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ELECTRO-KINETIC CONCENTRATION AND RETENTION OF NITRATE IN SANDY SOIL

By

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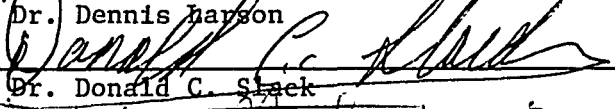
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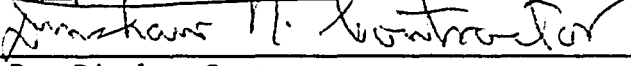
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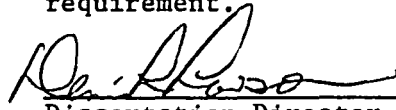
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DEDICATION

To my parents Layla and Mahmoud without whose love and support nothing in my live would have been completed.

TABLE OF CONTENTS

TABLES OF CONTENTS - Continued

TABLES OF CONTENTS - Continued

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS - Continued

LIST OF ILLUSTRATIONS - Continued

LIST OF ILLUSTRATIONS - Continued

LIST OF TABLES

ABSTRACT

Laboratory experiments utilizing closed and open system experiments were conducted in this study to evaluate the applicability of using an electro-kinetic process to concentrate and retain nitrate close to the anode. A finite difference model was developed to predict the pH gradient developed during the electro-kinetic process. Model results then were used with a derived regression equation between pH and NO_3^- to predict the nitrate gradient developed during an electr-kinetic process.

The results of this research revealed that an electrokinetic method is an effective means for concentrating and retaining nitrate close to the anode in saturated sandy soil even under a strong hydraulic gradient. Results also support the validity of using a finite difference and regression equation model to predict the spatial and temporal distribution of NO_3. developed under an electro- kinetic process for both closed and open system configurations.

CHAPTER ONE

INTRODUCTION

1.1 Description of the problem

Migration of contaminants to ground water aquifers has become a serious problem in many irrigated lands. In irrigated areas the chemical accumulation and subsequent movement to the water table is largely due to long term exposure of agricultural lands to extensive irrigation and heavy use of chemical fertilizers. Nitrate contamination of ground water is considered to be one of the more serious problems related to agricultural practices nation wide.

One means of reducing soil chemical pollution is by removing both the pollutant and the volume of ground water from the aquifer. Another means is to remove a chemical via leached water using a subsurface drainage system. The drainage system delivers the chemical to a collection point or dilutes chemical content to a level acceptable for effluent discharge to a lake or stream. Such methods are slow, costly and displace the problem without really solving it.

Electrokinetics, the process in which solutes are caused to migrate through a solution along an imposed voltage gradient, has been shown to be an effective means for removing chemicals from soils. Electrokinetics is an in-situ clean-up technique that could remove contaminants in ionic form. The method uses DC current in the mA range to remove/separate contaminant from soils. Electrokinetic benefits may include water

conservation, rapid removal, and small electrical power requirements.

The electrokinetic method is applicable to any electrically-charged species in ground water, organic or inorganic. Electrokinetic soil processing involves contaminant desorption, transport, capture and removal from soils by application of DC current across electrodes inserted in a soil mass (Acar et al, 1992). Under the influence of the electrical gradient, positively charged ions (cations) migrate towards the negative pole (cathode) and negatively charged ions (anions) migrate towards the positive pole (anode).

An electrical potential across a porous media can cause solute movement, electro-migration; liquid movement, electro-osmosis; and/or transfer of particles in solution, electro-phoresis (Probstein & Hicks, 1993). Elecrokinetics can also cause detachment of cations from clay particles and subsequent movement in solution toward the cathode.

1.2 Previous Studies

Karpoff (1953) established and applied an electro-osmosis technique for dewatering and stabilizing soil for foundation construction. Electrokinetics has shown a great success in removing organic chemicals. For example, Bruell and VanDoren (1987) reported benzene concentration was reduced to low levels in clay soil after two weeks of electrical treatment. Shapiro et al, 1989 examined the removal of acetic acid from soils using an electrokinetic process. A 94 percent degree of removal was achieved by the process and it was demonstrated that the pH variation can control the degree of removal of this organic acid. Acar et al (1992) studied the removal of Phenol from

koalinite soil by using an electrokinetic technique. Eighty-Five to ninety-five of the adsorbed Phenol was removed at an energy expenditure of 18-39 kWh/m³. Electro-kinetic effectiveness in removing salts from saline soils was examined by many researchers. For example, electro-kinetic soil desalination research in Russia and Egypt was reported to increase the salt content in drainage water using electro-kinetics when compared to leaching with water alone, but the differences decreased with time (El-sawaby & Vadyunina, 1977).

Bard and Faulkner (1980) discussed the theory of electromigration of ions in aqueous media. Hamed (1990) and Hamed et al (1991) reported a comprehensive study on the possibility of using electrokinetic process to remove Pb(II) from soil. Between 75 and 95 percent of Pb(II) was removed across the test specimens at an energy expenditure of 29-60 kWh/m³. Hamnet (1980); Renauld et al(1987); Acar et al.(1990) and Hamed et al. (1991) all did extensive studies of the possibility of using electro-osmosis to remove salts and organic and inorganic contaminants from soils. Larson (1980); Runnels and Larson (1986); and Wahli(1988), studied the movement of Cu and So_4 under a low DC current between metallic or carbon electrodes. Quellette et al (1978), described the use of electrolysis in the treatment of metal-contaminated acid in mine waters. Laboratory studies reported by Legeman (1989), Banarjee et al (1990), and Pamukcu et al (1990) substantiate the applicability of the electromigration technique to remove a wide range of inorganic contaminants from soils. Shmakin (1985) introduced an electrochemical technique to concentrate metal from bedrock as a means of exploring

for hidden mineral deposits. Talaptra (1986) set up a network of electrodes in the ground and imposed a high voltage (about 100 V) as a tool for geochemical prospecting of ore deposits. By this method, Talapatra was able to obtain information on the type of ore present in the area of study.

The fundamentals of removing contaminants from soils by electrokinetic processes, including electromigration, electro-osmosis, and electrophoressis, have been summarized by Acar et al (1990, 1992). They presented a theory , based on the Nerst-Planck equations, for pH gradient development during the electrochemical processing of soils. Also, a first-order finite element model was developed by them to evaluate the acid/base distribution and the flow patterns in electrochemical flow. Analytical solutions were compared with numerical results obtained by the finite element method and with some preliminary experimental results.

This study represents a continuation of the work by Cairo (1994), who studied the electromigration of nitrate through a porous medium. Cairo's study was conducted in a natural sandy loam field soil. A field lysimeter was used to evaluate an electrochemical technique using horizontal drainage tubing and parallel electrodes to concentrate nitrate near drains for hydraulic removal. Field results indicated that, immediately following application of ammonium nitrate and after opening drains, nitrate moved with the water towards the cathode (and the drain) in response to the hydraulic gradient. However, after several days, significant movement of water to the drains ceased and nitrate began to move towards the anode.

The reported research was a study of electromigration of nitrate through a porous medium as a possible method for in-situ removal of contaminants from ground water. Also, the effect of hydraulic flow superimposed on electromigration was tested. Laboratory experimental work used silica sand soil as the test soil. The test cell was a cylinder 25.0 cm long and 6.5 cm in diameter. Plate electrodes were inserted in the porous medium and at each end of the cylinder and constant DC current was imposed with an electrical power source. Different chemical concentration levels as well as different electrode materials and electrical currents were tested. A finite difference model was developed to estimate the pH gradient developed during the electrokentic process. The model development followed the theory of pH gradient developed by Acar et al (1990).

1.3 Objectives

The overall objective of this study was focused on the feasibility of using an electrokinetic method as an in-situ remedial technique for ground water contamination. The goal of this method is to increase the concentration of nitrate in the groundwater around the anode, so that intermittent pumping could remove volumes of water containing increased amounts of nitrate. Also, a horizontal drainage tubes and parallel electrodes configuration could be used to concentrate nitrate near drains for hydraulic removal.

Laboratory experiments were conducted to determine the mobility of nitrate in a saturated porous media in response to an electrical current imposed through the media. In addition, it was desired to determine if electro-kinetics could be used to retain nitrate in the media against a hydraulic flow.

Specific objectives of the research were:

1. Develop and evaluate the effectiveness of an electro-kinetic process to concentrate and retain nitrate close to the anode in a saturated sandy soil.

2. Test the effect of changing some of the design parameters on the performance of the electrokinetic process.

3. Evaluate the effect of super-imposed hydraulic flow on electromigration.

5. Predict the nitrate gradient developed in an electro-kinetic process as a function of electrical current and hydraulic flow.

4. Determine the limiting hydraulic velocity above which elecromigration effects are negated by hydraulic flow.

CHAPTER TWO

THEORETICAL BACKGROUND

This chapter summarizes the most important phenomena related to and resulting from an imposed voltage in a saturated porous media. The discussion first presents a brief approach to concepts of solutions and electrochemistry, followed by a discussion of some of the principles of migration phenomena. Finally, the theory of pH gradient development during the electrochemical process will be discussed as well as the details about a finite difference model for predicting the pH gradient. The purpose of this section is thus to define all the phenomena recognized as affecting the experiments involved in this research and provide the theoretical grounds for the interpretation of the results presented in subsequent chapters.

2.1 Solutions

Solutions are mixtures of two or more components. These components can be gases, liquids or solids. Gaseous solutions result from dissolving one gas in another. Liquid solutions are formed by dissolving gas, liquid, or solid in liquid(Michell and Robert,1961). If the liquid is water, the solution is called an **aqueous solution**. In solid solutions, one component is randomly dispersed on an atomic or molecular scale throughout another component. There are two definitions essential to describing any solution: **solute and solvent**. Solvent is the substance presented in larger amount.

Solute is the substance presented in smaller amount.

2.1.1 Concentration

The properties of any solution depend on it's concentration. There are many ways for describing concentration (Michel and Robert,1961).

The mole fraction : the ratio of the number of moles of one component to the total number of moles in solution.

Molarity (M) : the number of moles of the solute per liter of solution.

Molality (m) : the number of moles of solute per 1,000 g of solvent.

Normality : the number of gram-equivalents of solute per liter of solution.

Per cent by weight : the per cent of the total weight contributed by the solute.

Per cent by volume : the per cent of the solution volume represented by the volume of solute.

2.1.2 Electrolytes

There are many cases during the solution process in which molecules dissociate, or break apart. The dissociated fragments are called **ions** and they are usually electrically charged. Ions, moving in solution, constitute an electrical current. Substances that produce conducting solution are called **electrolytes** whereas substances that produce nonconducting solutions are called **nonelectrolyte** (Michel and Robert,1961). There are two groups of electrolytes : strong electrolytes, which yield

good conducting solutions, and weak electrolytes, which give mild solutions. Weak electrolytes differ from strong electrolytes in that weak electrolytes are only slightly dissociated into ions. Strong electrolytes are 100 per cent dissociated into ions.

Electrolytes (before being dissolved) may be ionic or molecular substances. For an **ionic substance**, the undissolved solid is already made up of charged particles. Ions may also be formed when certain **molecular substances** which are neutral are dissolved in the proper solvent. In this case, electrically neutral molecules interact with the solvent to form ions (Michel and Robert, 1961).

2.1.3 Solubility

Solubility describes the qualitative capability of the solution process. For any solute and solvent, unsaturated solutions, differing in concentration can be formed. However, at some point, a limit is reached beyond which the addition of solute to a specific amount of solvent does not produce another solution of higher concentration and the solute remains undissolved. The solution at this limit is called a **saturated solution** and the concentration of the saturated solution is called the **solubility** (Michel and Robert,1961). The solubility depends on the nature of the solvent, the nature of the solute, temperature, and pressure.

2.2 Electrochemistry

Electrochemistry is the field that considers the transport of electrical energy

through matter, the conversion of electrical energy into chemical energy, and the conversion of chemical energy into electric energy (Michell & Robert, 1961). Any chemical reaction is accompanied by a net decrease or increase in potential energy. In most cases, the change in potential energy appears as heat evolved or absorbed. Sometimes, however, the change in potential energy may be appear as electrical energy.

2.2.1 Electrical Conductivity

The transport of electrical energy by electric charge forms an **electrical current.** For the electrical current to exist, there must be charge carriers and there must be a force that makes the carriers move. The charge carriers can be positive and negative ions, as in case of electrolytic solutions where conduction is said to be **electrolytic,** or they can be electrons, as in case of metals where conduction is said to **metallic.** An electrical field is any space that has an electrical force across it(Michel and Rrobert,1961).

When an electrical field is applied to an electrolytic solution, the negative and positive ions experience a force in opposite directions. As a result, the negative ions move in one direction and the positive ions move in the other. The movement of the positive and negative ions in opposite directions constitutes an **electrical current.** The current would cease if positive and negative ions accumulate at corresponding electrodes. In order that the current continue, appropriate chemical reactions must occur at the electrodes to maintain electrical neutrality (Michel and Robert,1961).

2.2.2 Electrolysis

When an electrical current passes from a metallic conductor to a solution, electrons must be gained or lost by ions in the solution next to the surface of electrode. Thus, chemical reaction must accompany the passage of electrical current from one conductor to another (Daniles and Robert, 1956). At one electrode, electrons are lost from the ions in solution while electrons are released to the ions in solution at the other electrode. The electrode to which extra electrons are fed becomes negatively charged and attracts the positive ions (cations) and is called **cathode**. The other electrode becomes positively charged and attracts the negative ions (anions) and is called **anode**.

The removal of electrons is **oxidation**. It occurs at the anode. The addition of electrons is **reduction**. It occurs at the cathode (Danials and Robert, 1956). Usually, there are different ions at each electrode competing to give up electrons at the anode and take electrons at the cathode. If there are no easily oxidizable anions around the anode, water will react and hydrogen ions will be produced at the anode. If there are no easily reducible cations around the cathode, water will react and hydroxyl ions will be produced at the cathode.

2.3 Electromigration

In this section, the fundamental laws and the factors of importance of the electromigration process will be discussed.

Ohm's Law: When two plates of metals are placed in an aqueous solution of a salt or an acid, the resulting system becomes a source of electricity, generally referred to as a galvanic cell. The force that drives the electric current through a wire connecting the two plates is called the **electromotive force, or E.M.F.** There is a potential difference between any two points in a circuit carrying current. The algebraic sum of all potential differences constitutes the total E.M.F(Saumuel, 1978).

As early as 1827, Ohm observed that the current strength in a given circuit is dependent on the E.M.F. of the cell producing the current and the resistance of the circuit. The relation between the current strength (I), resistance (R), and the applied E.M.F.(E) is described by Ohm's law as:

$$I = \frac{E}{R} \qquad\qquad (2.1)$$

The resistance R of a uniform conductor is directly proportional to its length d and inversely proportional to its cross-sectional area A (Danial and Robert, 1956).

$$R = rd/A \qquad\qquad (2.2)$$

The proportionality constant r is called the **specific resistance** and is the resistance of a cube 1 cm on an edge.

Specific Conductance, the reciprocal of the specific resistance is usually used in

dealing with electrolytes.

$$L = 1/r = d/RA \qquad (2.3)$$

Equivalent Conductance. Is a term used to represent the conductance of an equivalent weight of an electrolyte. The equivalent conductance, Λ, is obtained by multiplying the specific conductance L by the volume V in milliliters that contains 1 gram equivalent of solute as :

$$\Lambda = V L = 1000L/c \qquad (2.4)$$

where c is the number of gram equivalent per liter. The dimension of Λ is cm^2 equiv$^-$ ^{1}ohm^{-1}. Λ° is the limiting equivalent conductivity at finite dilution.

