed out from the system.
A wide variety of physicochemical treatment technologies are currently available to treat soils contaminated with hazardous materials, including excavation and burial in a chemically secure landfill, vapor extraction, stabilization and solidification, soil washing, soil flushing, super critical fluid extraction, chemical precipitation, vitrification and incineration (U.S. EPA, 1988). One of the recent technological developments in the field of soil remediation is electrokinetics. The features of the electrokinetic method as an eminent technology have been promulgated by a number of investigators (Acar and Hamed, 1991; Acar and Alshawabkeh, 1993; Shapiro and Probstein, 1993). This emerging technology has the potential to remove organic and inorganic contaminants from soils by using very low DC currents in the order of mA/cm² of electrode area.

Most of the physicochemical technologies are not economically feasible. The high cost of remediation techniques ranges up to $1500 per cubic yard of soil (Acar, 1992). Many of the available technologies do not destroy the hazardous compounds. Rather, the chemicals are often transferred from one phase to another. Since these methods do not completely destroy the contaminants and they are often costly, alternative remedial techniques have been investigated.
Bioremediation is a very viable alternative technology because in many cases total destruction of organic contaminants are possible at a reasonable cost (Gupta and Djatari, 1994). Bioremediation, the utilization of microorganisms to metabolically mediate desired chemical reactions or physical processes, can often fill the need to detoxify contaminants or contribute to the solution in congruence with other technologies (Thomas and Ward, 1989).

Electrokinetic remediation is a technique where electrodes are placed (in a open flow or closed flow arrangement) across the soil mass to employ a very low DC electrical current density or low electrical potential difference to transport the species under coupled and/or uncoupled conduction phenomena, which result from the physicochemical and hydrological changes in the soil matrix (Acar et al., 1993; Acar and Alshawbkeh, 1993; Runnells and Wahli; 1993; Pamukcu and Whittle, 1993). Generally, externally supplied fluid, or groundwater, acts as the conductive medium (Acar and Gale, 1992; Acar and Alshwabkeh, 1993). The migrations of the species under electrical field are influenced by the prevailing electrolysis reaction at the electrodes and mechanisms that involve transporting species under an electrical field. The process additives can be injected into the system at the electrodes by the electrolysis reactions at the electrodes, or by cycling the processing fluid, and the species will move across the soil by coupled and/or uncoupled conduction phenomena under electrical fields. These electrical
conduction phenomena with other physical and chemical transformations in the soils will compose the basic mechanisms of the electrokinetics remediation technique. This technology has mainly been studied for inorganic species; however, it may be possible to employ electrokinetics in bioremediation to engender an effective level of uniform injection of nutrients, electron acceptors/donors, microbes or other process additives in a heterogeneous soil matrix which will simulate the annihilation process of contamination by the oxidation reactions catalyzed by microbes. Acar, 1990; Acar and Hamed, 1991; Acar et al., 1992a; Acar 1992; Acar and Alshawabkeh, 1993; Alshawabkeh and Acar, 1996; have adumbrated, “the opportunity exists to employ the multi-species transport phenomena under electrical fields to inject nutrients in enhancement of in-situ bioremediation and to initiate and sustain an effective level of bioremediation by microorganisms.”. The term bioremediation refers to the complete microbial destruction of contaminants (mineralization process), or transformation of an organic chemical into another form (biotransformation). This transformation may be minor, involving modifications such as simple oxidation, or reduction, or loss of functional groups from a molecule. Complete biodegradation to inorganic molecules is termed mineralization. Mineralization under aerobic conditions results in the formation of biomass, water and inorganic products such as CO₂. On the other hand, mineralization under anaerobic condition results in the formation of additional biomass, water, inorganic products, and
any one of a combination of partially oxidized carbon compounds (e.g. methane, organic acids, or others). In pollution control and site remediation industries, bioremediation is commonly assumed to mean mineralization (Slater and Lovatt, 1984).

Stimulation of microbial populations within a subsurface requires an appropriate carbon source, electron donors/acceptors for energy production, and inorganic nutrients such as nitrogen, phosphorous and some trace metals. Also, proper conditions within the soil environment such as appropriate pH, temperature, moisture content and redox potential are required which can adequately bolster the growth of desired organisms for a prolonged period. However, there also exist several major technical impediments to more widespread use of biological methods for the treatment of contaminated soils. The full potential of *in-situ* bioremediation are limited due to ignorance of coupled geological, hydrological, physical, chemical, and microbiological processes in the subsurface environment. Many intractable problems of the heterogeneous nature of the matrix and the contamination itself (Skladany and Metting, 1993) cannot even be adequately characterized. To develop an optimum and implementable bioremediation design, the site has to be fully characterized. Beside the extent, the type and the degree of contamination, the knowledge of hydrogeological properties is important to design an *in-situ* bioremediation operation (Gupta and Djatari, 1994). In conventional bioremediation, the permeability of the formation is
the primary limitation to delivering oxygen and nutrients to bacteria. Using a simplified (VS2DT) Variability Saturated 2 Dimensional Transport Model, Lappala et al., 1987; Healey, 1990), the feasibility was investigated of transporting oxygen and nutrients into a thin layer of waste (1 to 3 feet) with a much more permeable overlying aquifer material (permeability at $10^{-1}$ cm/s). The model results indicated that at a well spacing interval of 15 feet (total 100 to 150 injection wells per acre), only 0.3 to 0.5 percent of the solution will flow through the waste material and the reminder will bypass this waste layer (Djatari and Gupta, 1992). These results demonstrated the infeasibility of transporting process additives and further emphasize the ineffectiveness of bioremediation in low permeability deposits. The success of a biological treatment method depends on how efficiently and uniformly an engineered system can transport the required process additives, such as electron acceptors/donors, nutrients, surfactants and cometabolites, into the biologically active zones (BAZs). So the uniform and efficient introduction of process additives in BAZs is the bottleneck for a successful implementation of in-situ bioremediation (Suflita and Sewell, 1991; Zappi et al., 1993).

1.1 Objectives

It is required to develop electrokinetic techniques that will deliver necessary additives to optimize the conditions for microbial growth. Electrokinetic injection offers significant advantages over a conventional pump and treat system. It is essential to evaluate the technical merit of the
proposed scheme and several hypotheses need to be tested. The following hypotheses will be evaluated:

1. Selected electron acceptors and nutrients can be efficiently injected in deposits with varying degrees of permeability and pore fluid conductivities under electrical fields.

2. A uniform distribution of these process additives can be achieved across the electrodes.

3. Electric fields could effectively be used to direct the electron acceptors and nutrients in desired locations in a deposit with heterogeneities.

1.2 Scope Of the Research

It is well established that natural, indigenous microbial populations are always present in the vicinity of Non-Aqueous Phase Liquids (NAPLs) encountered in subsurface deposits (NRC, 1993). Nutrient deficiency and the resulting restriction in reproductive capacity of the microbial population constitute the reasons why these microorganisms cannot biologically oxidize the anthropogenic compounds. The poor bioavailability of NAPLs is another reason. The food sources (organic species) often need to be supplemented by nutrients and electron acceptors in order to initiate microbial enzyme release and transformation into active states. Transport of these species under electrical fields definitely poses an intriguing and viable alternative,
especially in soils with low hydraulic conductivities, as well as in heterogeneous media.

1.3 Organization of the Dissertation

The dissertation consists of five chapters. Chapter 1 introduce the motivations of the research and the objectives and scope of the research. Chapter 2 describes the background information about electrokinetic soil remediation and bioremediation. Identification and significance of the problem associated with the current available technologies in bioremediation also are summarized in this chapter. The proposed research scheme is also described in this chapter from the recent understanding of the electrical conduction phenomena in soil. All laboratory testing conducted and the methodology employed are described in Chapter 3. The results and discussion are presented in Chapter 4. Practical implications of the research are discussed in chapter 5. Chapter 6 summarizes the conclusions derived from this research work and recommendations for future research are presented in this chapter.
CHAPTER 2
BACKGROUND

2.1 Identification and Significance of the Problem

The ever-growing demand to introduce in-situ technologies in environmental restoration stimulated the vision and the desire to employ conduction phenomena under electrical fields for 1) extracting chemical species from soils under electrical fields (electrokinetic remediation) (Acar and Gale, 1992; Acar et al., 1992a; Acar et al., 1992b; Acar and Alshawabkeh, 1993), 2) remediation and separation of species in waste water (Yukawa et al., 1971), 3) constructing barriers that prevent migration of waste flumes (Mitchell, 1986), 4) repairing failed clay liners using electrophoresis (Yeung and Corapcioglu, 1994), 5) electrokinetic sampling and characterization of soil samples (Acar et al., 1988), 6) electrokinetic injection of grouts into soils (Acar and Gale, 1986; Mitchell, 1986), and 7) constructing barriers that prevent migration of waste flumes (Mitchell, 1986). This demand, along with the efforts by the engineering/scientific community in academia and national research laboratories, have already pushed the electrokinetic remediation technique to pilot-scale testing and demonstration stage evaluation. Currently, Electrokinetics Inc. is carrying out a demonstration study of lead extraction from soils for the DoD at a US Army Firing Range in Louisiana. USEPA is taking part in independent assessment of the results of this
demonstration study under the SITE program. The so-called Lasagna group (Dow Chemical, Monsanto, G&E and DuPont) is carrying out a demonstration study of electroosmotic extraction of nonaqueous phase liquids (NAPLs) from fine-grained soils into more permeable layers, where they can be bioremediated by conventional means. Preliminary results reported by the group in a meeting at the National Risk Management Research Laboratory (NRMRL) of the EPA are quite encouraging. Electrokinetic remediation technologies are expected to decrease the cost of remediating contaminated soils from $150/m³- $500/m³ to less than $100/m³, resulting in a significant savings potential in the 350 billion dollar site clean-up and remediation market in the USA (Acar and Zappi, 1995). Recent improvements in understanding the principles of electrokinetic remediation offer the opportunity to employ multi-component species transport mechanisms under electrical fields to inject nutrients and process additives for enhancement of \textit{in-situ} bioremediation and to introduce microorganisms to initiate and sustain an effective level of bioremediation (Acar and Alshawabkeh, 1994a; Acar and Alshawabkeh, 1994b; Acar and Alshawabkeh, 1996; Alshawabkeh and Acar, 1996; Acar \textit{et al.}, 1995).

\textit{In-situ} biotreatment is a desirable and promising technology (NRC, 1993). A review of the state of the art and practice for \textit{in-situ} biotreatment shows that most feasibility studies involved bench-scale column studies and ideal conditions generated in column studies have aimed at establishing
active microbial consortia by the uniform introduction of additives across homogenous, small-scale soil samples. One limiting aspect of successful implementation of the degradation rates obtained in bench-scale studies and in pilot-scale field studies has been ineffective introduction of process additives and nutrients into biologically active zones (BAZs). Key process additives are conventionally introduced by pumping a recirculated groundwater through the BAZ, relying upon the hydraulic gradients that can be developed across the BAZ. All biological processes require that macronutrients (e.g. nitrogen and phosphates) and electron acceptors (e.g. oxygen for aerobic systems) be supplied at appropriate amounts, stoichiometric ratios, and application rates. Some systems also require specialty additives such as surfactants and cometabolites (e.g., methanol, ethanol and toluene). Effective introduction and transport of these additives are hindered by preferential flow paths ("channeling"), heterogeneities, adsorption, biological utilization, and chemical reactions in the soil. A recent survey concludes that this ineffective transport of remediation additives is the primary cause of system failure for in-situ bioremediation efforts (Zappi et al., 1993; NRC, 1993). Lack of knowledge of geohydrology, additive transport and associated reaction processes, coupled with the observed inefficiency in the field, have been mostly approached by gross overinjection of the additives into BAZs. Excessive dosing coupled with the shortcomings of the hydraulically-driven transport processes can result in nutrient rich areas with
excessive biological growth (biofouling). Biofouling adversely impacts system implementation due to reduced conductivity by microbial growth plugging the flow paths. The need for uniform introduction of nutrients and cometabolites has been the principal bottleneck in the successful field implementation of \textit{in-situ} bioremediation (Suflita and Sewell, 1991; Zappi \textit{et al.}, 1993)

Electrokinetic remediation (EK) is an emerging \textit{in-situ} remediation technique that employs low level DC electrical potential differences (on the order of volts per cm), or an electrical current (on the order of milliamps per square cm of cross sectional area between electrodes), applied across a soil mass by electrodes placed in an open or closed flow arrangement (Acar \textit{et al.}, 1993; Acar and Alshawabkeh, 1993; Probstein and Hicks 1993; Runnells and Wahli, 1993; Pamukcu and Whittle, 1992; Whittle and Pamukcu, 1993; Acar \textit{et al.}, 1995). The groundwater in the boreholes, or an externally supplied fluid (processing fluid), is used as the conductive medium (Acar and Gale, 1992; Acar and Alshawabkeh, 1993). Open flow arrangement at the electrodes allows ingress and egress of the processing fluid, or the groundwater, into or out of the porous medium. The species input into the system at the electrodes (either by the electrolysis reactions, or through the cycling processing fluid) and the species in the pore fluid will be transported across the porous media by conduction phenomena in soils under electric fields. This transport coupled with sorption, precipitation/dissolution and
volatilization/complexation reactions comprise the fundamental mechanisms affecting the electrokinetic remediation process. Extraction and removal are accomplished by electrodeposition, precipitation, or ion exchange, either at the electrodes or in an external extraction system placed in a unit cycling the processing fluid.

The technique is currently a primary emerging technology for extracting inorganic species or selected organic species; however, as depicted in Figure 2.1, it is envisioned to use the scheme innovatively for the introduction of nutrients and process additives in soils. Species transport processes under electric fields also can be employed for the introduction of microorganisms in subsurface deposits. Such innovative uses of conduction phenomena under an electric field require an assessment of the electrokinetic scheme in line with the objectives of in-situ bioremediation.

The problems associated with aquifer heterogeneities can easily be overcome using EK opposed to conventional groundwater injection by hydraulic techniques. This project is initiated in order to employ and exploit the principles of multi-component species transport under electric fields as a means to supplement, enhance and engineer in-situ bioremediation systems.

2.2 Electrokinetic Phenomena in Soils

The clay surfaces are normally negatively charged because of isomorphous substitutions, the presence of broken bonds, and the surface

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Figure 2.1: A Schematic Diagram of a Possible Field Processing Configuration Depicting Uniform Transport of the Process Fluid and Ionic Species under an Electric Field

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ionizable groups. The negative charge deficiency of the clay particle surfaces are neutralized by tightly holding absorbed cations. Excess cations and their associated anions are present as salt precipitates. In clay-water system, the precipitated salts go into solution. Therefore, the clay particle surfaces-water-electrolyte system predominately consists of three different distinct zones: the clay particle surfaces are negatively charged, adjacent pore fluids are positively charged, and net charge of the free pore fluid would be zero. The quantity of exchangeable cations needed to balance the deficiency of negative charges of the clay particle surfaces is termed the cation exchange capacity (CEC, milliequivalent/100 grams dry soil).

Most natural soil surfaces are negatively charged and counter charges are necessary in order to maintain electrical neutrality. The counter charges that collect near the surface of the particle and extend in the adjacent solution phase are termed the diffuse double layer (DDL). Several theories have been developed to model the charge distribution adjacent to the clay surfaces. Detailed descriptions are available (e.g. Mitchell, 1986; Hunter, 1981; Stumm, 1992; Mitchell, 1993; Yeung, 1994). According to the Gouy (1910)-Chapman (1913) theory, the thickness of the DDL depends on the electrolyte concentration, cation balance, pH, temperature, and permittivity of the pore fluid.

Recent understanding of electrokinetics flow processes in porous media has generated tremendous interest in engineers and scientists from
different fields. The imposed electrical field or hydraulic gradient in a porous media may generate different types of flows which include fluid, electrical-induced forces, dissolved and undissolved chemical species, and colloidal particles. There are four basic electrokinetic phenomena in porous media, namely, electroosmosis, streaming potential, electrophoresis, and migration or sedimentation potential. Water and particles movement under imposed electrical fields are respectively known as electroosmosis and electrophoresis. Alternatively, water flow and suspended particles flow can generate electrical fields and are respectively known as the streaming potential and the sedimentation or migration potential.

2.3 Species Transport Under Electrical Field

Significant species transport processes under electric fields consist of mass fluxes generated by electromigration (or migration), electroosmotic advection (or electroosmosis), and to a lesser extent electrophoresis and diffusion. Several compositional and environmental variables affect the relative contribution of each flux: soil mineralogy, pore fluid composition and conductivity, electrochemical properties of the present, generated and introduced species in the pore fluid, and porosity and tortuosity of the porous medium. A sense of the magnitude of the contributions of each requires a scrutiny of how each flux is related to the prevailing electric field, the concentration of species, and the compositional/environmental variables. Electrophoresis is the movement of charged colloidal particles in a soil-liquid
system under an electrical gradient. This kind of transport has limited importance in Electrokinetics soil processing.

2.3.1 Ionic Migration

The transport phenomenon of charged ions is known as electromigration. The current in the soil-water system is accomplished by migration of these ions, which behaves similar to an electrochemical cell. The charge velocity \(v_i\) is proportional to the electrical field \(i_e\) strength and the proportionality constant is known as effective ionic mobility \(u^*\).

\[
v_i = u^* i_e
\]

There is no sound method yet devised to measure the ionic mobility in soils to estimate the \textit{migrational mass flux}; however, it can be theoretically estimated by assuming that the Nernst-Townsend-Einstein relation between the molecular diffusion coefficient, \(D_i\), assuming that the ionic mobility holds true for ions in the soil pore fluid (Acar and Alshawabkeh, 1993; Shackelford, 1991; Acar and Haider, 1990). The effective ionic mobility of a specific ion in the soil would then be a function of its molecular diffusion coefficient, tortuosity factor and its charge.

\[
u^* = u^* \tau n = \frac{D_i^* z_i F}{RT}
\]

\(u_i\) = the ionic mobility of the specie at infinite dilution
z = the charge of the specie

\( F = \) Faraday's constant (96500 C/mol electrons)

\( \tau = \) the tortuosity factor

n = porosity of the medium

\( R = \) the universal gas constant (8.3144 J/K.mol)

\( T = \) the absolute temperature (K)

Figure 2.2 shows the ionic mobility (\( u \)) at infinite dilution of some cations and the anions which are commonly found in soils and some of these ions are also important for active biological system in soils. The average ionic mobility of inorganic ionic species lies around \( 5 \times 10^{-4} \) cm\(^2\)/V.sec. The effective ionic mobility, \( u^* \), represents the mobility of the species in the porous medium. The effective ionic mobility, \( u^* \), is related to the ionic mobility in free solution at infinite dilution of the species, \( u \), by a factor that contains soil porosity (n), which may vary over a range of 0.1 to over 2 for fine-grained soils, and other factors that include the effect of tortuous flow path, anion exclusion by the clay surfaces, and the effect of counterions (Alshawabkeh and Acar, 1992; Shackelford and Daniel, 1991). The effects of all of these factors are lumped into a so-called tortuosity factor, \( \tau \). The tortuosity factor may vary between 0.01 to 0.5 for different types of soils (Shackelford and Daniel, 1991). It is also noticeable that effective ionic mobility is independent of the pore size distribution of the medium.
Figure 2.2: Ionic Mobilities for Representative (a) Cations and (b) Anions

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The effective diffusion coefficient $D^*$ in a soil-water system can be related by the diffusion coefficient ($D$) of the free solution,

$$D^* = D \tau n$$

Typical $D$ values range between $10^{-6}$ to $10^{-4}$ cm$^2$/sec. The proportionality constant relating the electrical potential gradient to the mass flux of species under electric fields is the ionic mobility, $u^*$, of the species. Acar and Alshawabkeh (1993) showed that the ionic mobility of a charged species is at least one order of magnitude higher than the diffusion coefficient of the same species at electric fields typically used in electrokinetic remediation; the ratio of the ionic mobility of a charged species under a unit electrical gradient to the diffusion coefficient of the same species is about 40 times the charge on the species. Therefore, migration becomes a major component of the total mass flux.

### 2.3.2 Electroosmosis

Electroosmosis occurs because the surfaces of soil particles are generally negatively charged. These charged negative surfaces attract counter positive ions in the pore fluid, which form a double layer. The outer mobile part of the double layer migrates towards the cathode under electrical field. Water in pores between particles is drawn along by viscous drag. The constant of proportionality between electrical gradient and flow rate is defined as the coefficient of electroosmotic permeability ($K_e$).
The Helmholtz-Smoluchowski theory is commonly used to describe the electroosmosis phenomenon and to quantify the volume flow rate ($Q_e$, cm$^3$/sec) of liquid through a porous medium under an electrical field ($i_e$, V/cm). One of the fundamental parameters involved in electrokinetic soil processing is the electroosmotic permeability ($k_e$, cm$^2$/V.sec), which is defined as the average velocity ($v_e$, cm/sec) achieved under an unit electrical field strength.

$$v_e = \frac{Q_e}{A} = k_e i_e$$

$A =$ cross sectional area

and

$$k_e = \frac{\varepsilon \zeta \eta}{\eta}$$

$\varepsilon =$ permittivity of the liquid (F/m)

$\zeta =$ the zeta potential, which is defined as the potential existing between the rigid and the movable parts of the double layer (V)

$n =$ porosity

$\eta =$ viscosity of the liquid (N·sec/cm$^2$)

The coefficient of electroosmotic permeability ($k_e$) is relatively independent of the pore size distribution, whereas the hydraulic conductivity ($k_h$) varies the square of effective pore size. $K_e$ is generally in the narrow
range of $10^{-5}$ to $10^{-4}$ cm$^2$/V-sec for a soils with a wide range of $K_h$ from $10^{-8}$ to $10^{-4}$ cm/sec. The average electroosmotic permeability has been calculated to be in the order of $5 \times 10^{-5}$ cm$^2$/V-sec. Factors that may effect $K_e$ include pH, electrolyte concentration, medium capacitance, and temperature.

The electroosmotic permeability varies with zeta potential ($\zeta$) and ionic concentration of the pore fluid, which may not be constant during electrokinetic treatment. The electrical potential at the junction between the fixed and mobile parts of the electrical double layer is defined as the zeta potential. $\zeta$ is usually negative due to surface charge, but it is strongly dependent on the pore fluid chemistry. For example, a number of investigators have studied variation of the zeta potential of kaolinite as a function of pH. They found that $\zeta$ for kaolinite reduces in magnitude (becomes more positive) as the pH drops (acidity increases). For kaolinite $\zeta$ varies from -40 mV at pH 10 to zero at pH 2.2 (Smith and Narimatsu; 1993). Subtle changes in initial and boundary conditions of the system chemistry are found to have a very large effect on electroosmosis in soils. The zeta potential is also reported to change linearly with the concentration described by (Kruyt, 1952)

$$\zeta = A - B \log C$$
where A and B are constants which can be determined by experiments, and C is the total electrolyte concentration.

The amount of electroosmotic flow depends on the magnitude and sign of the zeta potential. Zeta potential is strongly dependent on the local pH condition. Zeta potential values typically vary from 0 to -100 mV, with the more negative values at higher pHs.

Electroosmotic mass flux under electrical fields is controlled by the applied electrical potential gradient and the electroosmotic coefficient of permeability, $k_e$ (cm$^2$/Vs). The Helmholtz-Smoluchowski theory for electroosmosis has been widely used as a theoretical description of pore fluid transport through soils under an electrical potential difference (Hunter 1981). According to this theory, $k_e$ is a function of the effective bulk electrical conductivity, $\sigma_e$, of the soil pore fluid (S/cm) and is influenced by the zeta potential in the soil. Hamed et al. (1991) and Alshawabkeh (1994) have demonstrated that $k_e$ changes with time in response to changes in chemistry across the medium. While pore fluid flow under hydraulic gradients is significantly affected by the soil fabric and macrostructure, electroosmotic flow under electric potential differences is dependent primarily on the porosity and the zeta potential and hence it is independent of the pore size distribution or the presence of macropores. Therefore, electroosmosis is an
efficient method to generate a uniform fluid and mass transport in fine-grained deposits.

The relative contributions of electroosmosis and ion migration to the total mass flux vary for different soil types, water contents, and the types of species available in the pore fluid, their concentration and the processing conditions. In general, though, electroosmotic mass flux is at best on the same order of magnitude as the migrational mass flux, when the electroosmotic coefficient of permeability is high (of the order of $10^{-4}$ cm$^2$/V-s). High values of $k_e$ are obtained in soils with low conductivity (fine grained sands, silts and clays at high water contents). Acar and Alshawabkeh (1993) have demonstrated that mass transport by migration may be up to 300 times more than mass transport by electroosmosis in experiments carried out by placing electrodes on both sides of a soil specimen.

The complementary nature of electromigration and electroosmosis for the transport of species under an electric field renders the technique viable in all types of soil strata. The electroosmotic component of transport will almost disappear in coarse sands and high plasticity clays at low water contents. Transport of species will then be governed by electromigration. In fine-grained sands, silts and low activity clays at high water contents and low conductivities, electroosmotic transport would be as significant a transport mechanism as electromigration. It should be noted, however, when pore fluid conductivity increases significantly, electromigration of a specific
species may decrease due to a decrease in transference numbers of the specific species (Acar and Alshawabkeh 1993; Alshawabkeh and Acar 1996).

The effective transport rate of a single species in the pore fluid, $v_i$, (cm/s) under the electrical field is given by (Alshawabkeh and Acar 1996)

$$\overline{v_i} = (k_e + u^*_i) i_e$$

where $k_e$ is the electroosmotic coefficient of permeability (cm$^2$/V-s), and $u^*_i$ is the effective ionic mobility (cm$^2$/V-s), which could be in the same or in a reverse direction to electroosmosis and $i_e$ is the electrical gradient (V/cm).

Under special circumstances, it is also possible to have a reverse electroosmotic transport that may act against the transport of the species in the direction of the cathode (Eykholt and Daniel, 1994).

The velocity of transport of positively charged species by electromigration and electroosmosis would commonly be in the same direction increasing the magnitude of the rate of transport and total mass flux toward the cathode. The direction of transport for the negatively charged species by electroosmosis and electromigration, however, would oppose each other, retarding species transport to the anode compartment. If electroosmotic transport is very low compared to electromigration, transport of species will be governed by electromigration. Positively charged species will move towards the cathode and negatively charged species will move...
towards the anode at rates proportional to the transference number of the target species. It should be noted that, in each case, in the bulk pore fluid charge conservation will have to be met. When pore fluid conductivity increases significantly, transport rate of a species by electroosmosis and electromigration will decrease due to a decrease in the electroosmotic coefficient of permeability and a decrease in transference number of the species, respectively.

2.3.3 Current Flux

Ohm's law is the fundamental relationship governing the conduction of electricity in a soil-water system. This law states that when electricity flows through an electrical conductor, the current density ($\mathbf{I}_c$, A/cm$^2$) is proportional to the electrical gradient ($\mathbf{I}_e$, V/cm):

$$\mathbf{I}/\mathbf{A} = \mathbf{I}_c = \sigma \mathbf{I}_e$$

A = cross sectional area

I = total applied current

The constant of proportionality is defined as the electrical conductivity ($\sigma$, Siemens/cm). The electrical conductivity is a characteristic property of the conducting medium and does not depend on the geometry of the medium.

Ohm's law can be written in the following form to measure conductivity in a soil-water system by measuring voltage ($\Delta V$) at two points ($\Delta L$) under a constant current (I):
\[ \sigma = (\Delta L/\Delta V) \]

The electrical conductivity is usually 10 to 500 \( \mu \text{Siemens/cm} \) for natural soil. It depends on the following properties of the soil, including porosity; ionic concentration and mobility of the pore fluid; mineralogy as it affects particle size, shape and surface conductance, soil structure, including fabric and cementation; degree of saturation; and temperature.

The electrical conductivity \( \sigma \) can be derived in the following form to correlate with the ionic concentration \( (C, \text{eq/cm}^3) \) and mobility of all the species:

\[ \sigma = F \sum C_i u_i \]  

The fraction of the total current carried by a particular carrier is known as the transference or transport number of that species \( (t_j) \).

\[ t_j = \frac{F C_j u_j}{F \sum C_i u_i} = \frac{F C_j u_j}{\sigma} \]

It should be noted that the summation of transport numbers all the ions is equal to one in the pore fluid of a soil-water system,

\[ \Sigma t_j = 1 \]
Apparent conductivity \((\sigma_a, \text{ Siemens/cm})\) gives an equivalent conductivity value of the medium across the electrodes by neglecting the localized changes in the conductivity across the medium. The apparent conductivity can be calculated by:

\[
\sigma_a = (l/A)(L/V) = l/\sigma_e
\]  \hspace{1cm} 2.13

\(V\) = applied voltage (V)
\(l\) = total current (A)
\(A\) = cross-sectional area (cm\(^2\))
\(L\) = length of the specimen
\(l/\sigma\) = current density (A/cm\(^2\))
\(i_e\) = voltage gradient (V/cm)

The efficiency of electroosmotic \((k_i)\) dewatering can be defined as the amount of water transferred per unit charge passed, which can be quantified by the following equation:

\[
k_i = v_e / l = k_e / \sigma
\]  \hspace{1cm} 2.14

where \(v_e\) is the average pore fluid velocity under unit voltage gradient, \(k_e\) is the electroosmotic permeability, \(l\) is the total current and \(\sigma\) is the electrical conductivity. \(k_i\) varies over a wide range 0 to 1.2 cm\(^3\)/A-sec depending upon the conductivity of the medium.
2.4 Electrokinetic Remediation

In an unenhanced remediation technique, the electrolysis reactions at the electrodes will dictate the mechanisms involved in the transportation of species under electrical field (Acar et al., 1990a; Acar et al., 1992a; Acar and Alshawabkeh, 1994a, Acar and Gale, 1992; Wieberen, 1992; Acar et al., 1992; Pamukcu and Whittle, 1992; Acar and Alshawabkeh 1993; Lageman, 1993; Probstein and Hicks, 1993; Shapiro and Probstein, 1993; Runnells and Wahli 1993; Acar et al., 1995; Acar and Alshawabkeh, 1996; Alshawabkeh and Acar, 1996). At an early stage of processing, the oxidation reaction of water at the inert anode will cause the pH to drop below 2 whereas the reduction reaction at the cathode will cause it to increase over 12.

Anode reaction:

\[
2H_2O - 4e^- = O_2 + 4H^+ \quad (E_0 = -1.229)
\]

Cathode reaction:

\[
2H_2O + 2e^- = H_2 + 2O^2- \quad (E_0 = -0.828)
\]

where \( E_0 \) are the standard electrode potentials. The mechanisms involved in transportation of the acid front from the anode will include; electromigration by which ions will be driven by the attractive force of the charged electrode from the anode and cathode boundaries; and pore fluid advection; which will be driven by the existing electroosmotic flow, or a hydraulic gradient generated internally or externally, and diffusion which will be driven by the
potential difference of chemical gradient (Acar et al., 1990a; Acar et al., 1990b; Acar et al., 1992b; Acar et al., 1994a; Acar et al., 1994b). On the other hand the alkaline front from the cathode end will advance towards the anode by diffusion and electromigration. The advancement of the alkaline front in the soil will not be pronounced due to the electroosmotic flow. The alkaline front will have to encounter the electroosmotic flow from the anode to cathode and the faster rate of ionic mobility of hydrogen ion (H\(^+\)) will neutralize the transport of base front. As a consequence, the chemistry across the soil will be dominated by the movement of the acid front generated from the anode end, unless it is retarded by the inherent buffering capacity of the soil (Acar, 1992; Yong et al., 1990). When electrodes are placed in a pore fluid in the soil, electrolysis reactions prevail. Hydronium ions (H\(_3\)O\(^+\)) are generated at the anode and hydroxyl ions (OH\(^-\)) are generated at the cathode. In the electrokinetic decontamination of soils from inorganic species, generally conditions for the transport of the acid front across the soil are promoted, while generation of the base at the cathode is simultaneously suppressed (Acar et al., 1995; Alshawabkeh and Acar, 1996). The acid flush across the soil releases the adsorbed species in the pore fluid and transports them towards the cathode compartment, where they are precipitated, and/or electrodeposited. Details of the process are available elsewhere (Acar and Alshawabkeh, 1994a; Acar and Alshawabkeh, 1994b; Acar and Alshawabkeh, 1996; Alshawabkeh and Acar, 1996).
2.4.1 Enhancements/Conditioning and Injection of Species

The formation of base at the cathode end will cause precipitation of the inorganic species near the cathode boundary. Acar et al. (1992a; 1992b; 1993; 1994) have demonstrated a viable enhancement technique by depolarizing the cathode reactions in which the inorganic species can be efficiently transported into the catholyte without significant formation of precipitant. Acar et al. (1993) have also shown that 0.05 M acetic acid will be sufficient to depolarize the cathode reactions. The driving mechanisms of inorganic species in pore fluid or injected species are similar to the mechanisms involved in transportation of acid or base.

Previous studies investigating the potential to use electrokinetic phenomena to inject species attempted to employ electroosmosis and/or electrophoresis. Yeung (1994) reports a study by Holmes (1962) which applied electroosmosis to inject a bentonite slurry through a fine-grained soil. Yeung (1994) also discusses the potential use of electrophoretic transport to seal geomembrane liners. Similarly, electroosmotic injection studies evaluating the merit of exploiting the electrolysis reactions in soil stabilization have been reported (Gray and Schlocker, 1969; Gray, 1970; Madshus and Janbu, 1984; Sutton and Alexander, 1987). Gray (1970) presents the results of experiments carried out for electrochemical hardening of silica flour mixed with an illitic soil and a montmorillonitic soil. Aluminum electrodes and an aluminum chloride solution were used at the anode and aluminum
electrodes and a sodium chloride solution were used at the cathode. The aluminum electrode at the anode buffered the anolyte and a steady pH level of 3.8 was maintained (in comparison with a pH value of 1.2 with inert anode in water). In another batch of experiments, the catholyte was buffered by bubbling carbon dioxide and a final pH value of 10 was maintained (in comparison with a pH value of 12.8 with inert cathode in water). The provisions were taken to enhance movement of aluminum ions inside the soil and initiate a strength increase either by ion exchange or by 'mineralization' (Gray, 1970). The limited results indicated that there was up to 400 % increase in strength when the catholyte was not buffered and up to 100 % increase in strength with catholyte buffering. Madshus and Janbu (1984) also reported a field study of electrokinetic stabilization. Potassium chloride was placed in the anode compartment in order to increase the electrolyte concentration in the pore fluid and improve the shear strength of a quick clay deposit. The soils with a shear strength of about 20-25 kPa strengthened by about 100 % both due to a 45 °C increase in temperature under the electrical fields and also due to the increase in the electrolyte concentration in the pore fluid (Senneset and Acar, 1995).