Kohlrausch's law shows the dependance of Λ on concentration (Bockris and Reddy, 1970):

$$\Lambda_{(c)} = \Lambda^{o} - B\sqrt{c} \qquad (2.5)$$

where $\Lambda_{(c)}$ is the equivalent conductivity at concentration c and B is a positive constant. It is clear from Equation 2.5 that equivalent concentration decreases with an increase in the electrolyte concentration.

Equivalent Ionic Conductivity: Kohlrausch stated that the equivalent

conductance of the electrolyte Λ^o is equal to the sum of the equivalent conductances of

cations λ^+ and anions λ^-:

$$\Lambda^o = \lambda^o_+ + \lambda^o_- \qquad (2.6)$$

λ^+ and λ^- have different values because they are directly related to ionic mobilities

which differ from one ionic species to another.

Ionic mobility. The velocities of ions vary because of differences in charge,

hydration and size. Ionic mobility of an ion u (cm^2 $V^{-1}sec^{-1}$) is defined as the velocity

of the ion in a unit electrical field((Danial and Robert, 1956). Ionic mobility is a

property of the electrolyte defined as (Bard and Faulkner, 1980):

$$u_k = \frac{v_d}{E} \qquad (2.7)$$

where u_k is the ionic mobility for a specific ion k, v_d is the drift velocity in cm sec^{-1} and

E is the electrical potential in V cm^{-1}.

Ionic mobility and ionic equivalent are related to each other (Wahli, 1988) as:

$$u_k = \frac{\lambda_k}{F} \qquad (2.8)$$

where u_k, λ_k are the ionic mobility and ionic equivalent for a specific ion k, and F is the

Faraday constant.

Ionic Current Density: A difference in potential imposed through a solution creates an electric field and as a result a directional drift is imparted to ions (Bockris and Reddy, 1970). A flux of ions is created as a result of the applied electrical field (conduction phenomenon). The current density through an electrolytic solution is defined as the sum of the positive and negative current densities for the cation and anion respectively (Bockris and Reddy, 1970).

$$i_{tot} = -i_+ + i_-$$ (2.9)

Equation 2.10 relates the ionic current density to the ionic mobility (Bockris and Reddy, 1970):

$$i_k = z_k F c_k u_k E$$ (2.10)

where z_k is the charge and other terms are as previously described.

Transference number. Anions and cations in solution carry unequal fractions of the current depending on their current density and ionic mobility. The total current density is the sum of the current densities of each species present in solution. So, equation 2.9 can be presented as:

$$i_{tot} = \sum i_+ + \sum i_-$$ (2.11)

where i_+ does not equal to i_- (Bockris and Reddy, 1970).

The fraction of the current carried by any ion to the total current is defined as transference number, t_k:

$$t_k = \frac{i_k}{i_{tot}}$$ (2.12)

Combining Equation 2.10 and 2.12, transference number becomes:

$$t_k = \frac{u_k \, z_k \, c_k}{\sum_{k=1}^{n} u_k \, z_k \, c_k}$$ (2.13)

According to Equation 2.13, the portion of the current carried by ion k in a solution decreases as the number of species in the solution increase and as a result the current efficiency attributed to that single species diminishes. The pH of the solution also affects the current efficiencies of electrolytes. The fact that the ionic mobilities of H^+ and OH^- are an order of magnitude higher than other ions (Wahli,1988) implies that a high or low pH will decrease the efficiencies of other ions.

2.4 Acid/base Distribution in Electro-kinetic process.

In this section, a summary of the theory and the fundamental equations of pH gradient development, developed by Acar et al (1990), is discussed.

2.4.1 Electrochemical Reaction at Electrodes

Existence of a current in a porous medium implicitly necessitates Faradaic reaction at the electrode boundaries. Previous studies by Acar et al (1989) showed the electrochemical effects may significantly affect the results of the process and a pH gradient may be developed throughout the soil specimen. According to Mise (1961) and Gray (1970), the general trend is that the pore fluid gets acidic (pH=1-4) at the anode and basic at the cathode (pH = 10-13).

If there are neither easily reducible cations nor easily oxidizable anions in the pore fluid and for the case of inert electrodes, water electrolysis will take place at the electrode boundaries. According to Acar et al (1990), the primary electrode reactions then will be, at the anode,

$$2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+ \qquad (2.14\ a)$$

and, at the cathode,

$$4H_2O + 4e^- \rightarrow 2H_2 \uparrow + 4OH^- \qquad (2.14\ b)$$

As a consequence of the process described by equations 2.14a and 2.14b, two supplemental ionic species are generated. The ionic species generated by electrolysis together with ionic species available in the pore fluid will carry a portion of the current which depends on ion concentration and types (Acar et al, 1990).

2.5 Model Development

In this section, the equations describing the electrokinetic process, developed by Acar et al (1990), used in developing the model as long as the boundary and initial conditions are presented.

2.5.1 Assumptions

It is assumed that a constant current and a hydraulic potential difference are applied initially across a saturated, homogeneous soil. Also, ideal electrolyte solution properties are present in the soil matrix. The mass transfer chemistry is assumed to be dominated by the concentration profiles of acid and base. The current flow direction is always from the anode to the cathode.

2.5.2 Derivation of the Mathematical Equations

The total mass flux into an incremental element of thickness dx, q_{tc}, consists of three components:

$$q_{tc} = q_{cc} + q_{ch} + q_{ce} \tag{2.15}$$

where q_{cc} is material influx due to chemical gradient, q_{ch} is material influx due to hydraulic gradients which can be internal, electro-osmotic, or external, and q_{ce} is material influx due to electrical gradients. The Nernst-Plank equation (Ibi, 1983) describes the ionic flux q_{tc} into an element of thickness dx as :

$$q_{tc} = [-D_j \left(\frac{\partial c_j}{\partial x}\right) + v_x c_j - \frac{zF}{RT} D_j c_j \left(\frac{\partial \Phi}{\partial x}\right)] n dA \tag{2.16}$$

where j represents a specific ion, D_j is the dispersion coefficient, c_j is concentration of solute, mass of solute per unit volume of solution, v_x is average seepage velocity, F is Faraday's constant, R is universal gas constant, x is flow direction, T is temperature (°K), Φ is electrical potential, and n is porosity.

The solute flux due to a chemical gradient , as described in Eq. 2.16, is given by Fick's First Law:

$$q_{cc} = - D_j \frac{\partial c_j}{\partial x} n \tag{2.17}$$

where D_j is the longitudinal dispersion coefficient in saturated porous media. Gillham (1982) reported that D_j is composed of two components:

$$D_j = \alpha_x \ V_x + D^* \qquad\qquad (2.18)$$

where $\alpha_x \ V_x$ represents the dispersion of the species caused by the average linear seepage velocity, α_x is the longitudinal dispersivity which depends on the size and frequency of the pores in the medium and D^* is the molecular diffusion coefficient and represents the diffusion of the chemical in the pores (Gillham, 1982). The molecular diffusion coefficient D^* in the pore fluid is related to the diffusion coefficient in the free solution by

$$D^* = \rho D_o \qquad\qquad (2.19)$$

where ρ is a coefficient depending on porosity and tortuosity of the medium . Rowe (1987) reported that ρ values vary between 0.13 to 0.49.

The solute flux, q_{ch}, caused by the hydraulic gradients described by Dary's law; is:

$$q_{ch} = (k_x \frac{\partial h}{\partial x})nc_j \qquad\qquad (2.20)$$

where k_x is the hydraulic conductivity of the medium, h is the hydraulic potential and n and C_j are previously described.

In this model, the average seepage velocity is assumed to be linear, uniform, and equal to the macroscopic fluid velocity. Also, the electrical gradient $\partial \Phi / \partial x$ is assumed

be constant in time and space. These assumptions simplify Equation 2.16 to:

$$q_{cc} = [kc_j - D^* \frac{\partial c_j}{\partial x}]n \qquad (2.21)$$

The prameter k is defined by equation 2.22 as:

$$k = -\frac{zF}{RT}D^* \frac{\partial \Phi}{\partial x} + k_x \frac{\partial h}{\partial x} = -k_m + k_h \qquad (2.22)$$

where k is a constant with units of [L/T] representing the velocity of the pore fluid. The first term in Eq. 2.22 represents the flow of water molecules caused by the migration of H^+ ion and its hydrated water molecules under an electrical gradient, and the second term k_h describes the contribution to flow caused by the hydraulic gradient.

Conservation of mass balance across the element in one-dimensional condition must satisfy:

$$\frac{\partial q_{tc}}{\partial x} = -R \frac{\partial c}{\partial t} \qquad (2.23)$$

where R is the retardation coefficient, and $\partial c/\partial t$ is the rate of mass change. The retardation coefficient represents ant inter action between the different species and the adsorption and desorption. Parameter R can be evaluated from the bulk density of the soil and the partition coefficient (Acar et al, 1990) as:

$$R = 1 + \rho_d k_p / n \qquad (2.24)$$

with k_p is the partition coefficient.

Substituting Equations 2.16, 2.21 into Equation 2.23 gives

$$D_x \frac{\partial^2 c}{\partial X^2} - k \frac{\partial c}{\partial x} = R \frac{\partial c}{\partial t} \qquad (2.25)$$

where $\partial^2 c / \partial x^2$, $\partial c / \partial x$, $\partial c / \partial t$ represent partial derivatives of mass in space and time. If the experiment were conducted under constant hydraulic gradient, and if the water being transported with the migration of H ion is constant, k will simplify to V_x, the average seepage velocity.

$$D_x \frac{\partial^2 c}{\partial X^2} - V_x \frac{\partial c}{\partial x} = R \frac{\partial c}{\partial t} \qquad (2.26)$$

Equation 2.26 can be presented in normalized form by considering

$$X = x/L \qquad (2.27a)$$

$$C^* = 1 - \frac{c}{c_i} \qquad (2.27b)$$

$$P = V_x L / D_x \qquad \text{(2.27c)}$$

$$T = D_x t / R L^2 \qquad \text{(2.27d)}$$

where L is the length of the specimen, C_i is the initial concentration, P is the Peclet number, T is nondimensional time. Substituting Equations 2.27 into Equation 2.26 gives

$$\frac{\partial^2 C^*}{\partial x^2} - P \frac{\partial C^*}{\partial x} = \frac{\partial C^*}{\partial T} \qquad \text{(2.28)}$$

Equation 2.28 can be solved by a finite difference technique to estimate the pH gradient using the appropriate boundary and initial conditions.

As the species generated at the electrodes (inlet and outlet) are different, a neutralization reaction must exists at the location where they meet.

$$H^+ + OH^- \rightarrow H_2O \qquad \text{(2.29)}$$

2.5.3 Initial and Boundary Conditions

The initial condition is defined by the initial [pH] of the pore fluid for either H^+ or OH^-,

$$Ci(x,0) = Ci \qquad \text{(2.30)}$$

The boundary conditions are defined by the measured [pH] at the boundaries.

Since the species generated at the boundaries are different, a constraint exists at the boundary to ensure neutralization at the location where they meet.

$$H^+ + OH^- \leftrightharpoons H_2O \tag{2.33}$$

CHAPTER THREE

EXPERIMENTAL PROCEDURE

This chapter discusses the experimental procedures involved in this present research. The discussion includes a description of the characteristics of the porous medium, the preparation of the sodium nitrate solutions, the preparation and testing procedures used in both closed and open system tests, and finally a brief presentation of the numerical model used to analyze the experimental data.

The research was accomplished by two type of experiments: closed system experiments, and open system experiments. In both types of experiments, silica sand was used as a porous medium with the cylinderical column oriented horizontaly. Sodium nitrate was used as an interstitial solution in all experiments. Constant electrical current was obtained through the soil column by an electrical potential provided by power supply connected to electrodes located at both sides of the soil column.

In the open system experiments, different rates of hydraulic flow from the anode compartment to the cathode compartment were applied. In the closed system experiments no hydraulic flow was allowed.

Mass balance calculations found higher sodium output levels were higher than the input level in some of the closed system experiments, which indicated that the sand might initially have some sodium adsorbed on the surface of the particles. In order to check the adsorption premise, some separate beaker experiments were conducted.

3.1 Porous Medium

Silica sand was used as the inert porous medium in all the experiments. This section discusses some of the characteristics of the silica sand related to this research.

3.1.1 Bulk Density

The bulk density of the sand is a critical parameter in ensuring a homogeneous soil column. The sand was packed in layers and every layer had the same volume and mass of sand.

A tubular column whose volume and weight were known was filled with silica sand. The weight of the column was remeasured after filling it with dry silica sand. The bulk density was calculated using the exact measured weight of dry sand and the bulk volume of the column using the following relationships:

$$\rho_b = \frac{mass\ of\ dry\ sand}{bulk\ volume\ of\ the\ column} \tag{3.1}$$

Where ρ_b is the bulk density

The value of ρ_b determined was 1.53 g cm^{-3}, which falls within the range of values published in the literature for unconsolidated sand (Freeze and Cherry, 1979)

3.1.2 Porosity

Porosity is the parameter used to determine the volume of solution needed to

saturate the soil column in each experiment. The porosity of the sand used in this study was determined from:

$$n = 1 - \frac{\rho_b}{\rho_p} \qquad (3.2)$$

where ρ_b is the bulk density , and ρ_p is the particle density of the sand. A value of 2.65 was assumed for the particle density of the silica sand. The porosity value calculated using the experimental value of ρ_b = 1.52 and Equation 3.2 was 0.43, which is within the range of values published in the literature (Freeze and Chery, 1979).

3.1.3 Hydraulic Conductivity

Hydraulic conductivity of the test sand was an important parameter required for the calculation of the head needed for setting certain flow rates in the open system experiments.