Studies investigating the potential to use electrical fields to inject nutrients and process additives for in-situ bioremediation are limited. All of the prior studies attempted to use electroosmosis to transport the target nutrients and process additives. Segall and Bruell (1992) have reported the
results from a series of experiments where solutions of phosphorus- and/or nitrogen-containing anions were placed in column-influent (anode) reservoirs to inject these species in clay and soil mixtures. Column effluent was monitored on a daily basis and nutrient distributions in the column were measured by destructive sampling. The specimen length in the columns was 30.5 cm. Although 50 mg/L of NO$_3^-$ solution was fed at the anode for a period of 154 days, substantial amounts of nitrate never appeared in the effluent. Average concentration over the period was about 1.5 mg/L of NO$_3^-$ /N. The authors noted that difference between initial nitrate concentration and the monitored effluent values was ammonia gas generation. A second test also was carried out by Segall and Bruell (1992) to transport phosphorus into soil. It was concluded that "electroosmotic process does not facilitate sufficient phosphorus transport through fine-grained soils, even when feed water (anode) phosphorus concentrations are far in excess of potential bacterial nutrient requirements. This inability to move phosphate is a severe constraint on the potential of the in-situ biological treatment of organic contaminants".

The principal problem with the above experiments and other studies that attempted to inject chemical species with electrical fields for stabilization purposes (ASCE, 1987) was the hypothesis that the species can be transported by electroosmotic transport from the anode to the cathode. The goal to achieve electrokinetic injection of species under electrical fields
requires that the electrolysis reactions are considered together with conduction phenomena under electrical fields. The chemistry of the species input together with the prevailing electrolysis reactions will control the species that are transported by either electroosmotic advection, or electromigration, or both. Recent understanding developed in multi-species transport under electrical fields suggests that electrokinetic injection can in fact be efficiently used to overcome the difficulties associated with the hydraulic injection of species (Alshawabkeh and Acar, 1992; Alshawabkeh and Acar, 1996). The electrode depolarization technique could be effectively used to inject positively charged species at the anode and negatively charged species at the cathode, while the co-ions in the species introduced could facilitate depolarization of the electrode reactions to maintain a desirable pH environment and a low electrical conductivity. This idea, the envisioned procedure and the technique has been recently patented by Electrokinetics, Inc. (Marks et al., 1995).

2.5 Overview of Bioremediation Processes

In the bioremediation technique, hazardous organic compounds are oxidized into other nontoxic organic form (transformation) or completely mineralized into inorganic forms (mineralization). These oxidation reactions of organic compounds are mediated by enzymatic reactions of microorganisms. Generally, microorganisms use these hazardous compounds as their sole carbon and energy source. In addition to these
oxidation reactions, reduction reactions (by electron acceptors) also occur to metabolize the compounds (Figure 2.3). Generally, electron acceptors (or donors) and nutrients are limiting factors for indigenous microorganisms to degrade hazardous compounds in the subsurface environment.

*In-situ* bioremediation of hazardous organic compounds in the groundwater environment can be used cost effectively when proper engineering controls are available. Decontamination of organic compounds by microorganisms can minimize potential hazards by converting toxic reactants into harmless end products.

Biodegradation is site specific and varies with environmental and compositional variables of the site. As a result, the complexities of the biological response in different environments are not clearly understood. The success of *in-situ* bioremediation depends on several factors. According to Fredrickson *et al.* (1993), the most important factors which should be considered for successful implementation of *in-situ* remediation are:

1. Environmental variables (e.g., low temperature; non-optimum pH) may cause slow degradation.

2. Biodegradation of organic compounds is often hindered by the coexistence of other toxicants such as heavy metals.

3. Lack of efficient engineered system available to deliver electron acceptors and nutrients uniformly in a heterogeneous medium.
Organic acid

Cell mass (C₆₀H₇₀O₂₃N₁₂P)

Other metabolites (C₉H₄O₉N₉)

Adsorbed in soil

Nutrients (N⁰₃⁻, PO₄³⁻)

Temperature

pH

H₂O, N₂, H₂S

Electron acceptors (O₂, H₂O₂, NO₃⁻, SO₄²⁻)

Figure 2.3: Fate of Organic Contamination in Soils with Active Biological System
4. Contamination may be unavailable for biological activity due to low aqueous phase concentration or strong sorption by soil particles.

5. Biological mediated reactions may be result in more toxic metabolites.

6. Heterogeneous distribution and mixture of contaminants are, generally, found in the field.

7. Absence of microorganisms which have the necessary biochemistry to degrade the target contaminants.

The laminar flow condition of ground water causes minimum reaeration of the pore fluid. As a result, groundwater generally contains low concentrations of oxygen. Generally, oxygen is a limiting factor in subsurface environment for microbial activity. Microbes need oxygen (aerobic), or other inorganic (anaerobic) terminal electron acceptors, for their metabolism. The subsurface deposits also have low level of nutrients for biological activity.

A number of organic contaminants are candidates for biological remediation. A few are discussed below. Polynuclear Aromatic Hydrocarbons (PAHs) are composed of fused benzene rings. They are the byproducts of incomplete combustion of coal, oil, petrol, and wood. The daily uses of such materials by mankind as burning materials give substantial releases of PAHs in the ecosystem. PAHs and their transformed products (metabolic transformations by indigenous microorganisms) have been found
to exhibit mutagenic and carcinogenic effects. These materials can bind with DNA and RNA and disrupt normal functions. The malfunctions of cells can be the basis for tumor formation (Wild and Jones, 1995). As a consequence, the U.S. Environmental Protection Agency (USEPA) and the European Community (EC) have listed many PAHs as priority pollutants.

Gasoline and other fuels contain among other constituents, benzene, toluene, ethylbenzene, xylene (collectively known as BTEX). These are monoaromatic compounds with alkyl functional groups. These monoaromatic hydrocarbons have a relatively high potential to contaminate groundwater because of their high water solubility. Since these compounds are considered hazardous, they are regulated by the USEPA (1977).

The halogenated aliphatic compounds make up a major portion of the EPA (1991) priority pollutant lists. They include vinyl chloride, carbon tetrachloride, chloroform, trichloroethylene (TCE), 1,1,1-tri-chloroethane, and tetrachloroethane. These chemicals are produced in large quantities to use as solvents for cleaning and chemical synthesis. Around 350 sites are contaminated by TCE which is the leading chemical found in the 1250 NPL sites presented by EPA (1991).

A number of factors can influence the metabolism of the microbes, and hence, biodegradation. The factors that enhance microbial activity can be identified by shake-flask and bench-scale tests and methods can be implemented to control and to assure that optimum growth conditions can

2.5.1 Bioremediation

Bioremediation is a destruction or transformation of contamination in soil by the catalytic reactions onset by microbes. So, a successful bioremediation scheme always has as a prime target to achieve an innocuous form of the contaminant. As a consequence many technological strategies have been undertaken to exploit the potential of microbes to detoxify the hazardous materials. The innate response of natural microbes will be found in contaminated soils, only when they have ample opportunity to generate energy and new cells from the ambient environment. Intrinsic bioremediation is a process where contamination sites have all the essential growth materials in large enough quantities that can support the growth of natural microbes without human intervention. But in most cases in contaminated sites, a successful remediation action can be achieved by using engineered systems that can supply electron acceptors/donors, nutrients, and/or other growth-simulating materials to enhance the growth of microbes to degrade the contamination. In many cases, engineered bioremediation is an alternative remediation technique to intrinsic
bioremediation because it enhances degradation of contamination within a reasonable time frame and it reduces liability.

2.5.1.1 Basics of Microbial Metabolism

Microorganisms are capable of deriving their energy and carbon by directly transforming the organic species in soils. This biological mediated transformation of organic species serves two purposes of microbes: 1. the catabolic reactions, and 2. the anabolic reactions. Catabolic reactions (degradation process) are carried out by oxidizing the organic contamination into smaller molecules to produce energy:

\[
(CHON) + O_2 \rightarrow CO_2 + H_2O + \text{Small molecules} + \text{Energy}
\]

where CHON represents the organic contaminant.

The second (anabolic reactions) describes the resynthesis of these small molecules into the cell components required by the growing microorganisms, utilizing the energy generated in the catabolic reaction. This resynthesis process, which is known as anabolism consists of:

\[
\text{Small molecules} + O_2 + \text{Energy} \rightarrow C_5H_7O_2N + H_2O
\]

where \( C_5H_7O_2N \) is assumed to be a cell component. Under starvation condition, microbes are forced to oxidize their own carbonaceous materials in order to fulfill the energy necessary for their continued viability. This process is known as endogenous metabolism. Endogenous metabolism is represented the equation:
\[
\text{C}_5\text{H}_7\text{O}_2\text{N} + \text{O}_2 \rightarrow \text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O} + \text{Energy}
\]

Microorganisms get energy by mediating an energy-producing reaction that involves breaking down of chemical bonds and transferring electrons away from the organic carbon source (oxidation). Also, a reduction process (gain of electrons) has to occur to counterbalance oxidation. The carbon source is called the electron donor and the electron recipient is called the electron acceptor. These two essentials materials (electron acceptor and electron donor) are commonly referred to as primary substrates.

2.5.1.2 Electron Acceptors

Aerobic respiration

Detoxification of contaminants with the aid of O\(_2\) is called aerobic respiration. Most contaminants can be degraded under aerobic conditions. Therefore, in many cases sufficient oxygenation in the polluted matrix is the prime concern. In aerobic metabolism, part of the oxygen is used by microbes to oxidize the contamination to \text{CO}_2 and the rest is used to synthesize new cells. The amount of available oxygen will determine whether the system will be aerobic or anaerobic. The availability of oxygen (O\(_2\)) is a major limitation in many bioremediation projects because of the low solubility of oxygen (O\(_2\)) in soil solution (Lee et al., 1988; Thomas and Ward, 1989). Aerobic metabolism predominates in a soil solution when the dissolved oxygen (O\(_2\)) concentration is greater than 0.2 mg/l (Skladany and...
Metting, 1993). Maintaining an aerobic condition in the subsurface is problematic. For saturated soils, injection of aerated water or hydrogen peroxide ($H_2O_2$) is often practiced (Hinchee et al., 1991). When water is sparged with air and pure oxygen, concentrations of up to 8 mg/l and 40 mg/l of dissolved $O_2$ can be achieved, respectively. Application of $H_2O_2$ to in-situ bioremediation may also have adverse affects. Lee et al. (1988) and Pardieck et al. (1992) have reported significant toxic effects of $H_2O_2$ to microbes. Aquifer plugging is postulated to be a result of precipitants formed due to oxidation of organic and inorganic compounds in the presence of the highly reactive $H_2O_2$ (Spain et al., 1989; Morgan and Watkinson, 1992; Pardieck et al., 1992). Additionally, reductive dehalogenation does not proceed in the presence of $O_2$ and $H_2O_2$ (Young and Haggblom, 1989).

**Alternative electron acceptors: (Anaerobic respiration)**

Many subsurface environments are anaerobic. Recent studies have proven that, in many cases, successful remediation is possible as a result of utilization of alternative electron acceptors (Brown et al., 1990; Alvarez and Vogel, 1991). In anaerobic respiration, nitrate ($NO_3^-$), sulfate ($SO_4^{2-}$), metals such as iron ($Fe^{3+}$), manganese ($Mn^{4+}$) or even carbon dioxide ($CO_2$) can play the role of alternative electron acceptors. In anaerobic respiration, in addition to cell mass, end products include nitrogen ($N_2$), hydrogen sulfide...
(H₂S), reduced forms of metals (Fe²⁺ and Mn²⁺) and methane (CH₄) depending on the electron acceptors.

### 2.5.1.3 Inorganic Electron Donor

Autotrophic microbes can use inorganic molecules as electron donors. Generally these types of microbes use inorganic molecules such as ammonium (NH₄⁺), nitrite (NO₂⁻), reduced iron (Fe²⁺), reduced manganese (Mn²⁺) and hydrogen sulfide (H₂S), which are respectively oxidized to nitrite (NO₂⁻), nitrate (NO₃⁻), oxidized iron (Fe³⁺), oxidized manganese (Mn⁴⁺) and sulfate (SO₄²⁻). Autotrophic microbes generally use carbon dioxide (CO₂) and methane (CH₄) as their carbon source.

### 2.5.1.4 Cometabolism (Secondary Substrate Utilization)

When microbes use an organic as their primary substrate, coincidently they can also oxidize other organic substances. This process is defined as “cometabolism”. The cometabolism reaction (oxidation of secondary substrate) is catalyzed by enzymes involved in normal cell metabolism (by oxidation of primary substrate). For example, chlorinated solvents such as TCE are destroyed incidentally when microbes oxidize methane.

### 2.5.1.5 Inorganic Nutrients

Nutrient supply can be evaluated by considering whether the proper carbon-nitrogen-phosphorus (C: N: P) ratio is likely to be met by the soil
environment. An approximately average formula of a cell is $C_5H_7O_2N$ (Hoover and Porges, 1952). The formulation $C_{60}H_{87}O_{23}N_{12}P$ has been proposed when phosphorus is also considered (McCart, 1970). From the consideration of the cell formulation, McCarty has suggested for a balance growth of microorganisms in a reactor, C: N: P ratios of 100: 5: 1 in aerobic systems and 100: 2.5 : 0.5 in anaerobic systems, have to be maintained. Commonly employed values for biotreatability range from 100: 10:1 to 100: 4: 1. The lower ratio can be effective because all of the carbon (C) does not go in the production of new cells; some are used for energy production ending up as CO$_2$.

Paul and Clark (1989) have suggested that a C: N: P ratio 30: 5: 1 is needed for unrestricted growth of soil bacteria. Since nitrogen and phosphorus are inexpensive, however, they are often added at a higher rate as insurance. Nitrogen is commonly supplied in the form of NH$_4^+$, NO$_3^-$ or urea and phosphorus is supplied as rock phosphate, orthophosphate or triple superphosphate. Thus, an engineered bioremediation should be implemented in such a way to supply proper concentrations and ratios of these nutrients, if the natural habitat does not provide them.

2.5.1.6 Reductive Dehalogenation

Microbes can catalyze a reaction in which the halogen atoms of the organic species are replaced by hydrogen atoms. Generally in
dehalogenation reactions, electron donors are hydrogen and low molecular weight organic compounds such as lactate, benzoate, acetate, methanol and glucose.

2.6 Remarks on Conventional Hydraulic Injected Engineered System to Enhance Bioremediation

1) Generally rates of hydraulic flow greater than 0.003 cm/sec are required to continually replenish nutrients and remove waste products (Skladany and Metting, 1993).

2) For a system that circulates water, the hydraulic conductivity of the contaminated subsurface should be greater than $10^{-4}$ cm/sec (NRC, 1993).

3) For a system that circulates air, the intrinsic permeability should be greater than $10^{-4}$ cm$^2$ (NRC, 1993).

4) The efficacy of the remediation is commensurate with how uniform the process additives can be dispersed into the target contamination zone (Djatri and Gupta, 1992). So a nonuniform distribution of process additives, due to subsurface heterogeneity, may circumscribe the plausible implementation of in-situ bioremediation.

5) Residual concentrations of nonaqueous-phase contamination of less than 10,000 mg/kg of the soil do not significantly affect water or air flow, because at this level the contaminants are generally immobile and occupy much less space than the water (NRC, 1993).
6) Most of the organic species can be degraded with a cell concentration of approximately $10^5$ to $10^6$/gram of soil (Bartha and Bossert, 1984).

7) Excessive microbial growth can plug the permeable media and limit the reinjection of water due to an over-injection of process additives in the BAZs which has resulted from preferential flow caused by medium heterogeneities.

8) Bioaugmentation is the inoculation of soil or groundwater with naturally occurring or genetically engineered microorganisms. A successful microbial introduction into BAZs solely depends on the mechanisms by which the microorganisms are dispersing throughout the BAZs. The transportation process of cells within a soil matrix is a function of soil and the types of microbes. It is already well established that permeability of medium, ionic strength of flow, and the diameter of the cell are the primary conditions needed to promote the transportation of microbes in porous medium (NRC, 1993).

### 2.7 Problems to Overcome By Electrokinetics to Enhance Bioremediation

Electrokinetics transport phenomena can be used in the following diversified way to enhance bioremediation:

1. Injection of inorganic species (electron acceptors, nutrients)
2. Injection of organic species (cometabolites)
3. Bioaugmentation
4. Provide heat to enhance bacterial activity
5. Restoration of proper pH condition
6. Transport surfactants to release residual concentration

2.8 Enhance Soil Bioremediation with Electrical Fields

The species input at one electrode reservoir can be transported across the specimen to the other and under electrical fields and they could be available in appropriate stoichiometric ratios for the anticipated chemical reactions and/or biochemical processes only if the electrolysis reactions, aqueous phase reactions and the anticipated chemical/biochemical processes are considered together with multi-component species transport mechanisms in soils under electrical fields. Recent studies indicate that when the chemistry of the species input together with the prevailing electrolysis, sorption, precipitation/dissolution and aqueous phase reactions are considered, reasonable predictions of chemistry and mechanics in the soil across the electrodes are possible (Alshawabkeh and Acar, 1992; Alshawabkeh and Acar, 1996).