A constant-head permeameter method was used to measure the hydraulic conductivity (Fig 3.1). A constant hydraulic head was applied to obtain constant flow across a horizontal column of packed sand. Porous stone and a filter paper were placed at both ends of the soil column to permit only fluid entrance to and exit from the soil column. The length and area of the soil column were measured, and a Marriot bottle was connected to the permeameter. After equilibrium, the difference in head across the soil column was measured. The outflow water was collected in a graduated cylinder and
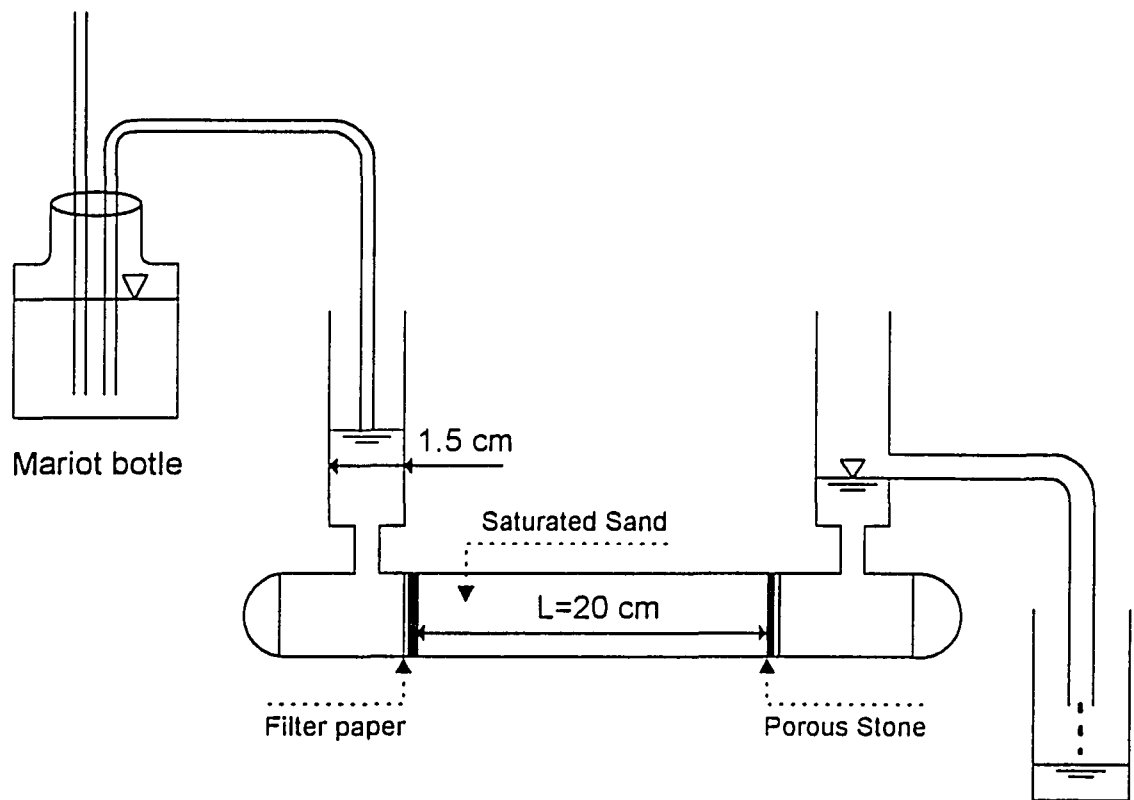
Figure 3.1 The Constant Head Permeameter to Measure k_s

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3.3 CLOSED SYSTEM

The purpose of these type of experiments was to study the chemical gradients developed in the presence of a DC electrical potential and to evaluate the effect of selected design parameters on the electro-kinetic process. This section summarizes the procedures involved in preparing the soil columns and setting up the electrical circuit, the sampling technique, and the method of extracting the interstitial solution.

3.3.1 Columns Preparation

In the first set of experiments (experiments 1 and 2), clear acrylic plastic tubes were used for the soil columns. The remainder of the columns were built from solid acrylic rods. All column tubes were 25 cm long and had 6.5 cm internal diameters. One end of the tube was closed while the other had a removable cap to close the tube after filling the column with soil and solution. The two electrodes were plates 4 cm in diameter and 0.2 mm in thickness for all experiments except the first experiment in which electrodes were rods 0.6 cm in diameter and 7 cm in length. Switching from rod to plate electrodes after experiment 1 was intended to bring the migration flow as close as possible to one dimensional flow. One of the electrodes was attached to the closed end of the tube while the other was attached to the cap (Fig 3.2). The plate electrodes were connected to both ends of the soil columns with a screw which extended from the end of the tube and thus provided the connecting point to a power supply with an alligator clip.
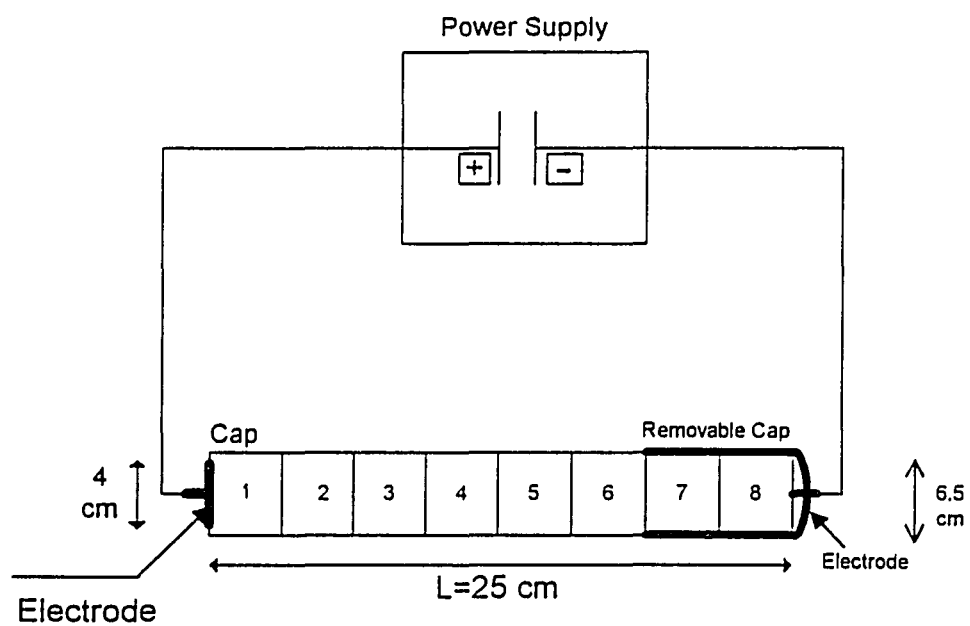
Figure 3.2 Sketch of the Closed System Apparatus

In experiment one, two holes were drilled in the column tube 5 cm from each end and 6 cm long rod electrodes were inserted into the column through small rubber stoppers. Silicon cement prevented leaks around the electrodes.

In all experiments, after filling the tube with sand and solution, the open end of the column was capped and sealed using silicon cement. The column was oriented in a horizontal position to minimize gravity effects. Before connecting the column electrodes to the power supply, the column length was divided into marked sections. Initial data recorded for each experiment included the column length; column diameter; volume of sand, volume of solution and initial concentration.

3.3.2 Electrical Circuit

A constant electrical current was input to the soil column by means of DC power supply connected in parallel with both electrodes. Constant current condition were used in all tests to keep the net rates of the electrolysis reaction constant and to minimize complicated current-boundary conditions. A voltmeter and ammeter were connected between electrode and the power supply. Since experiments were conducted with constant current levels, the voltmeter showed any variation in electrical conductivity during the experiment, indicating chemical changes in the column.

The current levels utilized in the closed system experiments: 1.5 ± 0.05 mA, 3.0 ± 0.05 mA, 5.0 ± 0.05 mA and 10.0 ± 0.05 mA. The voltages ranged from 30 to 90 volts. Gray (1970) reported secondary temperature effects decrease the efficiency of

electro-osmotic flow when the current density is greater than 5 mA/cm^2. To avoid such effects, the current density used in all test was about one order of magnitude lower than 5 mA/cm^2.

3.3.3 Freezing the Soil Column

To preserve the chemical gradient developed from the electrical gradient, the soil column was frozen before turning off the power supply. The freezing technique followed in this research was the same as discussed by Wahli (1988). After the experiment had run for the desired duration (which varied from one experiment to another), the soil column was horizontally laid in a large styfoam box and liquid nitrogen was poured into the space between the soil column and the box for a few minutes until the soil column was completely immersed. The power supply was turned off and the soil column was removed from the box. The soil column then was cut with electrical saw into 6-8 separate 2.5 to 3.5 cm long sections at the marks indicated on the column. The segments were stored in sealed beakers in a freezer until analysis. Before extracting the interstitial solution, each segment was allowed to thaw for one day.

3.3.4 Extracting the Interstitial Solution

All the extraction work and the analytical analysis of the solutions were conducted At UNIVERSITY OF ARIZONA SOIL AND WATER SCIENCE LABORATORY. A vacuum pump connected to a 0.45 μm filter funnel was used to extract the solutions from

the soil columns. The time required to extract solution from each segment was about 1 minute, consistent with a saturated coarse sand. The solution of each extracted segment was preserved in a 13 ml laboratory glass tube for later chemical analysis.

3.4 Beaker Experiments

Two sets of experiments were conducted to quantify the sodium initially in the sand. In the first experiment, beakers were filled with measured volumes of deionized water (100 ml) followed by measured amounts of sand (43 ml) so that the solution-to-sand ratio was equivalent to the porosity of the sand. After stirring the saturated sand, the beaker was sealed with parafilm paper to prevent evaporation and the sand and solution was left to equilibrate for 24 hours. Then, the solution was extracted from the sand using the method described above. The extracted solution was analyzed for Na, NO_3, and pH. In the Second experiment, beakers were filled with measured volumes of sodium nitrate solution (100 ml) followed by measured amounts of sand (43 ml) so that the solution-to-sand ratio was equivalent to the porosity of the sand. After stirring the saturated sand, the beaker was sealed with parafilm paper to prevent evaporation and the sand and solution was left to equilibrate for 24 hours. Then, the solution was extracted from the sand and analyzed for Na, NO_3, and pH.

3.5 Open System

The purpose of these experiments was to study the effect of a hydraulic flow superimposed on electromigration. These experiments were also used to determine the flow velocity at which electromigration of NO_3 no longer was sustained. Several different hydraulic flow rates were introduced in the direction opposite that of electromigration of No_3 (i.e., from the anode to the cathode).

3.5.1 Column Design And Experiment Set Up

Acrylic column 30 cm long and 6.5 cm in diameter were used in the experiments. The columns consisted of two parts; a 20 cm long column in which soil was placed and the two caps, 5 cm long each, used to seal the soil column after filling it with sand. Two plate electrodes were connected to the caps with screws which extended out of the tube to connect the electrodes to a power supply with an alligator clip. Six holes 5 cm apart were drilled along one side of the soil column to permit solution sampling. Rubber septums covered with filter paper were attached to each hole. Porous stone and filter paper were placed between the soil column and each cap to allow only solution to flow into and out of the caps. A hole 2.5 cm in diameter was drilled at the top of each cap and connected to a solid acrylic tube with silicon cement. Clear plastic tubes 2.6 cm in diameter were connected to each of the tubes through which sodium nitrate solution was allowed to flow into and out the apparatus. Figure 3.3 illustrates this apparatus.
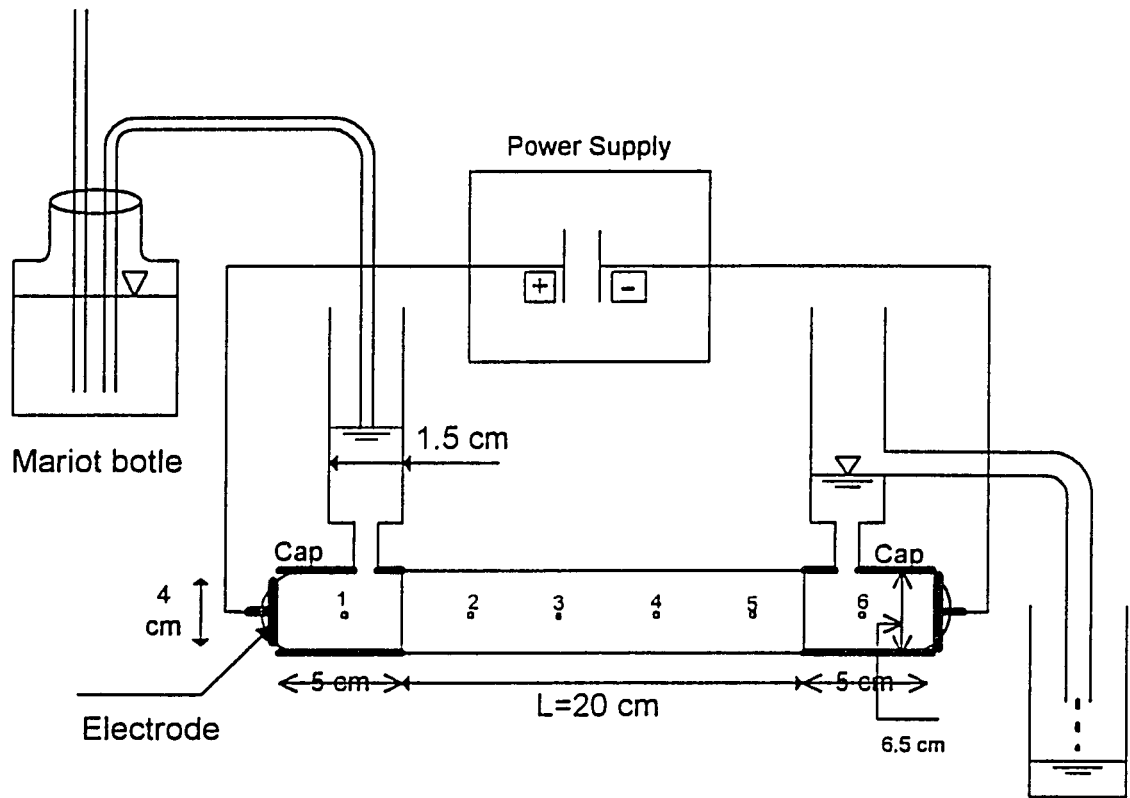
Figure 3.3 Sketch of the Open System Apparatus

The soil column was packed in four layers, each 5 cm long. To ensure homogeneous packing, the same measured amount of sand (254 gm) was placed in each layer. A glass rod was used to compact the sand in each layer.

In all experiments, a needle syringe was used to withdraw solution samples through the septums during the experiment. The diameter of the needle used was very small and the septum material was very elastic to ensure that the needle hole was sealed immediately after withdrawing the samples.

Four different hydraulic flow rates (9.5 cm/hour, 17 cm/hour, 32 cm/hour, 70 cm/hour) were tested in the open system experiments with the same current level (3 mA). Also, two different levels of current were tested with the 17 cm/hour flow rate, 3 mA and 6 mA. Two levels of sodium nitrate concentration were tested for the 17 cm/hour flow rate, 85 ppm and 170 ppm. A constant flow rate was accomplished by connecting a Marriot-type bottle to one end of the apparatus using the clear plastic tube. The other clear plastic tube was connected to a container to collect the outflow with a 0.3 cm in diameter clear plastic tube.

In each open experiment, the Marriot type bottle was filled with sodium nitrate solution and the solution allowed to flow through the soil column. A screw valve connected to the input tube was used to control the rate of flow coming from the Marriot bottle to the soil column. After equilibrium was reached and flow became steady, the difference in head across the soil column was measured using a scale and horizontal level. The outflow rate was calculated from:

$$v_x = \frac{V}{t\,A} = k_s\,\frac{H}{L} \tag{3.4}$$

where V_x is the flow velocity in cm/hr, V is volume of water collected in time t; K_s is the saturated hydraulic conductivity in cm/hr determined previously; H is the hydraulic head across the soil column(cm); L is column length in cm; and A is the cross sectional area of the column.

Each septum was pre-numbered according to its location (#1 referred to the septum closest to the anode, #6 referred to the septum closest to the cathode). Each experiment was continued for 12 hours. Six samples were drawn from the six septums at various test durations (0 hrs, 4 hrs, 8 hrs, and 12 hrs). The samples were reserved in 13 ml laboratory glass tubes until the experiment was terminated then analyzed for NO_3 and Na content. The pH levelsfor all samples also were measured using pH meter and glass electrode.

3.5.2 Electrical Circuit

The same power supply and electrical setup used with the closed system were also used with the open system.

3.6 Modeling

The applicability of electro-kinetic method to concentrating nitrate close to the

anode was the main goal of this research. Thus, analytical methods were sought to predict the nitrate gradient developed under specified electro-kinetic processes as a function of solution changes resulting from electrolysis. Important pH gradients were generated as a result of electrolysis. An inversely proportional relationship between the generated pH gradient and the generated nitrate gradient was observed from both closed system and open system experimental results. The regression relationship from test data had a high average correlation coefficients which suggested the use of the pH gradient developed under an electro-kinetic process and defined regression equations between pH and No_3 to predict the nitrate gradient.

A one dimensional finite difference model was developed to predict the pH gradient developed during the electro-kinetic process. The model followed the theory developed by Acar et al, (1991). A statistical program (Table curve) was used to find out the best regression equation relating the nitrate gradient to the corresponding pH gradient.

3.6.1 The pH Model

The equation that describes the H^+ and OH^- concentration in time and space, according to Acar et al (1990), is:

$$\frac{\partial^2 C^*}{\partial X^2} - P \frac{\partial C^*}{\partial X} = \frac{\partial C^*}{\partial T} \tag{3.5}$$

where C^* represents either H^+ or OH^- normalized concentration, T is nondimensional

time, P is the Peclet number; and X is nondimensional distance. C^*, P, X, and T are

further defined as:

$$C^* = 1 - \frac{C}{C_i}$$

(3.6a)

$$P = \frac{V_x L}{D_x}$$

(3.6b)

$$X = \frac{x}{L}$$

(3.6c)

$$T = \frac{D_x t}{R L^2}$$

(3.6d)

where C_i is the initial concentration of either H^+ or OH^-; L is the length of the column;

and t is the time.

The finite difference form of Equation 3.5 using a central difference implicit

solution scheme in X and the Crank-Nicklson scheme in T is:

$$[C^*_{i-1} - 2C^*_i + C^*_{i+1}]^{k+1} - 0.5 \ \Delta X \ P \ [C^*_{i+1} - C^*_{i-1}]^{k+1} - \frac{2 \ \Delta X^2}{\Delta T} \ [C^*_i]^{k+1}$$

$$+ [C^*_{i-1} - 2C^*_i + C^*_{i+1}]^k - 0.5 \Delta X \ P \ [C^*_{i+1} - C^*_{i-1}]^k + \frac{2 \Delta X^2}{\Delta T} [C^*_i]^k = 0$$

(3.7)

where ΔX is the length increment in the X direction; i is index of the increments in X

direction; ΔT is the time increment; and k is the index of the time increments.

Numerical solution using the above equation defines the solution at discrete points in the X-T plane. The initial condition defined the solution at $T=0$ and the boundary conditions define the solution at both $X=0$, and $X=1$.

The initial concentration was defined from the initial pH value of the solution, obtained experimentally. The boundary condition concentrations were defined from the pH values obtained experimentally at the boundary sections at termination of the electro-kinetic tests. The C^* values at each new time step (k+1), were initialized as the ones from the previous time step (k) and the boundary conditions.

The Newton-Raphson method of numerical integration was used to find the concentration residuals as:

$$D \, [\, Z \,] = [\, F \,]\qquad(3.8)$$

where [Z] is the vector of concentration residuals, and D is the matrix of Jacobians of F in the finite difference Equation (Equation 3.5).

Equation 3.8 represents a tri-diagonal system of equations in matrix form and was solved using the Gaussian elimination technique. C^* was updated in an iterative manner using [Z] as:

$$[C^*]^{n+1} = [C^*]^n - [\, Z \,]\qquad(3.9)$$

Iteration continued until convergence was achieved based on pre-specified tolerance so that the vector of residuals approached zero.

The model inputs were the length of the soil column, L, the number of equation solution points along the X direction, N_x, the total time the experiment was run, t, the number of time steps,N_t, the effective diffusion coefficients for both H^+ and OH^-, retardation coefficients for both H^+ and OH^-, the flow velocity, and the initial and boundary concentrations of H^+ and OH^-.

3.6.2 Material Constants

Diffusion coefficient, D. The diffusion coefficients in the free solution for both H^+ and OH^- were obtained from the literature (Acar el al 1993). It was, however, thought necessary to estimate an effective diffusion coefficient for H^+ and OH^- with respect to a counter ion species available in the original pore fluid (Acar et al 1993).

$$D_{effective} = \frac{D_+ D_- (Z_+ - Z_-)}{Z_+ D_+ - Z_- D_-}$$ (3.10)

where Z is ionic charge.

The effective diffusion coefficient for H^+ was calculated with respect to NO_3 while OH^- calculated with respect to Na. The diffusion coefficient in the porous medium was calculated from the diffusion coefficient in the free solution (Acar et al, 1993) as:

$$D^* = D_o \cdot \rho \qquad \qquad (3.11)$$

where D^* is the diffusion coefficient in the porous medium, D_o is the diffusion coefficient in the free solution, rho is a coefficient depending on porosity and tortuosity of the medium, varying between 0.13 and 0.49 (Acar 1993), and n is the porosity of the soil (0.43 in this study). Diffusion coefficients of 0.035 and 0.025 were calculated for H^+ and OH^- respectively.

The apparent diffusion coefficient, D, was calculated as:

$$D = \alpha \, V_x + D^* \qquad \qquad (3.12)$$

where V_x is the average seepage velocity in the porous medium, and α is the longitudinal dipersivity. A value of $\alpha = 0.01$ was chosen from Freez and Cherry(1989).

Retardation coefficient. The retardation coefficient, R, was calculated using dry bulk density of the sand, ρ_b, and the partition coefficient, k_p as:

$$R = 1 + \rho_b \, k_p/n \qquad \qquad (3.13)$$

Retardation coefficients of 5 and 1 were calculated for H^+ and OH^- respectively.

3.7 Statistical Analysis

The TABLE CURVE statistical program was used to find the best equation relating the nitrate gradient developed under an electro-kinetic process to the corresponding pH gradient.

The regression equation obtained from open system experiment results was:

$$\frac{C}{C^i} = a + b \; \frac{e^{pH}}{pH} + c \; \ln(t) \qquad (3.14)$$

The regression equation obtained from closed system experiment results was:

$$\frac{C}{C^i} = a + b \; \frac{\ln(pH)}{pH} \qquad (3.15)$$

CHAPTER FOUR

RESULTS AND DISCUSSION

Laboratory experiments utilizing closed and open systems were conducted to test the effectiveness of an electro-kinetic process in concentrating nitrate close to the anode for subsequent removal. In both sets of experiments, silica sand was used as the inert porous media and sodium nitrate was used as the interstitial solution.

In the open system experiments, a preset constant hydraulic flow rate was imposed across the porous media column (from the anode to the cathode) to test the effect of the hydraulic flow super-imposed on electromigration. These experiments were also used to determine the hydraulic velocity at which the effect of electromigration could be negated.

In the closed system experiments, the effects of some electrochemical parameters on the performance of the electro-kinetic process were tested. These parameters were duration of electrical input, electrode material, electrode spacing, current level, and the initial chemical concentration of sodium nitrate solution.

In this chapter, the results of the closed system experiments are first presented and discussed followed by presentation and discussion of the open system test results. The use of a one-dimensional finite difference model developed to predict the pH gradient developed by electrolysis during the electro-kinetic process is also presented and discussed.

4.1 Closed System

In closed system experiments, twenty tests were conducted to study the electrochemical gradients developed in an electro-kinetic process and the effects of changing some of the design parameters. The dimensions of the specimen, duration of the tests, current levels and other test parameters are presented in Table 4.1.

4.1.1 Mass Balance

Mass balance calculation determined the percent chemical recovery for each experiment. Results from beaker experiments indicated sand adsorbed a large amount of sodium The results of these experiments are presented in Appendix A.

The mass balance calculation was initiated by measuring the amount of salt introduced to the system and the output from the column as follows:

$$S_i = C_{it} * V_t \qquad (4.1)$$

where S_i is the amount of sodium or nitrate introduced to the Column (mg), C_{it} is the initial concentration in mg/l, and $V_t =$ the total volume of the solution present in the column calculated as:

$$V_t = L * A * n \qquad (4.2)$$

Table 4.1. Summary of the Closed System Experiment Data

Test #	Current (mA)	Length (cm)	Duration (hours)	Electrod Material	Initial C_o(ppm)
1	5	25	24	carbon	850
2	5	25	24	copper	850
3	5	25	5	steel	85
4	10	25	5	copper	85
5	5	25	5	copper	85
6	5	25	5	carbon	85
7	3	25	5	copper	85
8	3	25	5	steel	85
9	5	25	5	copper	85
10	5	12.5	5	copper	85
11	5	25	3.5	carbon	85
12	5	25	1.5	carbon	85
13	5	25	6.5	carbon	85
14	5	25	24	carbon	85
15	5	25	5	carbon	85
16	5	25	12	carbon	85
17	3	25	12	carbon	85
18	1.5	25	12	carbon	85
19	1.5	25	12	carbon	600
20	1.5	12.5	12	carbon	85

where L = the column length(cm), A = cross sectional area of the column, and n = porosity.

The output amount of salt was calculated as:

$$S_o = \sum S_i = \sum \frac{V_i C_i}{1000} \qquad (4.3)$$

where S_o is the calculated total amount of sodium or nitrate output from the column (mg), S_i the amount of sodium or nitrate in a column segment i(mg), C_i is the measured concentration in this segment, and V_i is the volume of fluid in segment i calculated as:

$$V_i = L_i *A *n \qquad (4.4)$$

where L_i is the length of the segment(cm) and A and n are defined above. The percent recovery for each experiment was calculated as:

$$R = \frac{S_o}{S_i} *100 \qquad (4.5)$$

The initial concentration of Na^+ and No_3^- was not measured prior to each experiment. Satisfactory mass balance calculations for both NO_3 and Na were obtained by considering the initial concentration to be the concentration the giving a percent recovery in the range of 100 ± 10. Results of the mass balance calculations are presented in Appendix A.

4.1.2 Chemical Gradients For NO_3 and Na and pH

Analysis of the interstitial solution revealed the same concentration gradient results for all experiments: a significant change in the nitrate concentration occurred throughout the experiment while significant sodium movement was only observed after the electrical field had been imposed for a considerable time period (24 hours). It is clear from the results that a nitrate concentration gradient was established as a direct response to the imposed electrical potential, with highest concentration adjacent to the anode and the lowest concentration adjacent to the cathode. Results also showed that sodium did not exhibit a similar response to imposed electrical potential of short durations (less than 24 hrs.). An almost uniform sodium gradient was established in the short duration experiments with only a slight increase in the Na concentration near the cathode and slight decrease near the anode; between the anode and cathode the concentration remained near the initial condition. The pH varied from high values at the cathode to low values at the anode.

Fig 4.1 illustrates the relative concentration gradients for NO_3, Na, and pH that were established after 3.5 hours of electrical input with a carbon electrode and 85 ppm initial concentration of sodium nitrate. Even though the experiment duration was short, a tendency for nitrate to move towards the anode is shown. The nitrate concentration in the section adjacent to the anode increased by two orders of magnitude from the initial concentration, dropped to almost zero in the two sections close to the anode and remained near the initial concentration($C/C_o = 1$) in the sections in between.
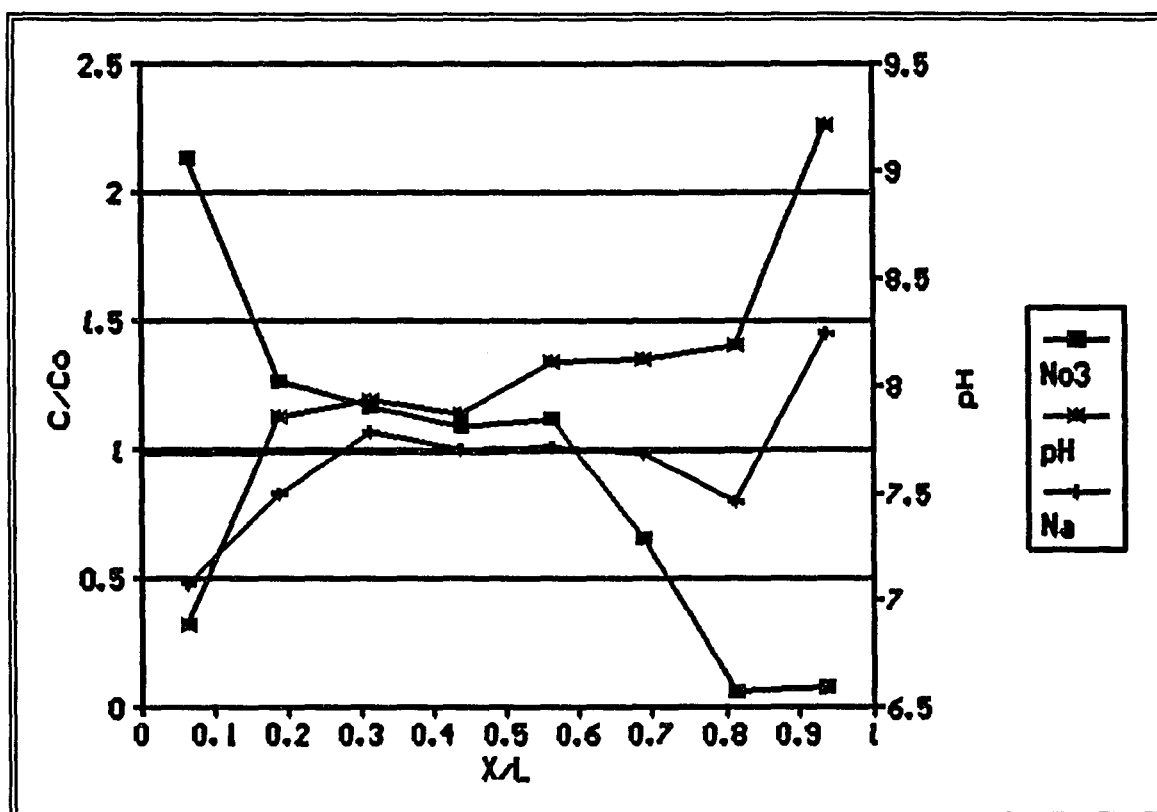
Figure 4.1. Sodium and nitrate concentration (c/c_o) and pH levels developed after 3.5 hours of 5 mA electrical ipnut with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

These results reflect the direct response of No_3^- to the imposed electrical potential. Rapid movement of nitrate towards the anode is a result of high nitrate solubility in both high and low pH environments and high ionic mobility ($155 * 10^{-6}$ $cm^2/v.s$). The uniform distribution of nitrate in the middle sections is likely the result of back diffusion acting against the migration.

The concentration gradient for sodium is shown in Figure 4.1. An increase in the sodium concentration to 1.5 times the original magnitude in the section adjacent to the

cathode and a decrease to 0.4 of the initial concentration in the two sections close to the anode is shown. Sodium concentration remained at the initial concentration ($C/C_o=1$) in the middle sections.

It is clear from the result shown in Fig 4.1 that the rate of nitrate migration is higher than that for sodium under the same electrical influence. This difference might be due to the difference in the ionic characteristics for NO_3^- and Na^+. Nitrate ionic mobility ($155 * 10^{-6}$ cm^2/v.s) is higher than sodium ($109 * 10^{-6}$ cm^2/v.s). As a result, the transference number for NO_3^- is higher than that for Na^+ which indicates a higher contribution of NO_3^- than Na^+ to the total effective electric conductivity.

Figure 4.1 shows an increase in the pH value developed at the cathode section(pH=9.3) and a decrease was accurred at the anode(pH=6.8). The initial pH for this experiment was 8.0. The change in the pH values near the boundaries is a direct result of the electrolysis by which H^+ and OH^- were generated at the anode and the cathode respectively as described above in equations 2.14a and 2.14b.