The pH value is a master variable in most chemical reactions and when electrolyte chemistry is not controlled, pH value changes within a wide range across the electrodes. In the electrokinetic decontamination of soils from inorganic species, the acid flush across the soil releases the adsorbed species into the pore fluid and transports them towards the cathode.
compartment, where they are precipitated, and/or electrodeposited. The electrolysis reactions are closely controlled and conditions for the transport of the cathode is depolarized to suppress generation of the base (Ugaz et al., 1994; Rødsand et al., 1995; Acar et al., 1995). Similarly, efficient transport and injection of species into soil is possible only if the electrolysis chemistry at the electrodes is considered together with transport phenomena under electrical fields.

A relatively stable pH environment is needed in the soil for in-situ bioremediation both to achieve reasonable transport rates for target species and also to optimize biological activity. Furthermore, the envisioned electrokinetic injection scheme should not prematurely and undesirably increase the ionic conductivity at the electrode reservoirs and the porous medium. The acid/base conditions generated as a result of the electrolysis reactions at the electrodes need to be neutralized/depolarized to achieve a desirable pH level. This provision requires exploiting electromigration in transport. It is possible to inject positively charged species at the anode and negatively charged species at the cathode. The co-ions of the target species introduced should be selected so as to facilitate depolarization of the electrode reactions, maintain a desirable pH environment and a low electrical conductivity. Furthermore, if the purpose of injection is in-situ bioremediation, the injected species at the anode and the cathode need to be perfectly soluble with each other for their efficient transport across the
porous medium. In electrochemical stabilization; however, these ions could also be selected to cause precipitation of species in the pore fluid resulting in cementation of the porous media. An experimental program is developed to investigate the efficiency and feasibility to inject species across soils for \textit{in-situ} bioremediation.

It is essential to develop this new, innovative and cost-effective remediation technique for full-scale field implementation to achieve faster, better, cheaper and safer environmental restoration. The fundamental advantages will be the versatility of the technique for injecting species in deposits with varying degrees of permeability, and across heterogeneities.
CHAPTER 3
METHODOLOGY

3.1 Experimental Program

It was decided to inject ammonium ions from the anode compartment and sulfate or nitrate or phosphate ions from the cathode compartment in order to evaluate the technical feasibility of simultaneous injection of a nutrient and an electron acceptor under an electrical field. Ammonium hydroxide (NH₄OH) at the anode compartment and sulfuric acid or nitric acid or phosphoric acid (H₂SO₄, or HNO₃, or H₃PO₄) at the cathode compartment were used for this purpose. The H₃O⁺ ions (co-ions), generated as a result of the anode electrolysis reaction were neutralized with hydroxyl ions injected into a conditioning reservoir via a pH controlled pump which maintained the pH at or about 7. Similarly, the OH⁻ ions (co-ions) generated as a result of the cathode electrolysis reaction, were neutralized by the hydronium ions in the acids (H₂SO₄, HNO₃, H₃PO₄). As a result, ammonium and sulfate or nitrate or phosphate ions (target species for injection) were transported from the anode towards the cathode and from the cathode towards the anode, respectively (Figure 3.1). These target species will provide a good understanding of the potential to transport species under
Figure 3.1: A Schematic Diagram of the Proposed Electrokinetic Injection Method
electrical fields with the specific scheme employed in this study. Other species could be selected and injected employing a similar technique.

Bench-scale tests were carried out using a fine sand, a kaolinite and a silty-clay. The use of artificial soils allowed maintenance of most compositional variables constant, while only the parameters essential for evaluation of the hypotheses could be changed. Two experimental set-ups were designed and a testing procedure and program were developed to meet the objectives.

3.2 Experimental Set-up

A schematic diagram of the set-up-1 used in this project is shown in Figure 3.2. A photograph of the flume is given in Figure 3.3. The flume depicted in Figure 3.3 was constructed of 5 mm thick acrylic plastic. Acrylic was selected since it has no known adverse effects (such as significant adsorption) on the transport of inorganic species under electrical fields and it facilitates visual inspection. The front and the back acrylic panels allowed placement of sampling ports on one face and voltage probes on the other. Sampling ports of 10 mm diameter were placed along the panels for intermittent extraction and chemical analysis of the pore fluid. Nine sampling ports were placed along the soil specimen at 95 mm spacing and another two were placed in each electrode chamber giving a total of eleven.

Three rows of sampling ports were available across the set-up: lower, middle and upper rows placed at 19.5 cm, 39 cm and 58.5 cm from the
Figure 3.2: A Schematic of the (a) Side View (b) Top View of the Electrokinetic Setup-1
Figure 3.3: A Picture of the Electrokinetic Setup-1
bottom of the set-up, respectively. Similarly, three rows of 10 mm ports were drilled across the back panel. The holes were sealed with Thermogreen™ LB-2 septa which prevented any leakage during sampling. All ports were sampled each sampling time in order to assess the extent of transport under electrical fields. Voltage probes were placed to determine the electrical gradient across the soil specimen. The electrical potential gradient is important in establishing the ionic mobilities and also in determining the change in conductivity across the specimen. This information provides an indirect assessment of the species transport across the soil.

The clear soil length between the electrode chambers was 80 cm, representing a reasonable distance to carry out experiments where transport of species in time will have to be established. The depth of the sample was taken to be 80 cm, in an attempt to establish any changes in transport on a vertical plane. Carbon (graphite) rod electrodes of 4.8 cm diameter were snugly placed in the two electrode chambers. Carbon electrodes were selected because they do not corrode and they do not introduce secondary products into the system. The distance between the electrodes was 110 cm. The thickness of the flume was 5.1 cm, in order to maintain one-dimensional flow and transport conditions across the electrodes.

The fluids in the electrode chambers were about 5.6 L each and the set-up allowed placement of about 31,400 cm³ of soil into the flume. The specimen chamber was separated from the electrode chamber by a
nonwoven geotextile supported by a geogrid. This support held the specimen within the set-up and avoided dispersion and/or collapse of soil particles into the electrode chambers. Each electrode chamber was connected to a bubble tube (Mariotte bottle) and an electrolyte conditioning system, as depicted in Figure 3.4. The bubble tube maintained the water level across the specimen constant and therefore prevented development of any external hydraulic gradient across the specimen. Transport of species was then due to conduction under electrical gradients and not due to an externally-applied hydraulic gradient. One other function of the bubble tube was to replenish fluid that may be lost in the electrode compartments due to any electroosmotic pore fluid flow.

Each electrode chamber was further connected to a fluid circulation system where the fluids within the chamber were recycled through the conditioning reservoir by two separate pumpheads connected to the same peristaltic pump driver. The pore fluid chemistry in the anolyte and the catholyte was separately controlled in these conditioning reservoirs (Figure 3.4). The circulation rate was maintained at a level which allowed displacement of all the solution in the electrode chamber within one to three minutes (2,000 to 4,000 mL/min). Two other pumps with pH controllers were connected to the two conditioning reservoirs. These pH controllers allowed setting the pH levels at a prefixed value and the pump intermittently injected the conditioning liquid from a separate container into the conditioning
Figure 3.4: A Schematic Diagram of the Test Set-up-1
reservoir to maintain the target pH value of the solution. The pH value in the pump controller was set to a value of 7.0. The pump injected the conditioning fluid intermittently adjusting the pH in the conditioning reservoir. Any excess fluid injected by the pH controlled pump and the fluid transported due to electroosmotic flow were collected in graduated cylinders placed at both ends of the set-up. Since the water level across the soil specimen was at the same level as the outflow holes at both ends, the electroosmotic flow rate would be determined after deducting the contribution of the species injected in the conditioning reservoir. Normally, the electroosmotic flow will be from the anode towards the cathode. The reservoirs are placed on both sides since there are data that display that electroosmotic flow may reverse direction in kaolinite.

A smaller bench scale horizontal column (set-up-2) used for the ion injection tests is shown in Figure 3.5. The glass cell had dimensions of 11.4 cm (4.5 in.) outside diameter, 10.1 cm (4 in.) inside diameter, and 30 cm (11.8 in.) in length. Two sets of ports at a designed spacing along the glass cell were available which can be voltage and/or temperature and sampling ports. The distances between electrodes were 34 cm. The electrolyte conditioning scheme at the boundaries and testing procedures were similar to that used in the set-up-1.
1. Bubble tube (Marriote bottle)-constant head supply reservoir
2a. Gas vent-anode;
2c. Gas vent-cathode
3a. pH sampling port-anode;
3c. pH sampling port-cathode
4a. End cap-anode compartment (made of Teflon™)
4c. End cap-cathode compartment (made of Teflon™)
5. Soil specimen (Glass sleeve of 20 cm long and 10 cm inside diameter)
6. Excess ports
7. DC supply to carbon electrodes in the end caps
8. Cathode overflow and measuring cylinder

Figure 3.5: A Schematic Diagram of the Test Set-up-2
3.3 Materials

Three experiments were carried out in the above test set-up 1. A fine sand bed was used in the first experiment. This sand was poorly graded with a $D_{10}$ size of 0.15 mm and it is depicted as SP in the Unified Soil Classification System (USC). It was decided to select a clay for the second experiment. Microbial growth would be hindered in clays of high plasticity because of the following reasons; 1) pore spaces in such clay deposits would be of a size (micrometer) on the same order of magnitude as that of the microorganisms, 2) osmotic component of suction in such clays will adversely affect microbial growth, and 3) very low hydraulic conductivity of intact and high plasticity clayey deposits often retard transport of non-aqueous phase liquids delaying their contamination in the first place. Georgia kaolinite, a low plasticity clay, was selected in the second experiment. The differences in geotechnical characteristics of the fine sand and the Georgia kaolinite are 1) about three orders of magnitude difference in hydraulic conductivity ($8 \times 10^{-4}$ cm/s versus $2 \times 10^{-7}$ cm/s), and 2) approximately one order of magnitude increase in electrical conductivity across the soil ($13.9 \pm 1.2$ $\mu$S/cm versus $124.1 \pm 6.6$ $\mu$S/cm). Other characteristics of Georgia kaolinite used in this study are given by Hamed et al. (1991). This soil is classified as CL in the USC system.

These first two experiments were carried out in order to establish the technical feasibility of injecting ammonium and sulfate ions in a highly...
permeable fine-grained sand bed with a lower pore fluid conductivity and a low permeability clay bed with a higher electrical conductivity. In the third experiment, the performance of the technique in a heterogeneous medium is evaluated by preparing a fine-grained sand layer overlying a kaolinite bed. The three experiments are depicted with the symbols BEK-01 (fine-grained sand), BEK-02 (kaolinite) and BEK-03 (layered media), respectively.

Another three experiments were carried out in the silty-clay (Argonne National Laboratory) which is depicted as SC-SM in the Unified Soil Classification System (USC). The hydraulic conductivity was around $3 \times 10^{-5}$ cm/s. In the same soil, different types of species were injected to understand how the boundaries effect the injection of ions and the changes in the pore fluid chemistry in response to different kinds of injected species. In the first experiment, ammonium and nitrate ions were, respectively, injected from the anode and cathode (BEK-04). In the second experiment, ammonium and nitrate ions were, respectively, injected from the anode and cathode with continuously flushing the anode compartment (BEK-05). In the third experiment, ammonium and phosphate ions were, respectively, injected from the anode and cathode with continuously flushing the anode compartment (BEK-06).

### 3.4 Selection of the Processing Current

As depicted in Equation 2.6, the transport rate of ions in soils under the electrical field will be affected by their effective ionic mobility, charge
(and hence their migration direction with respect to the electroosmotic transport), the local electrical potential gradient and the electroosmotic coefficient of permeability of the medium. In electrokinetic injection, a constant current, or a constant electrical potential, or a continuously changing current, or electrical potential, could be applied across the electrodes. When the constant current mode is selected, electrical potential across the electrodes floats with the changes in the electrical conductivity. The electrical conductivity of the pore fluid, in return, changes with the changing electrochemistry across the electrodes. The species input often increase the ionic concentration in the medium increasing the electrical conductivity and decreasing the electrical potential difference in time. Constant current density allows control and prediction of the electrolysis reactions at the boundaries. A better perception of the ongoing chemistry across the medium is hence obtained. Constant electrical potential lacks this control since the rate of production of the species by the electrolysis reactions at the boundaries will be changing with the floating current density.

A reasonable transport rate for an ion could be achieved if an initial electrical potential gradient of 1 V/cm is selected since the ionic mobility of most common ions with a valence of one would range between 30 cm²/V-day to about 120 cm²/V-day at infinite dilution. Hydroxyl and hydronium ions are special cases with about 180 cm²/V-day and 300 cm²/V-day, respectively (Lide and Frederikse, 1993). An electrical potential gradient of 1 V/cm is one
that is attainable in field implementation of the technique. Higher electrical potential gradients may result in undesirable increases in the temperature across the medium which may affect the transport rates (Acar and Alshwabkeh, 1996). Lower electrical potential gradients will decrease the transport rate of the target species and it will unnecessarily prolong the duration of the experiment.

3.5 Test Procedure

Two experiments were carried out in order to establish the technical feasibility to inject ammonium and sulfate ions in the highly permeable fine sand bed with the lower pore fluid conductivity and the low hydraulic conductivity clay bed with the higher electrical conductivity. The two experiments were depicted with the symbols BEK01 (fine sand) and BEK02 (kaolinite).

The following experimental procedure was used:

- Initially, soil characteristics were determined, which include grain size distribution, hydraulic conductivity, liquid limit, plastic limit, initial pH, maximum dry density and optimum water content.
- The fine-grained sand was compacted in layers in the flume at a final thickness of 70 cm in BEK-01. The clay in BEK02 was placed at a water content of 42 percent (slightly above the liquid limit of 38 percent). The need to place the kaolinite bed at about the liquid limit is due to the difficulty to saturate the specimen if it were placed at a lower...
water content. Processing an unsaturated deposit will bring in another factor outside the scope of the study at this stage. In the layered experiment (BEK03), kaolinite was first placed at a water content of 44 percent in the set-up and the fine-grained sand layer was compacted dry on top. Initial density and water contents of the specimen were measured. The silty-clay used in experiments BEK-04, BEK-05 and BEK-06 was placed at a water content of 34 percent, which was the water content near the liquid limit.

- The electrode reservoirs were filled with deionized and distilled water in order to facilitate any mass balance evaluations. The water level was flush with the outflow holes at both ends to allow for any electroosmotic flow measurements. For test set-up-1, the water level was 5 cm below the top soil level leaving 65 cm of soil under the water.

- The specimen was left overnight in the case of the fine-grained sand and about a week in the case of the clay and silty-sand in an attempt to increase the saturation in soils.

- Pore fluid across the specimen and in the reservoirs was sampled by extracting it with a disposable syringe through the ports. A separate syringe was used for sampling each port.

- Different levels of current were applied across the specimen momentarily and the developed electrical potential differences were
recorded. A current level which gives an initial potential gradient of about 1 V/cm was selected. Electrical gradients substantially lower than this level may prolong the time of testing and a potential gradient of 1 V/cm can be practically established in the field.

- The system was turned on at the selected current and the experiment was initiated.
- Samples of pore fluid were extracted across the specimen intermittently (every 6 hours to a day) and they were prepared for analytical work and sent for analysis.
- The experiment was continued until steady state conditions were achieved in transport and the experiment was terminated. In BEK-03, when steady state conditions were reached the electrolytes were drained and the process was reinitiated and continued until a second steady state was achieved.
- Samples extracted from the fine-grained sand layer in BEK-01 were diluted with distilled and deionized water and percolated through a 0.45 micrometer disposable syringe filter. All other samples collected were in the form of a slurry. These samples were mixed with 10 mL distilled, deionized water and the solution centrifuged for 30 minutes. The supernatant was collected, separated and was sent for analysis.
- The moisture content of the residual soil was determined in an oven using the ASTM method.
A Dionex 2010 series ion chromatograph (IC) is used for all anions including sulfate, chloride, phosphate and nitrate (EPA, 1994). Ammonium concentration was determined by using Wescam Model 360 ammonia analyzer (Alltech Associates, 1990; Carlson, 1978). Furthermore, the pore fluid was analyzed for twelve other predominant cations by using the inductively coupled plasma (ICP) technique (EPA, 1992).
4.1 Fine-grained Sand Bed (BEK-01)

4.1.1 Electrical Potential and Flow

The initial electrical potential difference developed across the specimen in BEK-01 is shown in Figure 4.1. Electrical gradients developed in response to the different current densities applied gave a bulk conductivity of 13.9±1.2 μS/cm. The conductivity across the saturated clean sand was quite low. Therefore, very low current densities could generate quite high electrical potential gradients across the saturated sand bed. A current density of 15 μA/cm², which renders an initial electrical gradient of 1.09 V/cm, was selected for processing. The current density was kept constant in the experiment. This allows better control of the electrolysis reactions and a better assessment of the transport across the cell. As the generated acid at the anode and the base at the cathode were neutralized and ammonium and sulfate ions were introduced into the system, the electrical conductivity across the specimen would increase and the electrical potential difference would decrease. This decrease in electrical potential difference across the cell with time is presented in Figure 4.2. The total electrical potential difference decreased from about 120 V to 25 V in time indicating that the electrical conductivity across the cell increased almost five times the initial
Figure 4.1: Initial Electrical Potential across the Sand Bed (BEK-01) under Different Current Densities

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Figure 4.2: Changes in Electrical Potential Difference across the Sand Bed (BEK-01) with Time
value. Electrical voltage distributions are directly related to changes in pore fluid chemistry of soil. It is also noted that relatively steady state conditions were reached within the first 300 hours of processing, or about 12 days of processing. A linear voltage across the soil specimen developed and decreased with time until a steady state condition was achieved. As a result, the voltage gradient dropped from 1.09 to 0.2 V/cm in the initial 300 hours of processing and achieved a constant value of 0.2 V/cm during latter stage of the processing period (Figure 4.3).