Figure 4.2 shows the concentration gradients for NO_3^-, Na^+, and pH that were established after exposure to 5 hours of electrical potential. The figure clearly shows that the migration of nitrate towards the anode is very dependent on the amount of electricity applied(duration in this case). The nitrate concentration near the anode increased to 3 times the initial level and decreased to near zero in the two sections adjacent to the cathode. Nitrate appears to concentrate up to a distance of 0.4 of the length of the column from the anode ($x/L = 0.4$) with highest value at the anode and decreasing along

the rest of the length.

The Na$^+$ gradient after five hours was almost exactly the same as that for the 3.5 hours duration experiment(Fig. 4.1) which reflects the slow response of Na$^+$ to amount of electricity applied (duration). This might be explained partially by the fact that Na$^+$ is not soluble

in a high pH environment (basic environment). Thus, the initial condition for the experiments did not favor Na$^+$ solubility. The increase in the sodium concentration near the cathode is a result of the high strength of the electrical potential in this section. The overall gradient of Na$^+$ concentration shows a slight tendency for migration towards the cathode.

Figure 4.2 shows the increase and decrease in pH valuesat the cathode and the anode, respectively. The pH value at the anode dropped to a value of 4.5 and increased to a value of 10.9 at the cathode while it remained as the initial value (8.0) in all other sections. The closed system configuration allowed the newly generated H$^+$ and OH$^-$ at the boundaries to be accumulated. As a result, the amounts of H$^+$ and OH$^-$ at the anode and the cathode increased with time, thus altering to the pH levels.

The nitrate gradient that was established after 24 hours of DC electrical current is illustrated in Figure 4.3. It is clear from this figure that nitrate was concentrated within a distance of 0.15 (x/L) of the length from the anode and removed from all the other sections. This figure clearly illustrates the possibility of using the electro-kinetic process to concentrate nitrate around the anode for further removal.
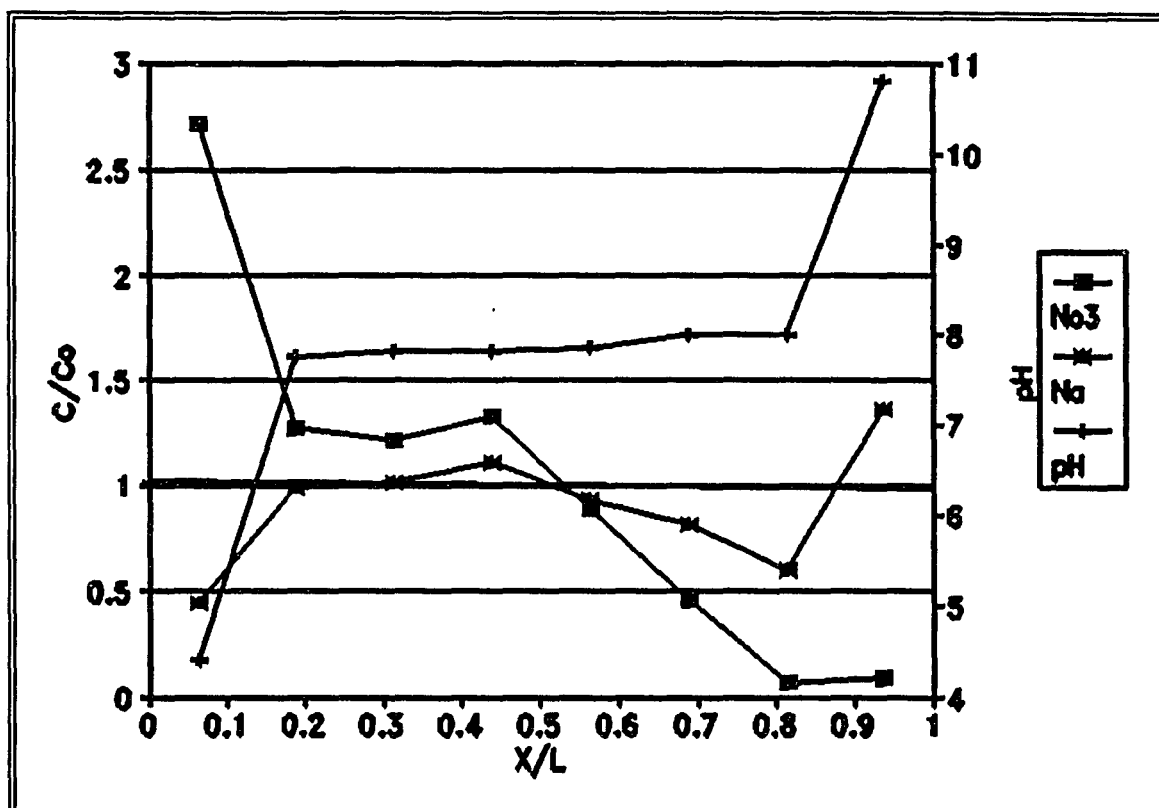
Figure 4.2.   Sodium and nitrate concentration (c/c$_o$) and pH levels developed after 5 hours of 5 mA electrical ipnut with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

Figure 4.3 shows a completely different sodium gradient than the ones found in

Figures 4.1 and 4.2. It can be seen from Figure 4.3 that sodium was concentrated within

0.15 of the column length from the cathode at about 12 times the initial

concentration and was completely removed from the rest of the length.

The pH gradient illustrated in Figure 4.3 shows a

uniform pH gradient (almost linear) along the whole length of the column. Increasing

the test duration to 24 hours increased the total amount of electrical energy and as a
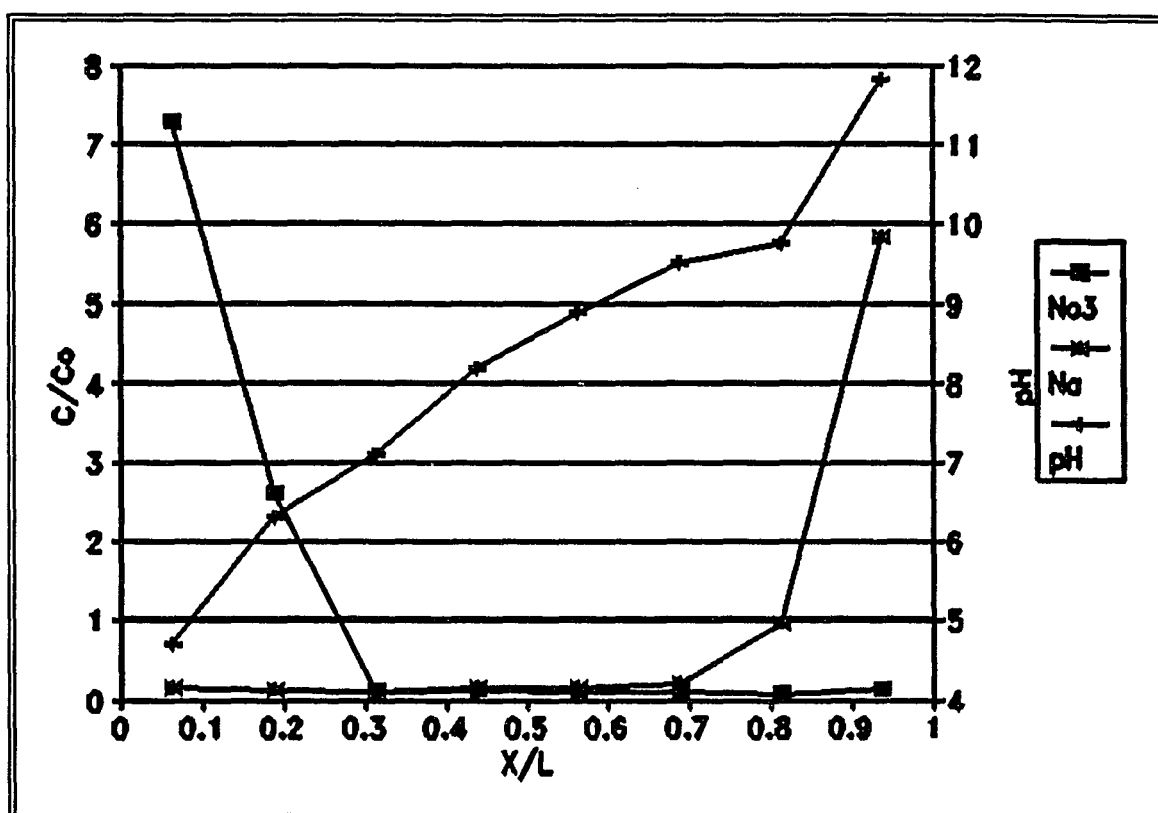
Figure 4.3.   Sodium and nitrate concentration (c/c$_o$) and pH levels developed after 24 hours of 5 mA electrical ipnut with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

result the amount of H^{+1} and OH^{-1} displaced to the boundaries was increased(notice the increase and decrease of pH values at the cathode and the anode respectively). The uniform distribution of pH in the central part of the column is a direct result of the migration of H^{+1} and OH^{-1} to their respective opposite electrodes.

Figure 4.4 represents the results for experiment # 16 in which a 5 mA current was maintained through the specimen for 12 hours. The main purpose of this experiment was to confirm the results obtained from experiment # 15 (Fig. 4.3).

The nitrate gradient shown in Fig 4.4 agrees with that shown in Fig 4.3 except for the concentration at the anode which was twice that shown in Fig. 4.3. Figure 4.4 clearly shows that NO_3^- was highly concentrated around the anode and completely removed from all the other sections.

The sodium gradient established in experiment # 16 and presented in Figure 4.4 is in a good agreement with ones established in all the close system experiments except experiment # 15 (duration = 24 hours). This indicates that Na^+ requires a considerably greater amount of electrical energy before it responds.

The pH gradient presented in Figure 4.4 again shows a drop in the pH value in the two sections near the anode and an increase in the two sections near the cathode while remaining near the initial value for the sections in between.

Figure 4.5 shows the results of experiment # 18 in which a 1.5 mA current was maintained through the specimen for 12 hours. The amount of electricity introduced in this experiment (12 hours*1.5 mA) is equivalent to the amount of electricity introduced in experiment # 11 (3.5 hours * 5 mA). Comparing the results presented in Figure 4.5 with the ones shown in Figure 4.1, it is clear that the same concentration gradients for No_3^-,Na^+ ,and pH were established in both experiments. This observation leads to the conclusion that the concentration gradient for No_3^- , Na^+ , and pH is highly dependent on the amount of electricity applied (current and duration). Tables of result data from all experiments are presented in Appendix B.
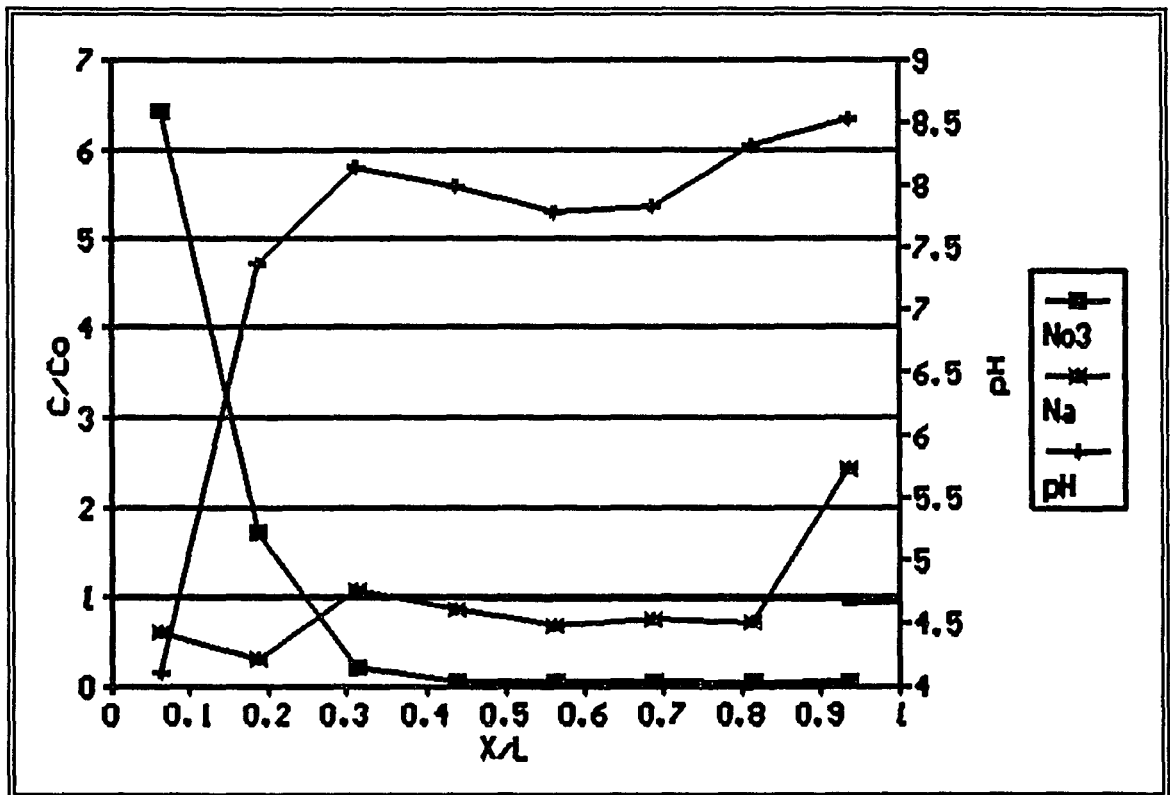
Figure 4.4 .   Sodium and nitrate concentration (C/C$_o$) and pH levels developed after 12 hours of 5 mA electrical input with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

4.1.3 Effects of Variables

The effect of closed system design parameters on the performance of the electro-kinetic process was tested under different conditions. The parameters which were tested are : duration of electrical input, current level, electrode material, electrode spacing, and the initial solute chemical concentration.

The results presented in the previous section indicated the initial condition for experiments did not favor sodium solubility and as a result no substantial movement of
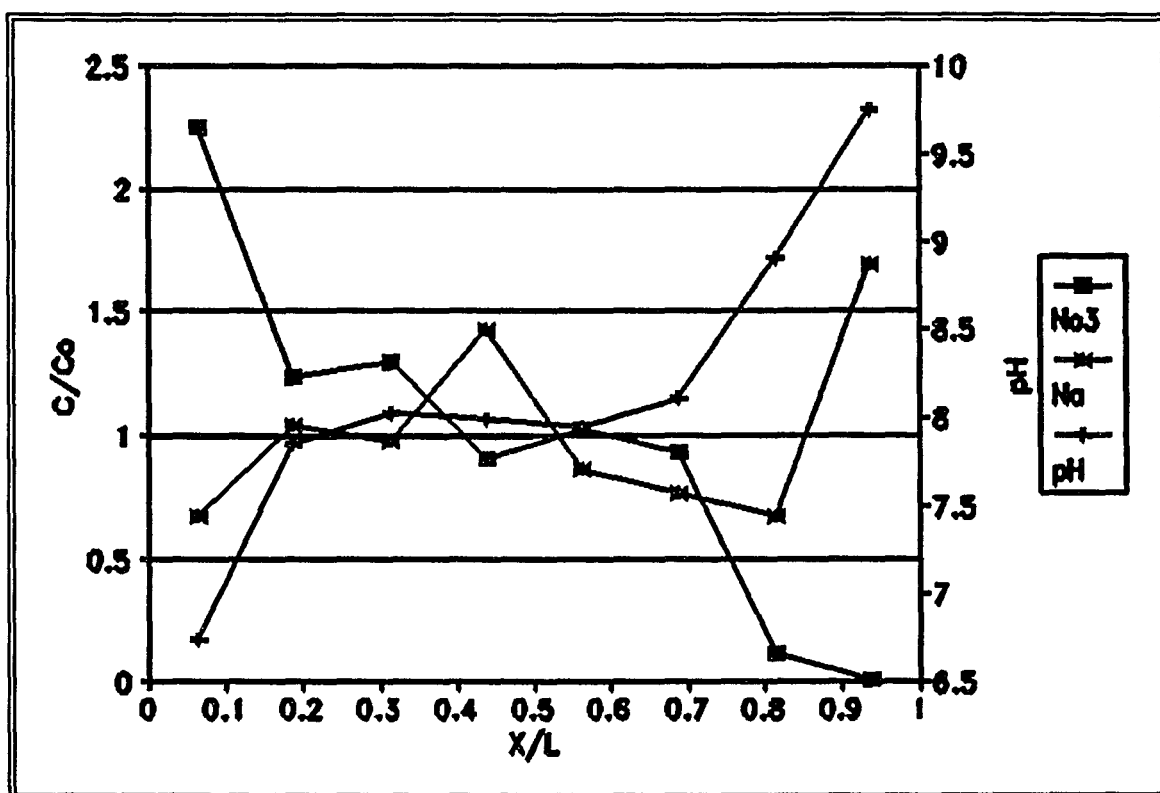
Figure 4.5. Sodium and nitrate concentration (c/c₀) and pH levels developed after 12 hours of 1.5 mA electrical input with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

sodium was observed except for the longest duration test, a 24 hour test. Thus, the tests reported below evaluated only the effect of design parameters on nitrate and pH levels.