Figure 4.4 displays that the electrical conductivity across the soil specimen increased from initial its value 13.9±1.2 μS/cm to a constant value around 63.2±4.3 μS/cm within the first 300 hours of processing. In order to maintain a constant current density, the electrical gradient would change according to the electrical conductivity. The injection of ions would increase the pore fluid conductivity, as a result the electrical gradient would decrease (Figure 4.3). It also indicates that conductivities across the soil specimen varied in a very narrow range and it almost linearly increased with time until the steady state condition was reached. The linear increase in the conductivity could be assumed to be due to the injection of ions. Conductivity is mainly a function of ion concentration, effective ionic mobility and the valency of ions. It can be postulated from such a behavior of conductivities in time and space that the effective ionic mobility of different inorganic species in the pore fluid were in the same range. The apparent
Figure 4.3: Voltage Gradient Developed across the Sand Bed (BEK-01) with Time
Figure 4.4: Changes in Electrical Conductivity across the Sand Bed (BEK-01) with Time

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Figure 4.5: Changes in Apparent Conductivity in BEK-01

Apparent Conductivity (μS/cm)

Time (h)
conductivity (Figure 4.5) showed the same trend and good agreement with the bulk conductivity diagram (Figure 4.4) which could be assumed as the average representation of the conductivities across the soil specimen with time.

The cumulative electroosmotic flow with time is shown in Figure 4.6. A total flow of 2100 cc or 0.2 pore-volume was collected during 528 hours of processing. Electroosmotic flow is a function of coefficient of permeability and the electrical gradient. The electroosmotic permeability ($k_o$) increased from $6 \times 10^{-6} \text{ cm}^2/\text{Vs}$ to $1.5 \times 10^{-5} \text{ cm}^2/\text{Vs}$ unit steady state condition was reached (Figure 4.7). Given the average values for the initial final voltage gradients of 1.09 and 0.2 V/cm, respectively, the electroosmotic flow rate decreased from 0.7 to a constant value 0.3 cm/day. It was possible to maintain constant pH with the procedure employed and the pH of the pore fluid at the electrode chambers and across the fine-grained sand bed ranged between 6.5 to 7.5 all throughout testing (Figure 4.8). A stable pH might sustain a electroosmotic flow throughout the testing period because the zeta potential is a function of pH. A constant pH environment can possibly maintain a constant zeta potential if other factors affecting zeta potential remains constant. But as the electrolyte concentration increase, the zeta potential decreases. So in a constant pH environment, the injection of ions would decrease the electroosmotic permeability. However, the results of the sand bed show that increase in the conductivity from 14 to a constant value 64 µS/cm had also
Figure 4.6: Electroosmotic Flow in BEK-01

Electroosmotic Flow (ml)

Time (h)

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Figure 4.7: Changes in Coefficient of Electroosmotic Permeability in BEK-01
Figure 4.8: pH across the Sand Bed (BEK-01) During Electrokinetics Processing
linearly increased the electroosmotic permeability from $6 \times 10^{-6}$ cm$^2$/Vs to a constant $1.5 \times 10^{-5}$ cm$^2$/Vs which contradicts conventional wisdom. Subtle changes in initial and boundary conditions of the system chemistry are found to have very large effect on electroosmosis in soils. The electroosmotic water transport efficiency ($k_e$) had dropped from an initial value of 0.35 cm$^3$/As to a constant value 0.22 cm$^3$/As (Figure 4.9), conforming with the electroosmotic flow rate data. Therefore, $k_e$ and $k_i$ are not constants for a particular soil but they are time dependable variables controlled by the dynamic chemistry generated at the boundaries, which are responsible for the changes in the pore-fluid and the surface chemistry of the soil.

4.1.2 Ammonium and Sulfate Profiles

Figure 4.10 presents the increase in ammonium profile across the sand bed with time in the middle row. It is interesting to note that within 476 hours (20 days) of testing, the cell was almost saturated with ammonium at a concentration of 25 mg/L to 30 mg/L. Ammonium ions reached the cathode compartment within the first 220 hours or 9.2 days (Figure 4.11) of testing rendering an effective transport rate of 12 cm/day. This transport rate, if achieved in the field and in different types of deposits, will be quite effective for in-situ bioremediation. The effective transport rate of a single species in the pore fluid, $v_i$ (cm/s), is given by (Alshawabkeh and Acar, 1996),

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Figure 4.9: Changes in Electroosmotic Water Transport Efficiency in BEK-01

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Figure 4.10: Ammonium Profile across the Middle Row of the Sand Bed (BEK-01)
Figure 4.11: Concentration of Ammonium across the Middle Row of the Sand Bed (BEK-01) in Time

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where $k_e$ is the electroosmotic coefficient of permeability (cm$^2$/V-s), $u_i^*$ is the effective ionic mobility (cm$^2$/V-s) and $i_e$ is the electrical gradient (V/cm). The transport rate due to the measured electroosmotic flow rate in this fine-grained sand bed was only about 0.7 cm/day. A major portion of the transport of the ammonium ion was thus due to ionic mobility of the species under the electrical gradient. The electrical gradient decreased from 1.09 V/cm to 0.22 V/cm (Figure 4.3). If an average electrical gradient of 0.65 V/cm was assumed to prevail during the test, the corresponding effective ionic mobility for the ammonium ion, $u_{NH_4}^*$, would be around 18 (cm/day)/(V/cm).

The ionic mobility of the ammonium ion at infinite dilution, $u_{NH_4}$, is 66 (cm/day)/(V/cm) (Linde and Frederikse, 1993). The mobility decreased to 27% of its value at infinite dilution due to the effects of porosity, tortuosity in the medium and other secondary factors. Considering the fact that the porosity of the compacted fine-grained sand was 0.39 (or 39% of the total area), the decrease in $u_{NH_4}$ was mostly due to the decrease in effective area for transport.

We note, however, that these results cannot be generalized for all systems and all soils. In fact, as depicted in Figures 4.10 and 4.11, the transport rates decreased in the latter stages of the test when the ammonium
concentration reached a level of ~ 20 to 25 mg/L. The transport rate of a specific ion under electrical fields is not only controlled by the ionic mobility but also by the concentration and charge of the specific species relative to the others in the medium. The transportability (or transference number) of a specific species is high when that species is the predominant one in the medium. Transport of other species, the need for charge balance and electrical neutrality may decrease the transference number when multi-species are transported across the soil under electrical fields (Alshawabkeh and Acar, 1996). The anode depolarization used in this study prevented introduction of other species (such as the hydronium ion) into the medium. This provision did not allow a premature increase in the ionic conductivity and hence, transference number for the ammonium ion remains high until the species available in the pore fluid and ammonium/sulfate ions moved across the specimen. The electrical conductivity in the medium would then increase and the electrical potentials would decrease (Figure 4.2), decreasing the transport rate of the ammonium ion. A more detailed numerical analysis of the results obtained in these experiments is being carried out at LSU using the numerical model developed for multi-component species transport model under electrical fields (Zheng, 1997; Alshawabkeh and Acar, 1996).

When the anolyte/catholyte conditioning techniques described in this study were employed and a current density of only 15 µA/cm² was
used, the electrical potential gradient of 1 V/cm or less would transport ammonium ion in a fine-grained sand bed at rates of 10 to 20 cm/day. The results demonstrate that the electrokinetic injection technique could be efficiently used to inject ammonium ion in clean fine-grained sands and the transport rates are of a magnitude that will allow practical use of the technique.

A comprehensive understanding of multi-species transport requires an evaluation of the concentration and transport of all the species across the bed since the interaction and the prevailing charge balance affects the transport rates. The predominant species in BEK-01 were the ammonium and the sulfate ions. These ions were available as a result of the depolarization of the electrode reactions. Figures 4.12 and 4.13 show the sulfate ion distribution across the bed in time. The results are quite interesting. The following observations are made:

- soil pore fluid had an initial concentration of about 5 mg/L of sulfate,
- the sulfate ion concentration increased across the cell while steady state conditions were reached at about 200 hours with a sulfate concentration of about 100 mg/L at the cathode and 20 mg/L at the anode.
- sulfate ion transport rate could not be evaluated accurately because of this initial concentration and the observed decrease in transport in time; however, a transport rate of anywhere from 12 cm/day to 20
Figure 4.12: Sulfate Profile across the Middle Row of the Sand Bed (BEK-01)

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Figure 4.13: Concentration of Sulfate across the Middle Row of the Sand Bed (BEK-01) in Time
cm/day was discernable within the first 200 hours of processing. The transport rate steadily decreased until the steady-state condition was reached.

- sulfate ion transported quite rapidly (12-20 cm/day) upstream from the cathode compartment to the anode compartment, although there was an electroosmotic fluid flux of 0.7 cm/day opposing transport of this species.

The ionic mobilities at infinite dilution for the sulfate and ammonium ions are 74 and 66 (cm/day)/(V/cm). Therefore, it is expected that the sulfate ion transport rate be greater than the ammonium ion. It is striking to note that the sulfate ion concentration ranges from 100 mg/L at the cathode to 20 mg/L at the anode under steady state conditions although the ammonium ion saturated across the bed at 25 mg/L to 30 mg/L. An appropriate assessment of results requires an evaluation of charge distribution, adsorption effects, and any solubility equilibria. The charge concentrations of these two species in the medium are given in Figure 4.14. There was an imbalance in charge concentration when only ammonium and sulfate ions were considered. The results could be better appreciated if the final ammonium and sulfate charge concentrations across the bed are evaluated together with the charge concentration of other species. A bar diagram of charge concentration for all species at 476 hours of processing is given in Figure 4.15. The results are quite interesting: the fine-grained sand used was a beach sand and sodium,
Figure 4.14: Ammonium and Sulfate Charge Concentration in the Sand Bed (BEK-01) after 476 Hours of Processing
Figure 4.15: Charge Concentration of Cations and Anions after 476 Hours of Processing in BEK-01

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chloride and calcium ions made up the major differences in charge concentration. Chloride ions at the anode and sodium ions at the cathode made up most of the rest of the deficient charge. Chloride ions moved towards the anode. Since these ions were not transported out of the system, they increased the ionic conductivity in the vicinity of the anode. They also provide the necessary negative charge to meet the electrical neutrality requirement. As a result, the sulfate ions originating in the cathode compartment could not move further into the anode compartment since electrical neutrality was maintained by the chloride ions that already moved into that space, the ionic conductivity had increased and the transference number for the sulfate ions had decreased. Any further increase in sulfate concentration after this time would be gradual and in line with the need for charge balance in the anode compartment. As for the ammonium ion, the higher ionic mobility of this species with respect to the other cations had resulted in its domination of charge and transport in positively charged species across the bed.

There were not any significant differences between the concentration profiles obtained in the upper, middle or bottom rows (EK, 1995) displaying the homogeneity of transport under electrical fields. Figures 4.16 and 4.17 show the final distribution of ammonium and sulfate profiles at different rows after 476 hours of processing. The profiles in different rows were mirror reflections of each other for both the injected ions. So, under electrical field
Figure 4.16: Final Ammonium Distribution across the Sand Bed (BEK-01) in Three Different Rows
Figure 4.17: Final Sulfate Distribution across the Sand Bed (BEK-01) in Three Different Rows
the injected ions showed similar profiles perpendicular to the current flow. It is also noted that the uniform profiles across the soil specimen depends on the conditions of the boundaries. A continuous electroosmotic flow from the anode to the cathode was responsible for flushing out the initial pore fluid cations of the soil, whereas the initial pore fluid anions were accumulated in the cathode and around the cathode regions because these ions were not flushed out from the system. As a result the injected cation (ammonium) was uniformly transported, whereas the injected anion (sulfate) was nonuniformly transported.

One direct implication of these results is the need to flush the electrolytes in the electrode reservoirs intermittently or continuously in order to decrease the electrical conductivity at the boundaries. This procedure and the prevailing depolarization reaction will stimulate charge deficiency in the electrode compartments enhancing the transport rate of both the ammonium and the sulfate ions. Membrane techniques that would selectively remove the undesirable species may also be used to enhance the process. A process optimization technique is necessary for the field implementation of the process.

The results obtained in the fine-grained sand bed are quite encouraging for electrokinetic injection of species for in-situ bioremediation. Ion transport rates of the order of 10 cm/day to 20 cm/day are obtained under electrical gradients of 1 V/cm or less. Both ammonium and sulfate ions were
transported across the specimen and at concentration levels that could be effectively used for in-situ bioremediation.

4.2 Kaolinite Bed (BEK-02)

4.2.1 Electrical Potential and Flow

Hydraulic conductivity of the kaolinite bed was on the order of $2 \times 10^{-7}$ cm/s, three orders of magnitude lower than the $8 \times 10^{-4}$ cm/s value obtained for the fine-grained sand bed. The initial electrical conductivity of the kaolinite bed was determined by momentary application of different current densities across the electrodes and by measuring the established electrical potential difference across the cell. The potential difference across the cell is shown in Figure 4.18. Current densities of 15 $\mu$A/cm$^2$ to 136 $\mu$A/cm$^2$ resulted in electrical potential gradients of 0.22 V/cm to 1.66 V/cm, respectively. An average electrical conductivity of $124 \pm 6.6$ $\mu$S/cm was calculated using the current density and the electrical potential gradients developed in the kaolinite bed. The conductivity level was ten times higher than the initial conductivity of the fine-grained sand bed ($13.9 \pm 1.2$ $\mu$S/cm). The increase in the concentration of chemical species in the clay results in an increase in ionic conductivity of the pore fluid. A current density of 123 $\mu$A/cm$^2$ was selected and this current rendered an initial potential gradient of 1.0 V/cm. During the 720 hours of processing, the potential difference decreased across the kaolinite bed with time due to the injection of species (Figure 4.19). The voltage gradient developed across the specimen with time is

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Figure 4.18: Initial Electrical Potential across the Kaolinite Bed (BEK-02) under Different Current Densities
Figure 4.19: Changes in Electrical Potential Difference across the Kaolinite Bed (BEK-02) with Time
Figure 4.20: Voltage Gradient Developed across the Kaolinite Bed (BEK-02) with Time

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shown in Figure 4.20. A linear voltage across the specimen was observed during the processing period. During 720 hours of processing, the voltage gradient was dropped from 1.0 to 0.35 in the soil specimen which indicates the ionic conductivity increased about three times.

The changes in electrical conductivity across the specimen with time is shown Figure 4.21. The conductivity increased from initial value 124±6.6 μS/cm to 290±110 μS/cm in 720 hours of processing. The dynamic pore fluid chemistry under electrical field may respond differently at various locations during processing. Initial ionic pore fluid concentration, charged clay surfaces and injected ions interact in a complex manner, which may affect the factors controlling the conductivity. These factors include the ionic pore fluid concentration, effective ionic migration (porosity, tortuosity) and valency of ions. The apparent conductivity (the average conductivity across the soil specimen) of the soil was increased 124 to 320 μS/cm in 720 hours of processing as shown in Figure 4.22.

Electroosmotic flow was from the anode compartment to the cathode compartment. A total flow of 15 liters or 1.2 pore volume was collected during 720 hours of processing (Figure 4.23). It was interesting to note that the electroosmotic coefficient of permeability increased from 1.5x10⁻⁵ cm²/Vs to 4.4x10⁻⁵ cm²/Vs (1.3 (cm/day)/(V/cm) to 3.8 (cm/day)/(V/cm)) within the 720 hours of processing (Figure 4.24). Given the average values for the initial and final electrical potential gradients of 1.00 V/cm and 0.35 V/cm,
Figure 4.21: Changes in Electrical Conductivity across the Kaolinite Bed (BEK-02) with Time
Figure 4.22: Changes in Apparent Conductivity in BEK-02
Figure 4.23: Electroosmotic Flow in BEK-02
<table>
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<tr>
<th>Time (h)</th>
<th>$k_e$ (cm²/Vs)</th>
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<tr>
<td></td>
<td>10^5</td>
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<td></td>
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**Figure 4.24:** Changes in Coefficient of Electroosmotic Permeability in BEK-02
respectively, the electroosmotic transport rate increased slightly from 1.3 to 1.35 cm/day. This gives an assessment of the magnitude of the electroosmotic transport rate of the pore fluid from the anode to the cathode compartment. It is also noticeable that increase in the conductivity from 124 to 320 µS/cm (Figure 4.22) had increased the electroosmotic permeability from 1.5x10^{-5} to 4.4x10^{-5} cm²/Vs (Figure 4.24) during 720 hours processing in the kaolinite bed. The initial soil pH was around 5.4. A constant pH (6.5 to 7.5) environment at boundaries had increased the soil pH to around 7.0 during the electrokinetic ions injection processing. The conductivity (inversely related to zeta potential) of the soil had increased three times whereas the pH (directly related to zeta potential) had increased at least 10 fold. As a net effect, the zeta potential had become more negative and the electroosmotic permeability had increased. So it is not unlikely that the electroosmotic flow rate increased, or decreased, or remained the same, when the electrical gradient decreased (i_e) and k_e increased. Figure 4.25 shows that the electroosmotic water transport efficiency had increased from 0.12 to 0.14 cm³/A.s during the processing period.

4.2.2 Ammonium and Sulfate Profiles

Figures 4.26 depicts the ammonium concentration profiles across the middle rows in the kaolinite bed during 30 days of processing. The transport across the clay bed was quite uniform. A relatively constant profile of ammonium at about 100 mg/L is achieved within the first 15 days of
Figure 4.25: Changes in Electroosmotic Water Transport Efficiency in BEK-02
Figure 4.26: Ammonium Profile across the Middle Row of the Kaolinite Bed (BEK-02)

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Figure 4.27: Concentration of Ammonium across the Middle Row of the Kaolinite Bed (BEK-02) in Time
processing. At this concentration level, the ammonium transport rate was in the order of about 9 cm/day (Figure 4.27). The process was continued after this time for experimental observation. The finding associated with the transport rate is interesting specifically when it is considered that the electrical conductivity in the kaolinite was significantly higher than that of fine-grained sand bed and the measured electroosmotic transport rate of pore fluid was in the order of 1.3 cm/day to 1.35 cm/day. Ammonium ion was transported at a rate significantly higher than the electroosmotic transport rate. The electrical gradient decreased from 1.0 to 0.35 V/cm (Figure 4.20). If an average of 0.7 V/cm was assumed to prevail during the test, the corresponding effective ionic mobility for ammonium ion would be around 12 (cm/day)/(V/cm). After 15 days of processing, the ammonium concentration was gradually increased. The final ammonium concentration varied from 250 to 150 mg/l across the anode to the cathode in the kaolinite bed after 720 hours or 30 days of processing.

The kaolinite had an initial sulfate concentration of about 200 mg/L. Injection and transport of sulfate ions become predominant only when the sulfate concentration at the anode increased beyond this initial concentration (Figures 4.28 and 4.29). The transport rate was not readily discernable; however, when the 200 mg/L level was reached at the cathode compartment, the rate of transport was about 10 cm/day (Figure 4.29) until the medium was saturated with ammonium and sulfate concentrations of 400 mg/L, or more,
Figure 4.28: Sulfate Profile across the Middle Row of the Kaolinite Bed (BEK-02)
Figure 4.29: Concentration of Sulfate across the Middle Row of the Kaolinite Bed (BEK-02) in Time
were reached. The effective ionic mobility for sulfate was around 16 (V/day)/(V/cm). From then on, sulfate concentration across the clay gradually increased with injection of the ion at the cathode compartment. Final concentrations after 30 days of processing varied from 600 to 1000 mg/l across the anode to the cathode. It should be noted that the sulfate accumulated near the cathode region was mostly transported from the initial sulfate of the pore fluid of soil.

Figure 4.30 displays the charge concentration of ammonium and sulfate ions. As in the case of the fine-grained sand bed, an assessment of charge equilibrium across the medium is essential to have a better appreciation of results.

A distribution of charges of other possible ions across the bed after 720 hours of processing is presented in Figure 4.31. Although most of the ions are accounted for, there was still some charge imbalance; possibly because the metals analyses were not yet all inclusive. The charge imbalance aside, most of the charge across the bed was accountable by the ammonia and sulfate injected in the soil. It is interesting to note that sulfate concentration at the anode was generally higher than the concentration across the bed mainly due primarily to transport of the initial sulfate across the specimen into the anode compartment. Homogenous distribution of the final ammonium and sulfate ions in three rows are respectively shown in Figures 4.32 and 4.33.
Figure 4.30: Ammonium and Sulfate Charge Concentration in the Kaolinite Bed (BEK-02) after 720 Hours of Processing

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Figure 4.31: Charge Concentration of Cations and Anions after 720 Hours of Processing in BEK-02

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Figure 4.32: Final Ammonium Distribution across the Kaolinite Bed (BEK-02) in Three Different Rows
Figure 4.33: Final Sulfate Distribution across the Kaolinite Bed (BEK-02) in Three Different Rows
The results obtained in the kaolinite bed are as encouraging as the results obtained in the fine-grained sand bed and they display the feasibility and the potential to employ the technique in soils with low hydraulic conductivities.

4.3 Fine-grained Sand/Kaolinite Bed (BEK-03)

4.3.1 Electrical Potential and Flow

Although the above experiments, first in a fine-grained sand bed and then in a clay bed, display the feasibility of injecting process additives under electrical fields and demonstrate the potential of the technique, it is necessary to evaluate performance in a heterogenous media. Heterogeneity can be in a direction perpendicular to the electrical field or, in the same direction with the electrical field. In the case of a perpendicular heterogeneity, such as a clay layer placed perpendicular to the electric field and sandwiched in between more permeable layers or vice versa, the results of the above study show that the transport rate in the clay layer will decrease slightly. However, it will still be possible to employ the electrokinetic injection technique efficiently to introduce and migrate nutrients and process additives across the medium since the transport rates will be within the same order of magnitude.

When the heterogeneity is in the same direction with the electrical field, there is the possibility that the layer with the higher electrical conductivity (clay layer in this case) would transmit most of the current,
hindering the transport of the species across the medium with the lower ionic conductivity (the fine-grained sand layer in the above case). It was decided to study this specific case involving two separate soil strata (having different hydraulic and electrical conductivities) overlying each other. The fine-grained sand used in BEK-01 and the clay used in BEK-02 were used to create a layered bed consisting of the two soils. The clay was first placed in the set-up at a water content of 45 % and at a thickness of 47 cm. The first two sampling ports remained within this layer. The fine-grained sand layer was placed on top of the clay layer at a thickness of 27 cm. The two rows of sampling ports were about 11 cm and 1 cm above the clay fine-grained sand interface and the water table was 15 cm above this interface. All ports were sampled to assess ion transport across the heterogenous medium.

The initial electrical potential differences under different current densities recorded across the two layers are depicted in Figures 4.34 and 4.35. The electrical gradient in the clay and the fine-grained sand layers were 1.6 and 2.5 V/cm, respectively under an average current density of 151 μA/cm². It is necessary to consider the different cross sectional areas of the two layers if an average electrical conductivity is to be calculated. The backcalculated conductivity of the clay layer was 80-90 μS/cm, while the conductivity of the fine-grained sand layer was 10-12 μS/cm. The conductivity in the clay layer was slightly lower than that measured in BEK-02, owing to the slightly higher water content of this layer in the flume in BEK-
Figure 4.34: Initial Electrical Potential across the Sand Layer of BEK-03 under Different Current Densities

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Figure 4.35: Initial Electrical Potential across the Kaolinite Layer of BEK-03 under Different Current Densities

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Initially, the clay layer was more conductive and its thickness was about three times the submerged thickness of the fine-grained sand layer. Therefore, most of the applied current would flow across the clay layer. The results of electrical potential difference of during 1028 hours of processing in BEK-03 are presented in Figure 4.36 and 4.37. As a result of the species injected across the bed and the increase in electrical conductivity, the electrical potential difference across the cell decreased. The anode and cathode liquid were flushed after 596 hours of processing. Immediately after that time the potential difference across both layers increased. The voltage gradients developed during processing in both layers are presented in Figure 4.38. Due to lower initial pore fluid concentration, the conductivity in the sand layer was lower than the clay layer. As a result to maintain constant current density the initial voltage gradient of the sand layer was higher than the clay layer. It was interesting to see that there was not any significant difference between the electrical potential difference and gradient (1.1 V/cm from Figure 4.38) across the two layers after about 200 hours of processing. Under the electrical field when ions were injecting at boundaries, it is simultaneously extracting ions from the pore fluid of the soil. When the electrical field was applied to the layered soil, the injection of ions would be more predominate in the lower conductivity soil than in the higher conductivity soil, because of lower ion concentration in the former. It is also noticeable that due to high voltage gradient in the sand layer, the ions were
Figure 4.36: Changes in Electrical Potential Difference across the Sand Layer of BEK-03 with Time
Figure 4.37: Changes in Electrical Potential Difference across the Kaolinite Bed of BEK-03 with Time
Figure 4.38: Voltage Gradient Developed across the BEK-03 with Time
transported at higher rate. As a result the conductivity increased in the sand layer more rapidly than clay layer, which means the voltage gradient dropped more rapidly in the sand layer than the clay layer. The species were transported across the fine-grained sand layer within the first 200 hours and the conductivity of the fine-grained sand layer increased. At this stage, both layers would behave as one layer in transport of the species under electrical fields. These results are quite interesting. The final voltage dropped to 0.4 V/cm in both layers after 1028 hours of processing (Figure 3.38).

The electrical conductivities developed during the processing in both layers are shown in Figure 4.39 and 4.40. The conductivity in the sand layer increased to around 500 μS/cm during the first 596 hours of processing and after flushing the anode and cathode compartments, the conductivity decreased to a value around 300 μS/cm (Figure 4.39). After flushing, the low conductivity at the boundaries had extracted the ions from the soil pore fluid, which resulted to decrease the conductivity of the soil. When ions at the boundaries increased by electrolyte conditioning, it again started injection of ions into the soil. As a result the conductivity again started to increase and after 1028 hours of total processing the conductivity increased to become around 550 μS/cm. Similar results were obtained for the clay layer (Figure 4.40). It is also noticeable that after flushing some locations across the clay-soil specimen, the conductivities were very high. It may be due to temporary
Figure 4.39: Changes in Electrical Conductivity across the Sand Layer of BEK-03 with Time
Figure 4.40: Changes in Electrical Conductivity across the Kaolinite Layer of BEK-03 with Time

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unstable voltage readings in soil when the compartments were flushed. The unstable reading was equilibrated with the system very shortly after flushing. The equivalent conductivity values (or apparent conductivity, which disregards the localized changes across the specimen) for both layers are presented in Figure 4.41. Depending upon the local pH and ionic strength, the electrical conductivity varies from one position to another. It seems that the apparent conductivity (Figure 4.41) is a good average approximate value for the specimen if we compared it with the local bulk conductivity diagrams (Figure 4.39 and 4.40).

Figure 4.42 displays the electroosmotic flow with time. During 1028 hours of processing, 35 liters or around 2.5 pore volume of water had transported from the anode to the cathode. The electroosmotic flow in BEK-03 is significantly higher than the tests with kaolinite (BEK-02) only. Similar to the previous experiments the electroosmotic permeability had increased with time. $K_e$ had increased from a initial value $1.5 \times 10^{-5}$ cm$^2$/Vs to final value $9.5 \times 10^{-5}$ cm$^2$/Vs (Figure 4.43) whereas in the kaolinite bed (BEK-02) the final value was around $4.5 \times 10^{-5}$ cm$^2$/Vs. The reasons for the increase in $K_e$ values with time is similar to those for the BEK-02 test. For the same soil, $K_e$ is a time dependent variable associated with the dynamic chemistry generated at the boundaries. Given the initial and final voltage gradients 1.6 and 0.4 V/cm, respectively, the electroosmotic flow rate had increased from
Figure 4.41: Changes in Apparent Conductivity in BEK-03
Figure 4.42: Electroosmotic Flow in BEK-03
Figure 4.43: Changes in Coefficient of Electroosmotic Permeability in BEK-03

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2.0 cm/day to 4.0 cm/day. So it is also very interesting to note that the electroosmotic flow rates had significantly increased with time by using the novel depolarization technique simulated in the experiment. One of the reasons is that the layered test (BEK-03) was conducted under a higher voltage gradient range from 1.6 to 0.4 V/cm, whereas the kaolinite test (BEK-02) was conducted at lower voltages 1.0 to 0.35 V/cm. Another reason is the higher water content of the kaolinite bed of layered soil than the kaolinite in BEK-02. Figure 4.44 displays the changes in electroosmotic water transport efficiency ($k_e$) with time. The $k_e$ values varied within a range of 0.14 to 0.18 cm$^3$/As during 1028 hours of processing.

4.3.2 Ammonium and Sulfate Profiles

The ammonium ion concentrations across the two layers are shown in Figures 4.45 and 4.47. First, ammonium ion was efficiently transported across both of the layers. The transport rate was faster across the fine-grained sand layer within the first 200 hours both due to the higher electrical gradient developed and lower conductivity (Figure 4.46). It is also interesting to see, during this period, the ammonium concentration was developing in the cathode chamber more rapidly than in the adjacent soil. The injection of sulfate ions in the cathode chamber might enhance the transport of ammonium ions from the adjacent soil to maintain electrical neutrality. The effective transport rate for the sand and clay bed were respectively 18 cm/day (Figure 4.46) and 13 cm/day (Figure 4.48). Subsequently, the transport rate
Figure 4.44: Changes in Electroosmotic Water Transport Efficiency in BEK-03

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Figure 4.45: Ammonium Profile across the Sand Layer in BEK-03
Figure 4.46: Concentration of Ammonium across the Sand Layer in BEK-03 in Time

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Figure 4.47: Ammonium Profile across the Kaolinite Layer in BEK-03
Figure 4.48: Concentration of Ammonium across the Kaolinite Layer in BEK-03 in Time

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decreased. After 596 hours of processing, the concentration of ammonium ion across the fine-grained sand bed was slightly higher than that in the clay layer, both around 250 mg/L. After 596 hours, both the anode and cathode compartments were flushed. After flushing, due to low conductivity at the boundaries, the concentration of ammonium decreased more rapidly in the sand bed than in the clay bed because ions mobilities were different in the two layers. Ion mobility generally depends on porosity and tortuosity of the medium. When the conductivity of the boundaries equilibrate with the pore fluid of the soil, again conductivity would increase with the injection of ions from the boundaries. After 1028 hours of processing, the final concentration of ammonium varied in the sand layer within a range of 300 to 350 mg/l and in the clay layer within a range of 250 to 300 mg/l.

Sulfate transport across the layers is even more interesting (Figures 4.49, 4.50, 4.51 and 4.52). In the clay layer (Figure 4.51), there was no transport until the boundary concentration at the anode increased above the initial sulfate concentration. It is also noticeable that this transport from the clay to the anode compartment prevailed even though there is an electroosmotic transport rate around 3 cm/day from the anode to the cathode in the clay layer. There was a wave in the sulfate profile developing close to the anode compartment as the species already available in the clay transported out of the medium to the anode compartment. As the sulfate concentration at the anode built up (around 200 hours), it also provided the
Figure 4.49: Sulfate Profile across the Sand Layer in BEK-03
Figure 4.50: Concentration of Sulfate across the Sand Layer in BEK-03 in Time
Figure 4.51: Sulfate Profile across the Kaolinite Layer in BEK-03
Figure 4.52: Concentration of Sulfate across the Kaolinite Layer in BEK-03 in Time

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anions necessary in charge conservation at the anode compartment. It is also noticeable that initially, some of the sulfate was built up in the sand layer close to the anode compartment, which did not transport from the cathode through the sand layer. It was the direct consequence of the initial pore fluid sulfate concentration in the clay layer, which were transported from the clay and accumulated in the anode chamber. Then, these sulfate ions were transported into the sand layer by electroosmosis and/or to maintain electrical neutrality. So it should be noted that the ionic concentration of initial pore fluid of the layers in the heterogeneous media may affect the transport efficiency of the injected ions of each other in a complicated fashion. A hypothetical case is considered, where a condition is simulated to inject any other anions rather than sulfate from the cathode compartment into heterogeneous media consisting of the same layers as this test, the initial high concentration of sulfate in the clay bed will accumulate in the anode compartment and the adjacent clay soil, which will lower the transfer efficiency of the injected anions in the clay. Similar results were obtained in BEK-01. These accumulated sulfate ions (from the initial pore fluid of clay) will also be transported in the sand layer by electroosmosis, which will also lower the transfer efficiency of the injected anions in the sand bed. So it may be necessary to revise the technique. One hypothesis is to process both the layers separately, or together by intermittent or continuous flushing at the
anode chamber. Secondly, membrane techniques might be applied to remove these undesirable initial pore fluid ions.

After 596 hours processing, the sulfate ions saturated both the fine-grained sand and clay layer at about 700 mg/L to 800 mg/L. After flushing, the sulfate ions profiles in both layers were similar to the ammonium profile because underlying reasons for both the cases are the same. The final concentration of sulfate in the sand layer (Figure 4.49) and clay layer (Figure 4.51) were, respectively, within the range of 900 to 1000 mg/l and 1200 to 1000 mg/l.

The final distribution of ammonium and sulfate ions at different rows in the clay (two rows) and sand (two rows) layers are presented in Figures 4.53 and 4.54. The depolarization technique can be used to uniformly inject species in heterogeneous media for in-situ bioremediation.