4.1.3.1 Duration Effect

Figure 4.6 illustrates the nitrate gradients which were developed in five time periods (1.5 hrs., 3.5 hrs., 5 hrs., 12 hrs., 24 hrs.). As previously discussed, the nitrate gradient seemed to be very dependent on the amount of electricity applied. It can be clearly seen from Figure 4.6 that there is an advance in the movement of NO_3^- towards

Figure 4.6.   Nitrate concentration (c/c$_o$) developed after 1.5 to 24 hours of 5 mA electrical input with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

the anode with time. It took only 1.5 hours for the nitrate concentration to drop to 0.7 of the initial at the cathode end and to increase to 2.0 times the initial level at the anode end of the test column. Nitrate concentration remained near the initial concentration in the middle sections. Increasing the electrical input time from 1.5 hours to 3.5 hours resulted in a drop in the nitrate concentration to nearly zero in the two soil column sections adjacent to the cathode(0.15 of the soil column). The relative nitrate concentration at the anode end remained almost the same as that for the 1.5 hour test, but nitrate concentration increased in the middle sections. The NO_3^- concentration front

continued to advance towards the anode with time and as result more nitrate was accumulated at the anode with time . Finally, the system appeared to reach equilibrium after 12 hours of electrical input, with nitrate completely removed from 70 % of the column length nearest the cathode and concentrated mostly in the 15 % portion of the column nearest the anode. Increasing the electrical input time from 12 hours to 24 hours showed almost no effect on the nitrate gradient and nitrate still seemed to be concentrated in 0.15 of the column length nearest the anode.

The results shown in Figure 4.6 show the dependence of the nitrate gradient on the duration of the applied electricity at a given current level and illustrate the possibility of using an electro-kinetic process to concentrate nitrate close to an anode for further removal as an in-situ clean up technique.

The response of the NO_3^- gradient with different time durations was clearer than the performance of pH gradient. As stated before, H^+ and OH^- were generated by electrolysis at the anode and cathode, respectively. The electrolysis process resulted in a decrease and an increase in the pH values at the anode and cathode, respectively. Hammed et al (1992) showed the amount of H^+ and OH^- accumulated at the boundaries is highly dependent on both time and current.

Figure 4.7 shows the pH gradients which were developed in tests of five different durations. It is clear from the results shown in Figure 4.7 that the pH value at the anode decreased gradually with time, a change attributed to the increase in the amount of H^+ generated in this region. On the other hand, the pH value at the cathode responded

differently than expected. The pH at the cathode increased with time for shorter time periods (up to 5 hrs.), decreased with time for the intermediate test duration (12 hrs.) and then started to increase again with tests of longer duration (24 hrs.).

The pH values at the cathode and the pH gradient along the column seemed to be highly affected by nitrate movement. In the shorter time period tests , the amounts of H^+ and OH^- generated at the cathode and anode accurred as though neither substantial migration nor diffusion was expected. OH^- seemed to be dragged with NO_3^- towards the anode while H^+ movement towards the cathode seemed to resisted by the movement of NO_3^-. A basic environment was established along the length of the specimen as OH^- was moved with NO_3^- to the cathode (see Fig 4.1).

Increasing the test duration to 5 hours resulted in an increase in the generated amounts of H^+ and OH^- (for the same quantity of electricity, twice as much H^+ as OH^- was generated). As a result, the acidic front started to advance towards the cathode by both migration and diffusion and thus began to neutralize the basic front in the middle sections of the column where initial pH level was present. The pH level at the cathode implies that as time increased, the acidic front continued to advance across the specimen without significant retardation (the buffering capacity of the sand soil is very low and nitrate movement quickly reached equilibrium). The front reached the cathode after a 12 hours test duration and neutralized the basic condition generated at the cathode, lowering the pH at the cathode(see Figs. 4.4 and 4.7).
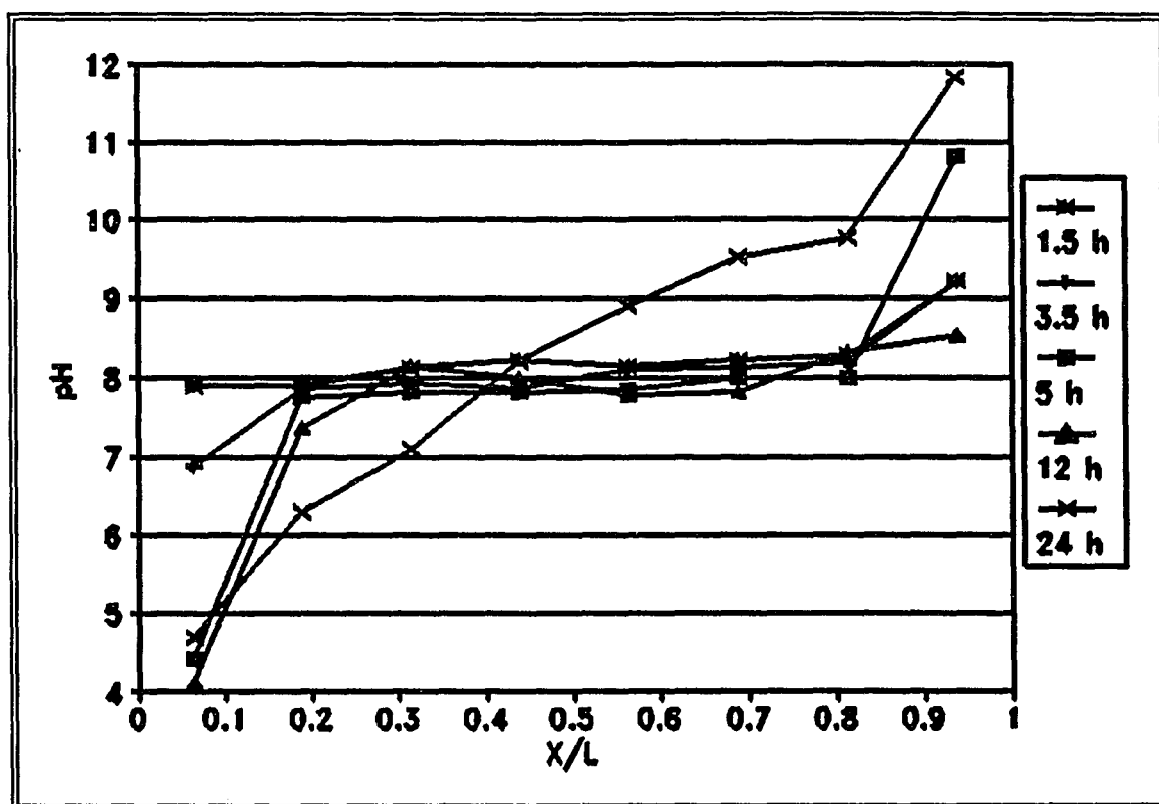
Figure 4.7.   The pH gradients developed after 1.5 to 24 hours of 5 mA electrical input with carbon electrodes and initial pH level of 8.0.

Applying the current through the specimen for 24 hours (note that the NO_3^- gradient had reached equilibrium at 12 hrs. test duration) allowed H^+ and OH^- to again be generated at the anode and cathode, respectively, which resulted in an increase and decrease in the pH values at the cathode and anode, respectively. The generated acid and base fronts advanced towards their respective opposite electrodes by both diffusion and migration, which contributed to a nearly linear pH gradient along the whole length of the column(see Fig. 4.3).

4.1.3.2 Current Level

Figure 4.8 shows the nitrate gradients with a carbon electrode tests which were developed under three different current levels (5 mA, 3 mA, and 1.5 mA). It is clear from the results shown in Figure 4.8 that the current level had a direct effect on nitrate movement. The higher the current level, the faster the movement and greater the concentration of nitrate around the anode. As shown in Figure 4.8, slow movement of nitrate occurred with a 1.5 mA current and nitrate was concentrated at a relative distance of 0.7 of the column length from the anode. On the other hand, rapid movement of nitrate was observed with the 5 mA current and nitrate seemed to be concentrated at a relative distance of only 0.15 from the anode. Figure 4.8 also shows intermediate nitrate movement for the 3 mA current level and nitrate appeared to be concentrated within a relative distance of 0.3 from the anode.

The results shown in Figure 4.8 substantiated a prior conclusion ; namely, that nitrate migration is highly dependant on the amount of applied electricity (duration and current level). The results presented in Figure 4.8 also suggest that 3 mA should be the minimum current level to use to concentrate nitrate with the given experimental configuration (carbon electrode and 12 hrs duration).

Figure 4.9 shows the pH gradients that were developed under three different current levels(5 mA, 3 mA, and 1.5 mA). It is observed from the results presented in Figure 4.9 that the higher the current level, the lower the resulting pH at the anode. These results are in a good agreement with the pH gradient theory developed by Acar
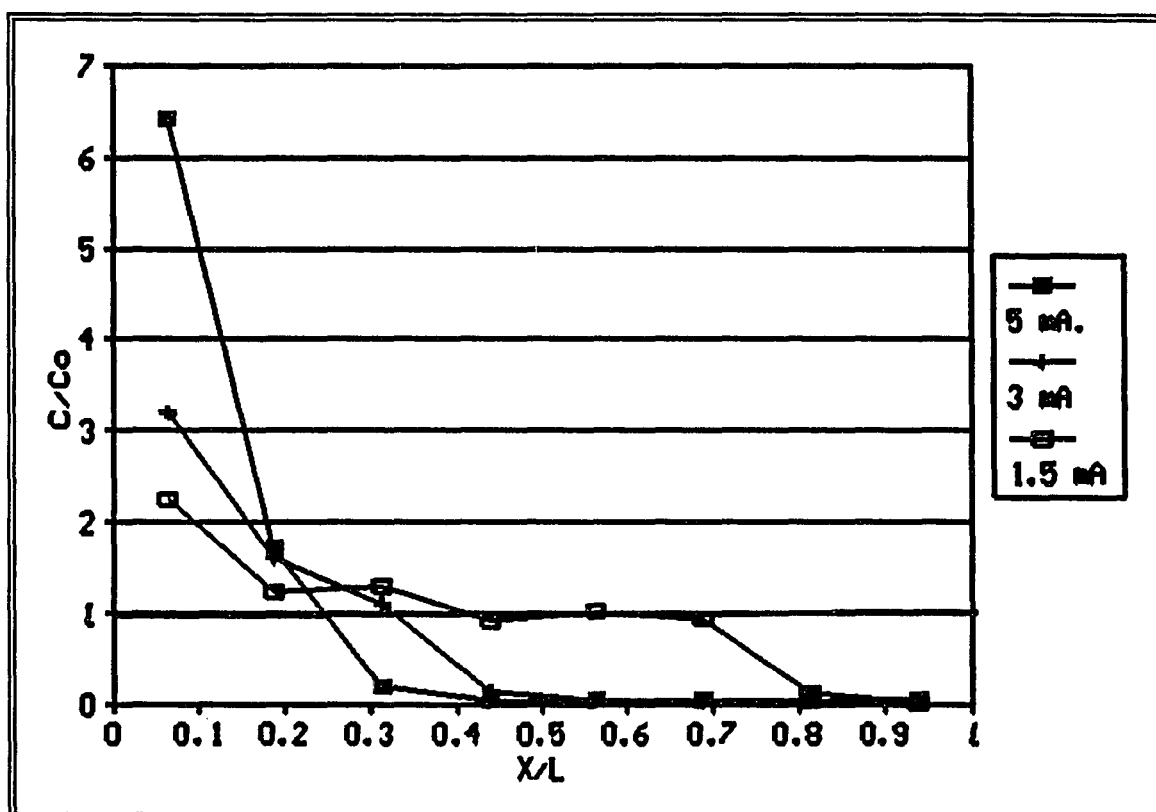
Figure 4.8.   Nitrate concentration (C/Co) developed after 12 hours of 5 mA, 3 mA, and 1.5 mA   electrical inputs with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

et al (1990). The results shown in Figure 4.9 confirm the conclusion that the pH value at the cathode as well as the pH gradient along the whole column is highly affected by No_3^- movement.

Introducing a 1.5 mA current for 12 hours resulted in the generation of H^+ and OH⁻ at the anode and cathode ,respectively, and to the decrease and increase in pH values at these electrodes respectively. Although the amount of H^+ generated at the anode was 2 orders of magnitude more than the amount of OH⁻
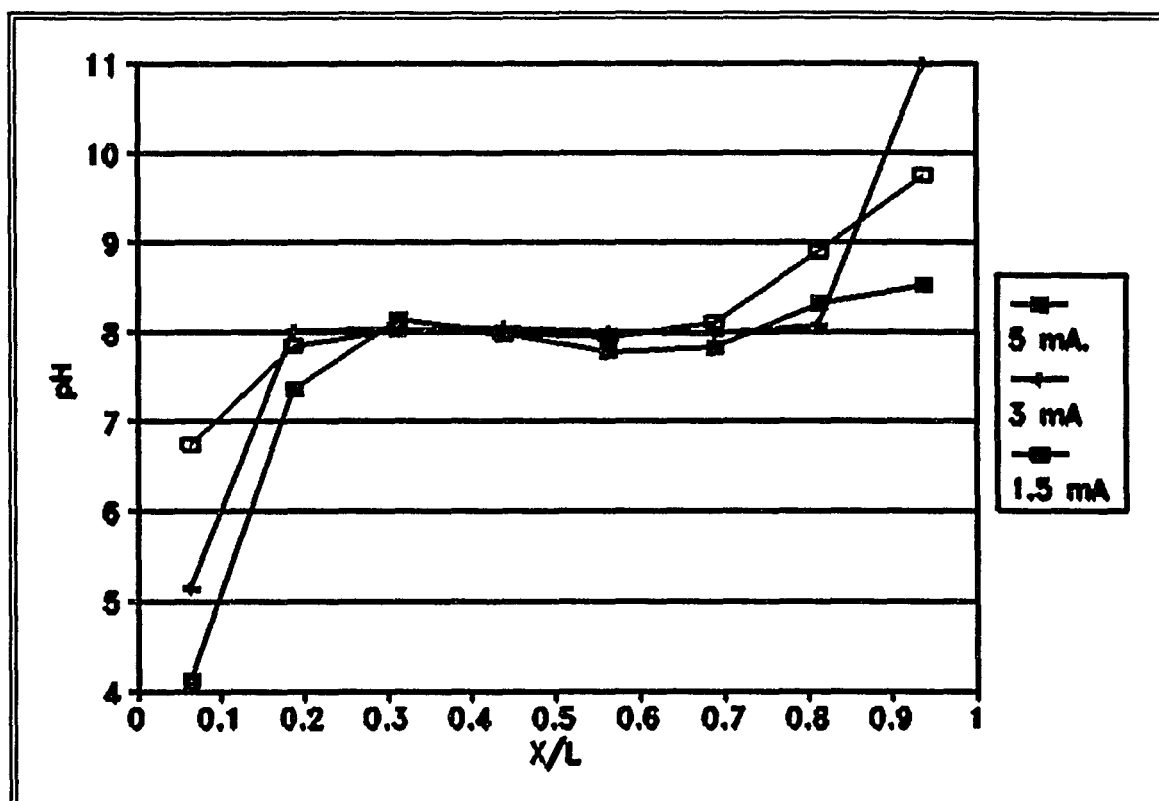
Figure 4.9. The pH gradients (C/Co) developed after 12 hours of 5 mA, 3 mA, and 1.5 mA electrical inputs with carbon electrodes and initial pH level of 8.0.

generated at the cathode, the basic front generated at the cathode was dragged with NO_3^- towards the anode. On the other hand, the movement of H^+ towards the cathode was retarded by No_3^- movement.

Increasing the current level to 3 mA generated more H^+ and OH^- and as a result the acidic front generated at the anode advanced towards the cathode by migration and diffusion and neutralized the basic front along the length of the specimen. The higher the current level, the faster the advance of the acidic front across the specimen. At the 5 mA current level, the acidic front reached the cathode and neutralized the base

generated at the cathode, lowering the pH at the cathode.

Figure 4.10 shows the NO_3^- gradients for copper electrodes which were developed under three different current levels (10 mA, 5 mA, and 3 mA). It is clear from Figure 4.10 that the movement of nitrate was considerably less with the 3 mA than with 5 mA or 10 mA input current levels. On the other hand, no significant difference in NO_3^- concentration gradient was observed between the 5 mA and 10 mA tests. However, increasing the introduced current from 5 mA to 10 mA doubled the amount of H^+ and OH^- generated at the anode and cathode, respectively.

Figure 4.11 shows the pH gradients developed after input of the three different current levels (3 mA, 5mA, and 10 mA). With the 3 mA current level, the acid and base generated at the anode and cathode, respectively, diffused almost at the same rate to their respective opposite electrodes. As a result, basic and acidic environments were established near the cathode and the anode. Introducing either a 5 mA or 10 mA through the specimen using copper electrode resulted in much faster advance of the acid front to the cathode (for the same quantity ofelectricity twice as much H^+ as OH^- is generated), lowering the pH at the cathode (see Fig. 4.11).

4.1.3.3 Electrode Material

The nitrate gradients developed with a 5 mA electrical current for three different electrode materials (copper, carbon, and steel) are illustrated in Figure 4.12. The results show that under identical conditions except for electrode material, the copper yielded similar results as the carbon electrode tests. A fairly high NO_3^- movement was obtained
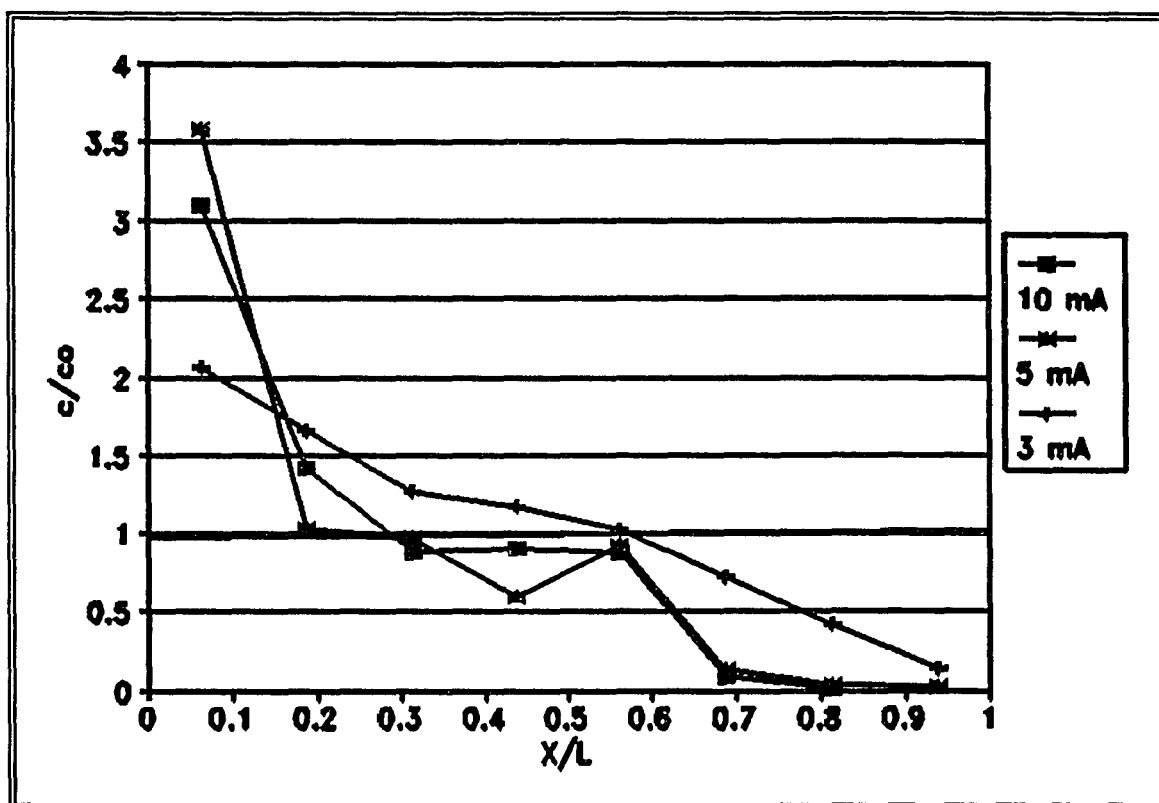
Figure 4.10 . Nitrate concentration (C/Co) developed after 5 hours of 10 mA, 5 mA, and 3 mA electrical inputs with copper electrodes and initial sodium nitrate concentration of 85 ppm.

using either carbon or copper electrodes. On the other hand, slow nitrate movement was obtained using the steel electrode. The differences in rate of nitrate movement among the electrodes is basically attributed to the fact that carbon and copper are inert electrodes that do not participate in the chemical reactions at the boundaries while participation is expected with steel. Also, both carbon and copper are somewhat better electrical conductors than steel.
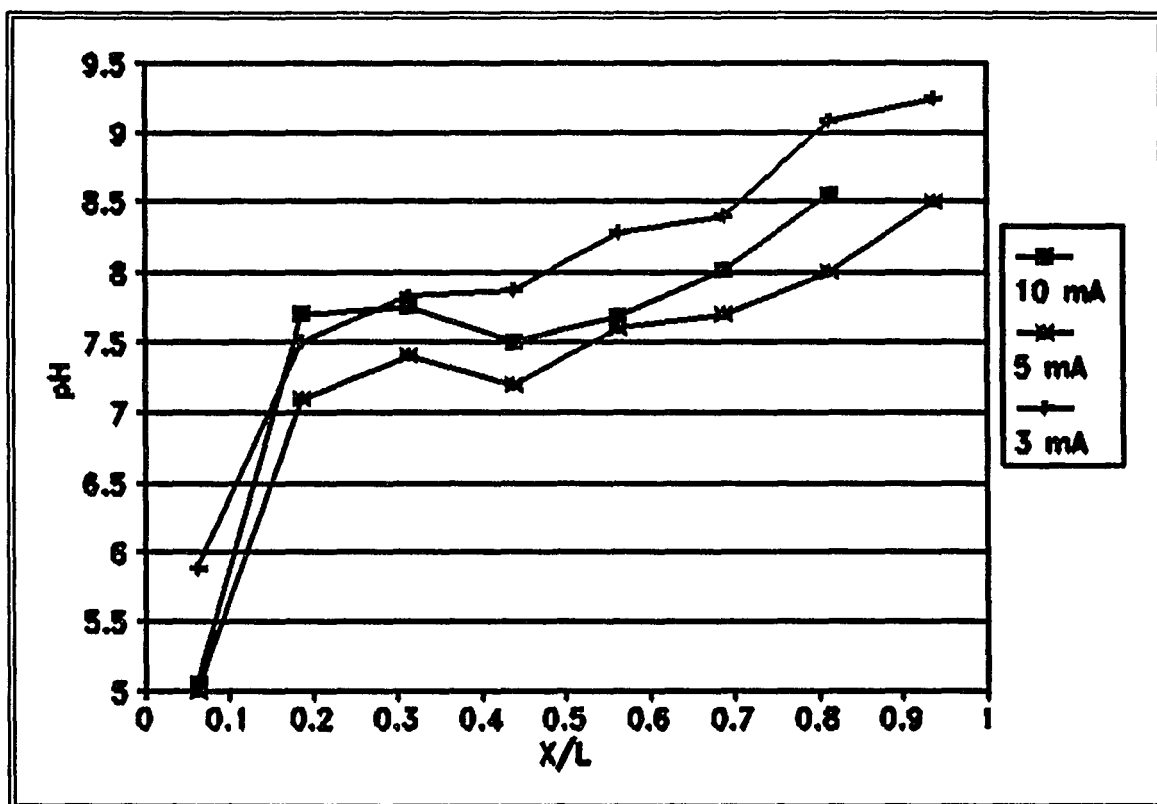
Figure 4.11. The pH gradients developed after 5 hours of 10 mA, 5 mA, and 3 mA electrical inputs with copper electrodes and initial pH level of 8.0.

Figure 4.13 shows the pH gradients that were developed with the three different electrode materials. With steel electrodes, only a relatively small amount of H^+ and OH^- was generated at the boundaries. The pH gradient developed with the steel electrodes varied from a basic environment near the cathode to an acidic environment near the anode.
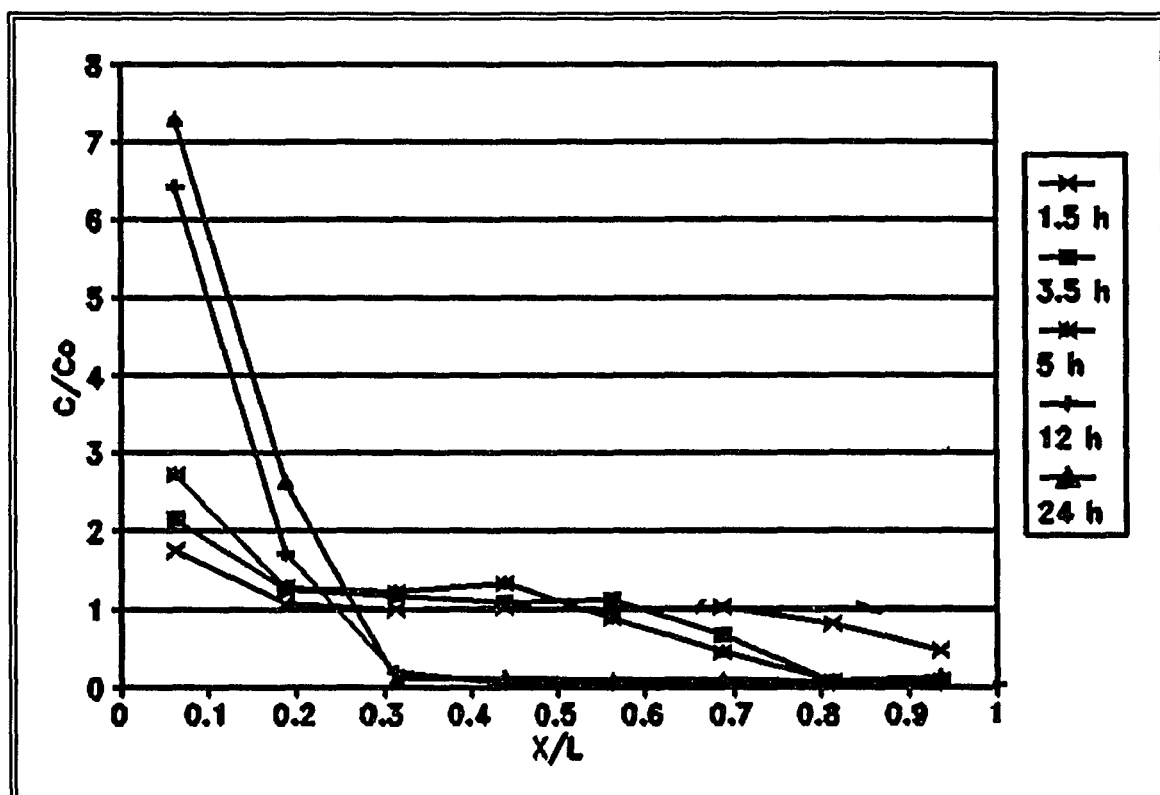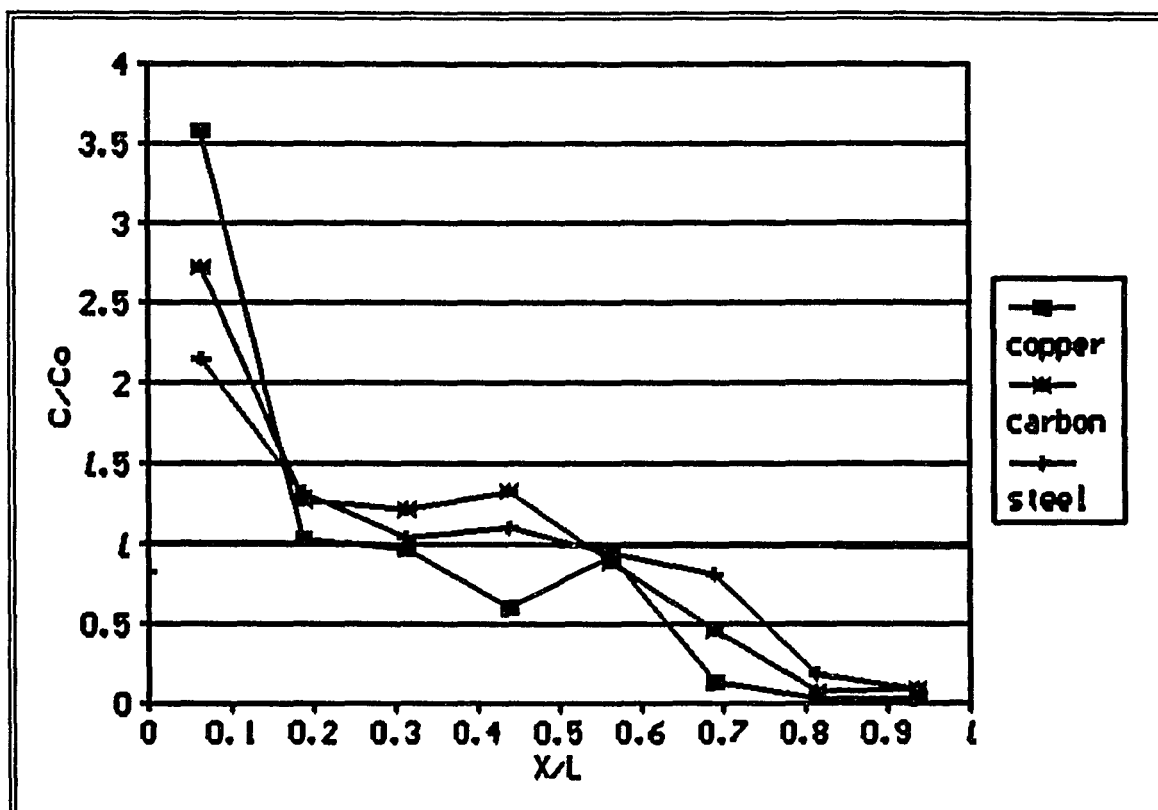
Figure 4.12 . Nitrate concentration (C/Co) developed after 5 hours of 5 mA electrical input with copper, carbon, and steel electrodes and initial sodium nitrate concentration of 85 ppm.