The results of the three experiments demonstrate the potential and feasibility to inject species into soils under electrical fields. Transport rates on the order of 10 cm/day to 20 cm/day were achieved for sulfate and ammonium ions in both a fine sand bed, a clay bed and a layered bed. The electrical gradients of 1 V/cm or less constituted the predominant driving force for transport under current densities of 15 to 150 µA/cm². In all the experiments conducted, the results obtained in different rows, within the same layer, were mirror reflections of each other displaying the uniformity of transport under electrical fields. The electrode depolarization technique
Figure 4.53: Final Ammonium Distribution across the BEK-03 in Different Rows
Figure 4.54: Final Sulfate Distribution across the BEK-03 in Different Rows
described in this study, coupled with electrolyte conditioning techniques, could be exploited to inject nutrients and process additives for *in-situ* bioremediation systems.

### 4.4 Silty-Clay Soil Specimen

In the previous experiments, it is clearly demonstrated that the efficiency of uniform transport of the injected ions in the media under electrical field also depends on the initial pore fluid conductivity and the boundary conditions. The ions transport mechanisms involved, from the anode to the cathode and the cathode to the anode, are different due to electroosmosis. Generally, electroosmotic flow is from the anode to the cathode. An asymmetrical ion transport mechanisms occurs, in which the injected cations migrate from the anode to the cathode by electromigration accelerated by electroosmosis, whereas the injected anions migrate from the cathode to the anode by electromigration opposed by electroosmosis. As a result, initial pore fluid cations are flushed out from the system, which renders the injected cations more uniformly transported in the media. On the other hand, the initial pore fluid anions are transported to the anode and to the adjacent soil, which hinders the uniform transportation of the injected anions. The transport rate of the injected ions under the electrical field is not only a function of the ionic mobility but also depends on the concentration and charge of the injected ions relative to the other competing ions in the medium. The transportability (or transference number) of the injected ions is
high when that ion is the predominate ion in the medium. The accumulation of other competing pore fluid ions may decrease the transference number of the injected ions when multi-species are transported across the soil under electrical fields. Due to limited knowledge on electrokinetic injection of ions in soil, improvements and changes made in each test parameter depend on the results of the previous tests. Hypotheses were made and tested by experiments. It is hypothesized that by continuous flushing of the anode compartment, it is possible to decrease the conductivity, which will increase the extraction of the initial pore fluid anions from the soil specimen that will be flushed out from the system. As a result the transportability of injected anions will increase.

Three experiments were conducted in the silty-clay soil under the same electrical field. The three experiments are depicted with the symbols BEK-04, BEK-05 and BEK-06. Ammonium and nitrate were injected in BEK-04 without continuous flushing the anode compartment, whereas in BEK-05, the anode compartment was continuously flushed. These two experiments were carried out to test the hypothesis that continuous flushing at the anode will increase the transportability of the injected cations. The third experiment, BEK-06 was carried out with different species. Ammonium and phosphate were injected from the anode and cathode, respectively, with continuous flushing of the anode compartment. This experiment was carried out to compare the results of BEK-05 to see how the pore fluid chemistry would
response due to injection of different kinds of species under the same electrical field with the same soil.

The initial electrical potential difference developed across the silty-clay specimen due to momentary application of different current densities are presented in Figure 4.55. Electrical gradients developed in response to the different current densities gives a bulk electrical conductivity of $46\pm3.2$ \(\mu\text{S/cm}\). A constant current density $47$ \(\mu\text{A/cm}^2\), which renders an initial electrical gradient around $1.05$ V/cm, was selected for processing in these three experiments. The electrolysis oxidation at the anode and reduction at the cathode, respectively, would generate acid and base. The acid at the anode was neutralized by the base ammonium hydroxide and the base at the cathode was neutralized by either nitric or phosphoric acid. As a consequence, ammonium ions and nitrate or phosphate ions would be introduced, respectively, from the anode and the cathode into the soil and transported across the soil under electrical fields.

4.4.1 Ammonium and Nitrate Injection without Flushing the Anode Compartment (BEK-04)

4.4.1.1 Electrical Potential and Flow

The electrical potential developed during the processing is shown in Figure 4.56. It is interesting to note that during the first 70 hours of processing the voltage difference across the specimen decreased with time and afterward it was increased with time. Initially, due to the injections of ions in
Figure 4.55: Initial Electrical Potential across the Silt-Clay Specimen under Different Current Densities
Figure 4.56: Changes in Electrical Potential Difference across the Soil Specimen in BEK-04 with Time
the soil specimen, the conductivity would increase and the electrical potential would decrease. When the process continued, due to dynamic chemistry across the specimen under electrical field, some of the controlling parameters might change the conductivity, which decreased, and increased the electrical potential. Insoluble chemical precipitants, undefined change in structure or complex interaction of the ions of the initial pore fluid, injected species and charged soil surface may have caused changes in these parameters, which include ionic concentration, effective ionic mobility, porosity and tortuosity. It may also be possible that the extraction of the pore fluid might govern over the injection of ions in the latter stage, which might be due to the secondary electrolyte reactions.

Figure 5.57 shows that the voltage gradient (linear across the specimen at any time) decreased from an initial value 1.05 V/cm to 0.5 V/cm during the first 70 hours of processing. Then, the voltage gradient increased with time to a value 0.75 V/cm after a total 196 hours of processing.

The changes in electrical conductivity across the specimen with time are presented in Figure 4.58. Initially, with the injection of ions from the boundaries the conductivity increased from 46±3.2 to 95±12 μS/cm during the first 70 hours of processing. Then, the conductivity decreased with time to a value around 65 μS/cm after a total 196 hours of processing. The probable reasons have already been stated, which might have caused the decrease in the conductivity of the soil during the last stage (70 hours to 196 hours) of
Figure 4.57: Voltage Gradient Developed across the Soil Specimen in BEK-04 with Time
Figure 4.58: Changes in Electrical Conductivity across the Soil Specimen in BEK-04 with Time
processing and in turn increased the resistivity of the soil such as to maintain the constant current density condition. An appropriate assessment of such kind of results may be better evaluated by multi-species (injected, pore fluid and adsorbed ions) charge distribution, adsorption effects and any solubility equilibria. The changes in the apparent conductivity during processing are presented in Figure 4.59. These results have the same trend as the bulk conductivity diagram (Figure 5.58) and provide a better average representative value across the soil specimen during the processing period.

A cumulative electroosmotic flow of 2 liters or 1.5 pore volumes was collected during 196 hours of processing (Figure 5.60). The electroosmotic flow rate is a function of electroosmotic permeability \( k_e \) and electrical gradient \( i_e \). Figure 4.61 shows the changes in electroosmotic permeability with time. Electroosmotic permeability increased from an initial value \( 3 \times 10^{-5} \) cm\(^2\)/Vs to \( 9 \times 10^{-5} \) cm\(^2\)/Vs within the first 70 hours of processing. Then it decreased with time to a value \( 5 \times 10^{-5} \) cm\(^2\)/Vs, after a total 196 hours of processing. The changes in electrical gradient are presented in Figure 4.57. The electroosmotic flow rate varied within a range of 2.7 to 3.9 cm/day during the first 70 hours of processing and then remained constant to a value 3 cm/day, in conformity with the electroosmotic water transport efficiency (Figure 4.62). Therefore, electroosmotic flow changes would be due to changes in electrical gradient and/or a change in the electroosmotic
Figure 4.59: Changes in Apparent Conductivity in BEK-04
Figure 4.60: Electroosmotic Flow in BEK-04
Figure 4.61: Changes in Coefficient of Electroosmotic Permeability in BEK-04
Figure 4.62: Changes in Electroosmotic Water Transport Efficiency in BEK-04
permeability. Both are time dependent variables due to associated chemical changes in pore fluid and soil surface. The change in electro-osmotic water transport efficiency ($k_i$) with time is depicted in Figure 4.62. $k_i$ sharply increased from 0.7 cm$^3$/As to 1.15 cm$^3$/As within the first 25 hours of processing. Then, it decreased to a value 0.8 cm$^3$/As at 100 hours and afterwards it remained constant around that value. The $k_i$ value for the silty-clay soil was much higher than those of kaolinite or sand used in previous experiments. $k_i$ indicates how efficiently water can be transported under unit charge. It generally varies from 0 to 1.2. So in the silty-clay soil, the water can be transported more efficiently than in the other soils (kaolinite and sand) used in these experiments.

4.4.1.2 Ammonium and Nitrate Profiles

Figure 5.63 displays the profile of ammonium concentration across the specimen with time. The cell was almost saturated with ammonium at a concentration 65 mg/l to 55 mg/l after 196 hours of processing. Ammonium ions reached the cathode within the first 72 hours or 3 days (Figure 4.64) of testing, rendering an effective transport of 10 cm/day. The ammonium ion was transported from the anode to the cathode due to additive effect of the electroosmosis and the effective ionic mobility. The transport rate due to the measured electroosmotic flow in the silty-clay bed was around 3 cm/day. A major portion of the transport of the ammonium ions was thus due to ionic
Figure 4.63: Ammonium Profile across the Soil Specimen in BEK-04
Figure 4.64: Concentration of Ammonium across the Soil Specimen in BEK-04 with Time
mobility (7 cm/day) of the species under the electrical gradient. It could be assumed that ions were transported under an average electrical gradient of 0.75 V/cm (Figure 4.57). If an average electrical gradient of 0.75 V/cm was assumed to prevail during the test, the corresponding effective ionic mobility of the ammonium $u^-_{\text{NH}_4^+}$, would be around 9 (cm/day)/(V/cm). The ionic mobility of ammonium ion at infinite dilution, $u^-_{\text{NH}_4^+}$ is 66 (cm/day)/(V/cm). The mobility decreased 14% of its value at infinite dilution due to the effects of porosity, tortuosity in the medium and other secondary factor.

The profile of nitrate concentration across the soil specimen with time is presented in Figure 4.65. After 196 hours of processing, the nitrate ion was not uniformly distributed across the soil specimen. Due to injection of nitrate from the cathode, the final concentration at the cathode was around 250 mg/l and remained constant up to a distance 17 cm from the anode and linearly decreased to be around 50 mg/l at the anode compartment. Nitrate ions reached from the cathode to the anode within the first 96 hours of processing of testing, rendering an effective transport rate 8.5 cm/day (Figure 4.66). The nitrate ion was quite rapidly transported from the cathode to the anode by the effective ionic migration opposed by electroosmosis. The average measured electroosmosis during the processing was around 3 cm/day. So the effective ionic migration was around 11.5 cm/day. If an average electrical gradient of 0.75 V/cm was assumed to prevail during the test, the corresponding
Figure 4.65: Nitrate Profile across the Soil Specimen in BEK-04
Figure 4.66: Concentration of Nitrate across the Soil Specimen in BEK-04 with Time
effective ionic migration or mobility of nitrate $u^{\text{e}}_{\text{NO}_3^-}$ would be around 15 (cm/day)/(V/cm). It is very interesting to note that after 196 hours of processing the nitrate ion concentration ranges from 250 mg/l at the cathode to 50 mg/l at the anode, whereas the ammonium ion was saturated across the specimen 65 mg/l to 55 mg/l. The result requires an evaluation of charge distribution, adsorption effects, and any solubility equilibria effects to be assessed. The final charge concentration of these two species in the soil specimen are given in Figure 4.67. There was an imbalance in charge concentration when only ammonium and nitrate ions were considered. The results would be better appreciated if the final ammonium and nitrate across the bed are evaluated together with the charge concentration of the other predominate ion species. The predominate speciation across the soil specimen before and after 196 hours processing is respectively presented as bar diagrams in Figures 4.68 and 4.69. The initial predominate cations in the pore fluid were sodium (Na$^+$) and calcium (Ca$^{2+}$), whereas the anions were chloride(Cl$^-$) and sulfate ($\text{SO}_4^{2-}$). The initial charge concentration in the pore fluid for both cations and anions was around 2.75 meq/l. It is reasonable to assume that the effective ionic mobility ($u^*$) of different species are in the same range. As a charge carrier, all the species will behave the same if their concentrations are expressed in eq/l. Due to electrical neutrality, the charge (in meq/l) of cations and anions should be same. Under the electrical field,
Figure 4.67: Ammonium and Nitrate Charge Concentration in BEK-04 after 196 Hours of Processing
Figure 4.68: Initial Charge Concentration of Cations and Anions in BEK-04
Figure 4.69: Final Charge Concentration of Cations and Anions in BEK-04 after 196 Hours of Processing
the effective transport rate for cations is $\left( u^+ + K_e \right)$ and anions is $\left( u^- - K_e \right)$. The initial conductivity of the soil specimen was around $47 \ \mu S/cm$ and the initial voltage gradient was $1.05 V/cm$. From the following conductivity equation with the approximation stated above, the approximate effective ionic mobility should be $7.67 \ (cm/day)(V/cm)$.

$$\sigma = F \Sigma C_i u_i$$

The final pore fluid charge concentration for both cations and anions was around $5.5 \ meq/l$ after 196 hours of processing. The final conductivity and voltage gradient were respectively were $65 \ \mu S/cm$ and $0.8 \ V/cm$. From the above equation, with the approximation stated before, the effective ionic mobility should be around $5.3 \ (cm/day)(V/cm)$, which is less than the initial value. The ionic mobility is lower due to the effects of porosity, tortuosity in the soil specimen and other secondary factors.

It is also interesting to note that the chloride and sulfate ions made up the major differences in the final anion charge concentration (Figures 4.68 and 4.69). Chloride and sulfate ions moved towards the anode. Since these ions were not transported out of the system, they increased the ionic conductivity in the vicinity of the anode. They also provide the necessary negative charge to meet the electrical neutrality requirement. As a result, the nitrate ions originating in the cathode compartment could not move further into the anode compartment since electrical neutrality was maintained by the
chloride ions that already moved into that space, the ionic conductivity had increased and the transference number for the nitrate ions had decreased.

4.4.2 Ammonium and Nitrate Injection with Flushing the Anode Compartment (BEK-05)

4.4.2.1 Electrical Potential and Flow

The experiment was initiated to assess whether or not the transportability of the injected anions could be increased by continuously flushing the anode compartment. A constant current density of 47 mA/cm$^2$ which rendered a electrical gradient of 1.1 V/cm was selected for processing. The ammonium ions from the anode and the nitrate ions from the cathode were injected into the soil specimen, as for experiment BEK-04. The only difference in the test conditions between BEK-04 and BEK-05 was that the anode compartment was continuously flushed in BEK-05, whereas the anode was not flushed in BEK-04.

The changes in the electrical potential difference with time are shown in Figure 4.70. The injection of ions in the pore fluid decreased the resistivity of the soil with time, with the result to maintain the constant current condition, the electrical potential difference decreased with time. It is also noted that relatively steady state conditions were reached within the first 100 hours of processing. The potential difference in BEK-04 initially decreased in the same trend as this and other previous experiments, but in the latter stage the
Figure 4.70: Changes in Electrical Potential Difference across the Soil Specimen in BEK-05 with Time
potential difference increased with time. The probable reasons have already been stated. Comparing the simulated test conditions in BEK-04 and BEK-05, it seems to be very difficult to clearly explain this kind of dynamic behavior of pore fluid chemistry under the same electrical field.

Figure 4.71 shows the changes in the voltage gradient with time. A linear voltage drop across the specimen was observed throughout the test period. The voltage gradient was dropped from initial at 1.1 to 0.5 V/cm during the first 100 hours of processing and remained constant around 0.5 V/cm during the processing period of 100 hours to 196 hours.

The electrical conductivity across the soil specimen increased from an initial 46±3.2 to 96±5 μS/cm during the first 100 hours of processing. It is also noticeable that conductivities across the soil specimen varied in a very narrow range and they almost increased linearly with time, during this period. After this time the conductivity at some locations across the specimen increased variably and final conductivity was 117±15 μS/cm. The dynamic pore fluid chemistry under an electrical field may respond differently at various locations during processing. Initial ionic pore fluid concentration, charged clay surfaces and injected ions interact in a complex manner, which may affect the factors controlling the conductivity. These factors include ionic pore fluid concentration, effective ionic migration (porosity, tortuosity) and valency of ions. The apparent conductivity of the soil was increased from 47 to 112 μS/cm during 196 hours of processing, as shown in Figure 4.72.
Figure 4.71: Voltage Gradient Developed across the Soil Specimen in BEK-05 with Time
Figure 4.72: Changes in Electrical Conductivity across the Soil Specimen in BEK-05 with Time
Electroosmotic flow was from the anode compartment to the cathode compartment. A total flow of 2.2 liters or 1.65 pore volume was collected during 196 hours of processing (Figure 4.73). It was interesting to note that the electroosmotic coefficient of permeability increased from $3.2 \times 10^{-5}$ to $8.5 \times 10^{-5}$ cm$^2$/Vs (2.7 to 7 (cm/day)/(V/cm)) within the 196 hours of processing (Figure 4.74). Given the average values for the initial and final electrical potential gradients of 1.05 V/cm and 0.4 V/cm, respectively, the electroosmotic transport rate increased from 2.57 cm/day to 2.8 cm/day. This gives an assessment of the magnitude of the electroosmotic transport rate of the pore fluid from the anode to the cathode compartment. It is also noticeable that an increase occurred in the conductivity from 47 to 112 μS/cm (Figure 4.73) and this increased the electroosmotic permeability from $3.2 \times 10^{-5}$ cm$^2$/Vs to $8.5 \times 10^{-5}$ cm$^2$/Vs (Figure 4.75) during 196 hours processing in the silty-clay specimen.

Initial soil pH was around 5.8. A constant pH (6.5 to 7.5) environment at the boundaries had increased the soil pH to around 7.0 during the electrokinetic ion injection processing. The conductivity (inversely related to zeta potential) of the soil had increased two times, whereas the pH (directly related to zeta potential) had increased at least 10 fold. As a net effect, the zeta potential had become more negative and the electroosmotic permeability had increased. So it is not unlikely that the electroosmotic flow rate increased or remained the same when the electrical gradient decreased.
Figure 4.73: Changes in Apparent Conductivity in BEK-05
Figure 4.74: Electroosmotic Flow in BEK-05
Figure 4.75: Changes in Coefficient of Electroosmotic Permeability in BEK-05
Figure 4.76: Changes in Electroosmotic Water Transport Efficiency in BEK-05

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and $k_e$ increased. Figure 4.76 shows the electroosmotic water transport efficiency with time. An average value of 0.8 cm$^3$/As could be assumed during the processing period. Similar results were obtained in the previous experiment (BEK-04).

4.4.2.2 Ammonium and Nitrate Profiles

Figure 4.77 presents the change in the ammonium ion profile across the specimen with time. The final ammonium ion concentration varied within a range of 70 to 80 mg/l after 196 hours of processing. During the first 72 hours or 3 days the ammonium ions reached from the anode to the cathode rendering an effective transport rate 10 cm/day (Figure 7.78). A similar result was obtained for BEK-04. So the effective ionic mobility would be around 9 (cm/day)/(V/cm), as for BEK-04.

The development of nitrate ion concentration across the soil specimen during the processing is shown in Figure 4.79. The final concentration across the soil specimen after 196 hours of processing varied within a range of 325 to 300 mg/l. A uniform distribution of nitrate was achieved by continuously flushing the anode compartment. The effective rate (Figure 4.80) and the ionic mobility were the same as for BEK-04.

The final charge distributions of the injected ammonium and nitrate ions across the specimen are presented in Figure 4.81. Both the charge of the ammonium and nitrate ions were around 5.5 meq/l across the specimen and the electrical neutrality was maintained by each other. The final
Figure 4.77: Ammonium Profile across the Soil Specimen in BEK-05

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Figure 4.78: Concentration of Ammonium across the Soil Specimen in BEK-05 with Time
Figure 4.79: Nitrate Profile across the Soil Specimen in BEK-05

Concentration (mg/l)

Distance from Anode (cm)

Time (hr)

Concentration (mg/l)
Figure 4.80: Concentration of Nitrate across the Soil Specimen in BEK-05 with Time
Figure 4.81: Ammonium and Nitrate Charge Concentration in BEK-05 after 196 Hours of Processing
Figure 4.82: Final Charge Concentration of Cations and Anions in BEK-05 after 196 Hours of Processing
predominate speciation is presented in Figure 4.82. Comparing this Figure with the final speciation (Figure 4.69) of the previous experiment, it is clearly shown that initial the pore fluid anions (chloride and sulfate) had flushed out from the system and increased the transportability of the injected anions (nitrate).

4.4.3 Ammonium and Phosphate Injection with Flushing the Anode Compartment (BEK-06)

4.4.3.1 Electrical Potential and Flow

Similar to the previous two experiments (BEK-04 and BEK-05), a current density of 47 mA/cm², which rendered an initial electrical gradient 1.15 V/cm, was selected for the processing. The acid at the anode was neutralized by ammonium hydroxide and base at the cathode was neutralized by phosphoric acid. The anode was continuously flushed to increase the transportability of the injected phosphate anions. As a consequence, ammonium and phosphate ions were respectively introduced from the anode and the cathode and transported across the soil under the electrical field.

The changes in the electrical potential difference across the soil specimen are presented in Figure 4.83. During the first 100 hours of processing, the electrical potential difference decreased with time and afterwards it increased with time. A similar kind of behavior was observed in
Figure 4.83: Changes in Electrical Potential Difference across the Soil Specimen in BEK-06 with Time

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Figure 4.84: Voltage Gradient Developed across the Soil Specimen in BEK-06 with Time
BEK-04. The explanation of such kind of voltage trend has already been discussed for BEK-04.

The voltage gradient which developed during 240 hours of processing is displayed in Figure 4.84. The voltage gradient decreased from an initial value 1.05 V/cm to 0.6 V/cm during the first 100 hours of processing. Then, the voltage gradient increased with time to a value 0.85 V/cm after a total of 240 hours of processing.

Figure 4.85 displays the changes in the electrical conductivity across the soil specimen with time. During the first 50 hours of processing, the conductivity increased from the initial 46±3 to 80±5 µS/cm. After that, the conductivity was variably increased or decreased across the soil specimen during the processing period of 50 hours to 240 hours. The final conductivity was around 60 ±12 µS/cm after 240 hours of processing. The dynamic nature of pore fluid chemistry generated by the electrical field would respond differently at different locations due to changes in ionic pore fluid concentration, valency of ions, pH, ionic mobility, tortuosity, porosity, adsorption effects and solubility equilibria.

The apparent conductivity of the soil specimen with time is presented in Figure 4.86. The apparent conductivity increased from an initial value of 47 µS/cm to around 80 µS/cm during the first 100 hours of processing and then
Figure 4.85: Changes in Electrical Conductivity across the Soil Specimen in BEK-06 with Time

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Figure 4.86: Changes in Apparent Conductivity in BEK-06
Figure 4.87: Electroosmotic Flow in BEK-06
Figure 4.88: Changes in Coefficient of Electroosmotic Permeability in BEK-06
decreased with time to a value 55 μS/cm after a total of 240 hours of processing.

The cumulative electroosmotic flow with time is shown in Figure 4.87. A total flow 2400 cc, or 1.8 pore volumes, was collected during 240 hours of processing. The electroosmotic coefficient of permeability increased from an initial 3x10^{-5} cm²/Vs to 7x10^{-5} cm²/Vs during the first 70 hours of processing (Figure 4.88). Then the electroosmotic coefficient of permeability decreased with time to a value 4x10^{-5} cm²/Vs. Given the average values for the initial and the final voltage gradients of 1.05 and 0.85 V/cm, respectively, the electroosmotic transport rate increased from 2.1 cm/day to 2.9 cm/day. The change in the electroosmotic water transport efficiency (kₐ) with time is depicted in Figure 4.89. kₐ increased sharply from 0.7 cm³/As to 1.1 cm³/As during the first 15 hours of processing. Then, kₐ decreased with time to a value 0.7 cm³/As at 100 hours and remained constant around that value from 100 hours to 240 hours of the processing period.

4.4.3.2 Ammonium and Phosphate Profiles

The ammonium ion profile across the soil specimen with time is displayed in Figure 4.90. The final concentrations of ammonium ion across the soil specimen were within a range of 50 to 55 mg/l. The effective transport rate (Figure 4.91) and the effective ionic mobility were in the same range as the other two previous experiments (BEK-04 and BEK-05).
Figure 4.89: Changes in Electroosmotic Water Transport Efficiency in BEK-06
Figure 4.90: Ammonium Profile across the Soil Specimen in BEK-06
Concentration (mg/l)

Figure 4.91: Concentration of Ammonium across the Soil Specimen in BEK-06 with Time
Figure 4.92: Phosphate Profile across the Soil Specimen in BEK-06
Figure 4.93: Concentration of Phosphate across the Soil Specimen in BEK-06 with Time

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Figure 4.92 shows the profile of phosphate ion concentration across the soil specimen with time. The phosphate ion concentration across the soil specimen varied within a range of 85 to 140 mg/l. Phosphate ions reached from the cathode to the anode within the first 100 hours of processing, rendering an effective transport rate of 7.2 cm/day (Figure 4.93). The average electroosmosis transport rate was around 3 cm/day. So, the effective ionic migration rate was 10.2 cm/day. If an average electrical gradient 0.8 V/cm (Figure 4.84) was assumed to prevail during the testing period, the corresponding effective ionic migration or mobility of phosphate, $u_{PO_4^{3-}}$, would be around 13 (cm/day)/(V/cm). The phosphate ion concentration was not uniformly distributed, although the anode was continuously flushed. The final charge distribution of these two species in the soil specimen is presented in Figure 4.94. Most of the charge imbalance was observed in the soil region close to the cathode. In this region, the charge of phosphate was more than the charge of ammonium. This kind of result would be better appreciated by speciation of the other predominate ions in the pore fluid. But unfortunately, the final predominate speciation was not carried for this experiment.

Ammonium ion charge was saturated across the soil specimen at concentration around 4 meq/l, whereas in the previous experiment the final charge concentration value for ammonium ion was around 5.5 meq/l. So under the same test conditions, with the only difference being injection of
Figure 4.94: Ammonium and Phosphate Charge Concentration in BEK-06 after 240 Hours of Processing
another type of anion from the cathode, a great influence in the overall process chemistry has been demonstrated.
CHAPTER 5
PRACTICAL IMPLICATIONS

The electrolyte conditioning technique described in this study could be used to inject chemical species, nutrients and process additives to enhance in-situ bioremediation, to induce chemical oxidation/reduction and also to stabilize soils. An important consideration in any field implementation is the power consumption and the associated cost. Power consumption in electrokinetic injection will be directly related to the electrical conductivity of the medium. Electrical conductivity of saturated soil deposits would range between 10 μS/cm for sands with pore fluids of low conductivity to over 8,000 μS/cm in high plasticity clays (Mitchell, 1993; Yeung, 1994). Considering the fact that high plasticity clays would limit their contamination in the first place, a conductivity range of about 10-500 μS/cm represents most deposits which may necessitate electrokinetic injection for in-situ bioremediation. This estimate agrees with the experience of the authors in real-world contaminated deposits and also with the conductivity values reported for most soils in the literature (Yeung, 1994). A current density of 500 μA/cm² will generate an initial electrical potential gradient of 1 V/cm in a soil with an initial electrical conductivity of 500 μS/cm. If a one-dimensional electrical field is maintained between a series of anodes and a series of cathodes, a
maximum power consumption of about 12 kWh/m$^3$-day or about 360 kWh/m$^3$-month would be anticipated.

The duration of the electrical injection scheme will depend upon the spacing between the anode series and the cathode series and the purpose of the injection scheme. If the electrode spacing is kept short (e.g. 1-2 m), the time necessary for processing will be lower since the distance traversed by the ions injected under the electrical field will decrease. However, the cost of conventional rotary or auger borings for electrode installation in a contaminated site and installation of the associated circulation system in these borings may increase to the overall cost substantially, unless cost-effective electrodes and/or well installation techniques are devised and/or adopted. If a total processing time of about four months is targeted, the maximum energy expenditure will be about 1,300 kWh/m$^3$ of soil, translating to a total energy cost of about $39-$65/m$^3$ ($0.03-0.05$/ kWh). Even when other fixed costs double this energy cost, the cost of *in-situ* bioremediation by electrokinetic injection will be set at the lower end of the categorical range of $100$-$1,000/m$^3$ cost reported for the available soil/water remediation technologies (Acar and Zappi, 1995). In some instances, regardless of its cost, the technique may be the only available technology for the *in-situ* bioremediation of organic species in heterogenous deposits. Process optimization by intermittent application of the electrical field in tune with the intended use of the injection scheme, the use of unconventional sources of
electricity, accurate conditioning of the electrolytes and development of innovative, cost-effective electrodes and electrode insertion techniques could further decrease the total costs.

Another important consideration in field implementation of the electrokinetic injection technique in bioremediation would be an assessment of the final concentrations of species achieved with respect to the cost of injection. The concentration of electron donors and nutrients necessary for effective bioremediation is often in the order of tens of mg/L. Therefore, the final concentration of the ammonium ion in this study would be acceptable for bioremediation, while the concentration of the sulfate ion may be too high. Lower concentrations could be achieved by appropriate control of the electrode reactions and conditioning chemistry. When the concentrations of process additives and nutrients necessary in field implementation is significantly lower than the concentration of other species in the pore fluid, the low transference number for the target species may hinder their effective transport into soil. In this case, it may be possible to enhance transport rates by reducing the ionic conductivity of the pore fluid at the electrode reservoirs.

Finally, the conditioning scheme and testing procedure described in these experiments could be used to measure the effective ionic mobility of ionic species in porous media; however, a more rigorous analysis of the results is needed if accurate estimates are required. The conditioning chemistry at the reservoirs and the associated mass/charge balance has to
be incorporated in the computer models presented by Alshawabkeh (1994), Jacobs et al. (1994), Alshawabkeh and Acar (1996), or others. The aqueous phase and sorption chemistry specific to the problem will have to be input. Since the mass/charge balance in the reservoirs is also directly related to the mass/charge balance across the soil, the analysis becomes challenging (Zheng, 1997). With some sacrifice in accuracy, it is possible to make assumptions that could simplify the problem. The equations describing the transport of the ammonium ion and the sulfate or nitrate or phosphate ion could be decoupled and the measured concentrations of the species in the reservoirs could be input as boundary conditions.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following conclusions are derived from the study:

- The electrolysis oxidation and reduction will respectively generate acid in the anode and base in the cathode, which need to be neutralized/depolarized to achieve a desirable pH condition. The co-ions of the targeted species introduced should be selected so to facilitate depolarization of the electrodes reactions, maintain a desirable pH environment and low electrical conductivity. The hydronium ions of the anode electrolysis reaction will be neutralized by the hydroxyl ions in the base solution and the hydroxyl ions of the cathode electrolysis reaction will be neutralized by the hydronium ions in the acid. As a result, co-ions of the base (base conjugate, or injected cations) will be transported from the anode towards the cathode, while co-ions of the acid (acid conjugate, or injected anions) will be transported from the cathode towards the anode. The neutralized bases and acid should be selected in such a way that common electron acceptors (sulfate and nitrate) and nutrients (ammonium and phosphate) as co-ions from the two boundaries will inject into the soil specimen in between them. Furthermore, if the
purpose of injection is *in-situ* bioremediation, the injected species at
the anode and cathode need to be perfectly soluble with each other
for their efficient transport across the soil specimen.
• It is essential to employ an electrolyte conditioning scheme to exploit
ionic mobility and electroosmosis for electrokinetics injection of
species. The injected cations will migrate by ionic mobility accelerated
by electroosmosis, whereas the injected anions will migrate by ionic
mobility opposed by electroosmosis.
• The transportability of the injected ions also depend on the charge
centration of the other competing ions on the pore fluid. The
accumulation of these pore fluid ions in the system would decrease
the transference number of the injected ions.
• The transportability of the injected ions could be increased by
flushing intermittently or continuously the electrodes compartments to
decrease the conductivity at the boundaries, which would increase the
initial pore fluid ions to be flushed out from the system.
• The injections of ions into the system would increase the conductivity
across the specimen which in turn would decrease the resistivity of the
specimen. To maintain a constant current condition the electrical
potential would decrease accordingly. In some cases, the electrical
potential had increased during the latter stage of processing. When
the process continued, the dynamic chemistry across the specimen
under electrical field might change some of the controlling parameters of the conductivity, which decreased the conductivity and increased the electrical potential. Insoluble chemical precipitants, undefined change in structure or complex interaction of the ions of the initial pore fluid, injected species and charged soil surface may have changed these parameters, which include ionic concentration, effective ionic mobility, porosity and tortuosity. It is also possible that the extraction of the pore fluid might govern over the injection of ions in the latter stage, which might be due to the secondary electrolyte reactions.

• This depolarization technique could be used to sustain an effective level of electroosmotic flow. The electroosmotic permeability increased during the processing with the increase in conductivity. Initial soil pH was below that of the conditioning boundaries pH. A constant pH (6.5 to 7.5) environment at boundaries had increased the soil pH around to 7.0 during the electrokinetic ion injection processing. The pH (directly related to zeta potential) had increased many times more than the conductivity (inversely related to zeta potential) of the soil. As a net effect, the zeta potential had become more negative and the electroosmotic permeability had increased. So it not unlikely electroosmotic flow rate increased, or decreased, or remained same when the electrical gradient decreased ($i_e$) and $k_e$ increased in view of these competitive mechanisms.
• Ionic species were transported in different kind of soils at rates of 8 to 20 cm/day under different current densities 15 to 150 mA/cm² and a voltage gradient less than 1 V/cm.
• Electrical fields could be used to direct the electron acceptors and nutrients in desired locations in deposits with heterogeneities.
• A uniform distribution of the process additives could be achieved across the electrodes.
• In-situ bioremediation by electrokinetics injection might fall at the lower range of $100/m^3 to $1000/m^3 cost for other available technologies.

6.2 Recommendations

Some recommendations for future work in the light of the conclusions derived from this study are:

• Introduction of other additives, such as non-ionic electron acceptors (oxygen or hydrogen peroxide), comtabolites, surfactants, Fenton’s reagent and colloidal gas aphrons by electrokinetics should be studied.
• It should be noted that the increase in ionic conductivity of the pore fluid in soils with high pore fluid conductivity may lower transport rates by decreasing the transference numbers for the target species. Under such circumstances, it will be necessary to employ process optimization techniques that will enhance the transport rates.
- To evaluate the feasibility of enhancing *in-situ* bioremediation by electrokinetics injection, media contaminated with toxic organics should be tested.
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DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Md. Fazle Rabbi

Major Field: Civil Engineering

Title of Dissertation: Injection of Species under Electrical Field to Enhance Bioremediation

Approved:

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Major Professor and Chairman

Dean of the Graduate School

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Date of Examination: July 7th, 1997