The pH gradient developed with the copper electrodes showed an acidic environment along the whole length of the column. Copper electrodes are characterized by their high hydrogen over voltage, thus lower pH levels were obtained along the length of the column with copper than with carbon electrodes.

4.1.3.4 Electrode Spacing

Figure 4.14 shows the nitrate gradients with carbon electrodes which were established with two different electrode spacing(14 cm, 25 cm). A relatively slow nitrate
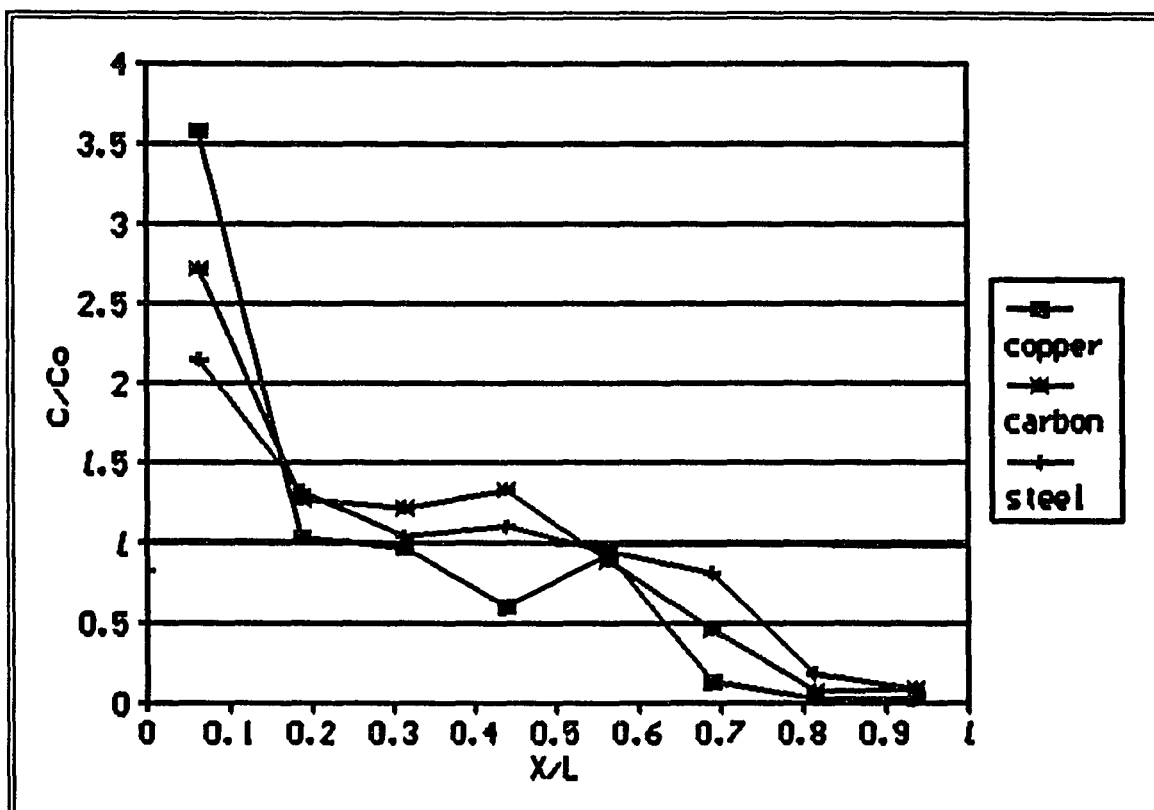
Figure 4.13 . pH gradients developed after 5 hours of 5 mA 3 mA electrical input with copper, carbon, and steel electrodes and initial pH level of 8.0.

migration rate was observed for the 25 cm electrode spacing. More rapid movement of nitrate occurred with the 14 cm electrode spacing. Differences in the rate of movement are basically attributed to the principle that with a shorter spacing between electrodes, the higher the strength of the electrical potential and the shorter the distance each ion has to travel to reach its respective opposite electrode.

Figure 4.15 shows the pH gradients developed with two different electrode spacing. The results shown in Figure 4.15 confirm the previous observation that the pH levels near the cathode and along the length of the column are highly dependent on
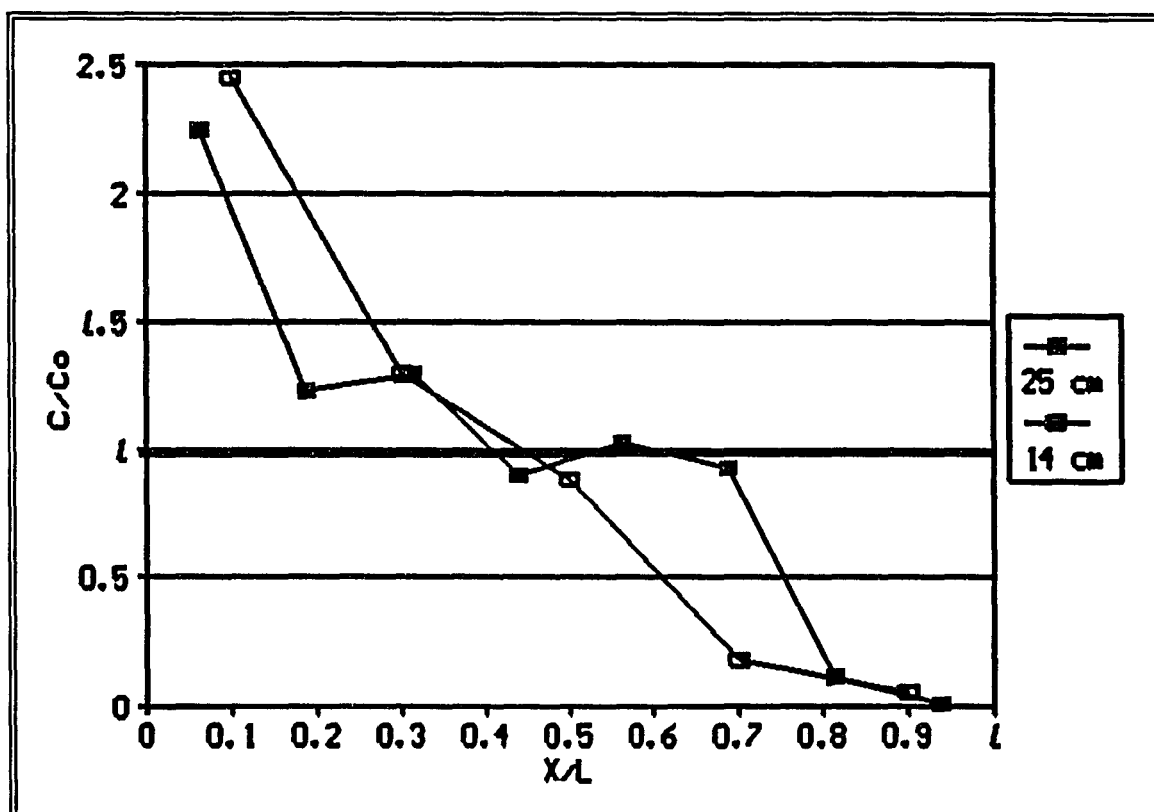
Figure 4.14 . Nitrate concentration (C/Co) developed after 12 hours 1.5 mA electrical inputs for two different column lengths, 14 cm and 25 cm, with carbon electrodes and initial sodium nitrate concentrations of 85 ppm.

nitrate movement. In the 14 cm electrode spacing experiment, nitrate movement towards the anode apparently also affected pH; as a result the basic front advanced faster than the acid front. In the 25 cm electrode spacing experiment, NO_3^- moved slowly and the acid and base fronts advanced to their respective opposite electrodes in similar ways.

4.1.3.5 Initial Concentration

The initial concentration of the sodium nitrate solution seemed to have a direct effect on the movement of NO_3^- under an electrical potential. Figures 4.16 shows the
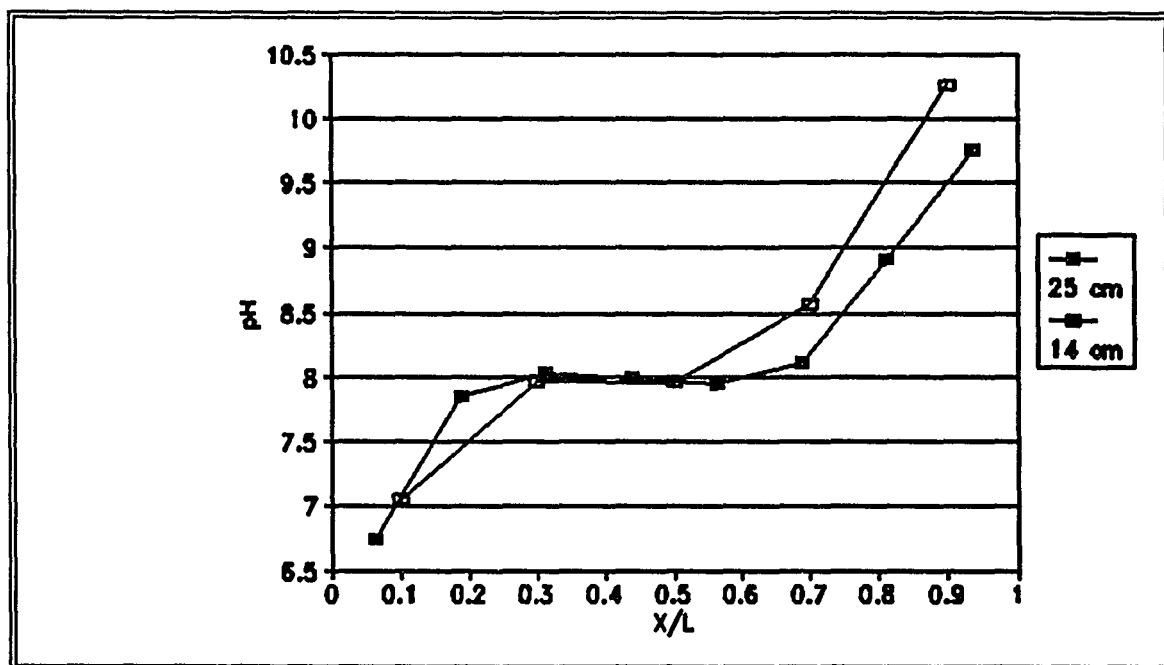
Figure 4.15 . pH gradients developed after 12 hours of 1.5 mA electrical input for two different column lengths, 14 cm and 25 cm, with carbon electrodes and initial pH level of 8.0.

No_3^- gradients which developed with a 1.5 mA current for two different initial concentrations of sodium nitrate solution (62 ppm and 440 ppm). It is clear that nitrate movement was greater in the 62 ppm initial concentration experiment than in the 440 ppm test. The lower the initial concentration of the solution, the farther apart the ions are and the less the opportunity of the ions to be held back by ions of opposite charge which they tend to drag along. Also, increasing the initial concentration increases the back diffusion which acts against migration.

Figure 4.17 shows the pH gradients for two different initial concentration solutions developed with a 1.5 mA electrical current. The acidic front advance was
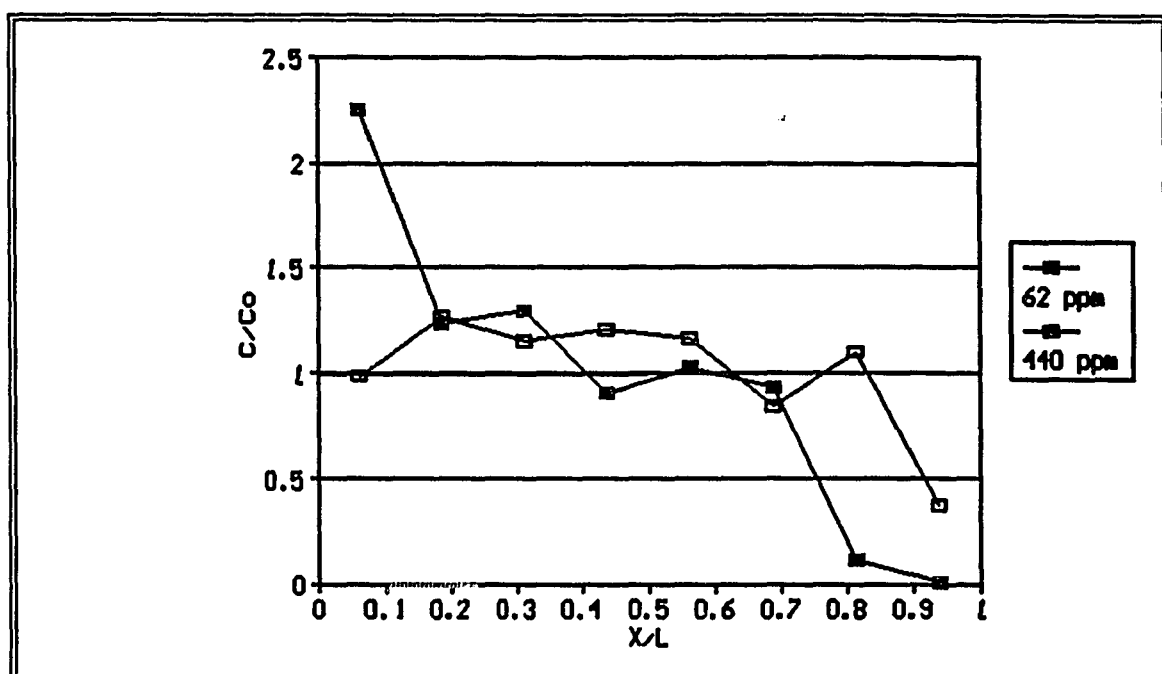
Figure 4.16 . Nitrate concentration (C/Co) developed after 12 hours of 1.5 mA electrical input with carbon electrodes and initial nitrate concentrations of 62 and 440 ppm.

greater than the basic front advance in the 440 ppm initial concentration experiment.

The slow response of NO_3^- to the imposed electrical current in the 440 ppm initial condition experiment may have allowed the acidic front , generated at the anode, to advance towards the cathode with almost no retardation. In the 62 ppm initial concentration tests, a basic environment was established near the cathode. On the other hand, no change in the acid front was observed, perhaps because, H^+ movement towards the cathode was retarded by the movement of NO_3^- to the anode.
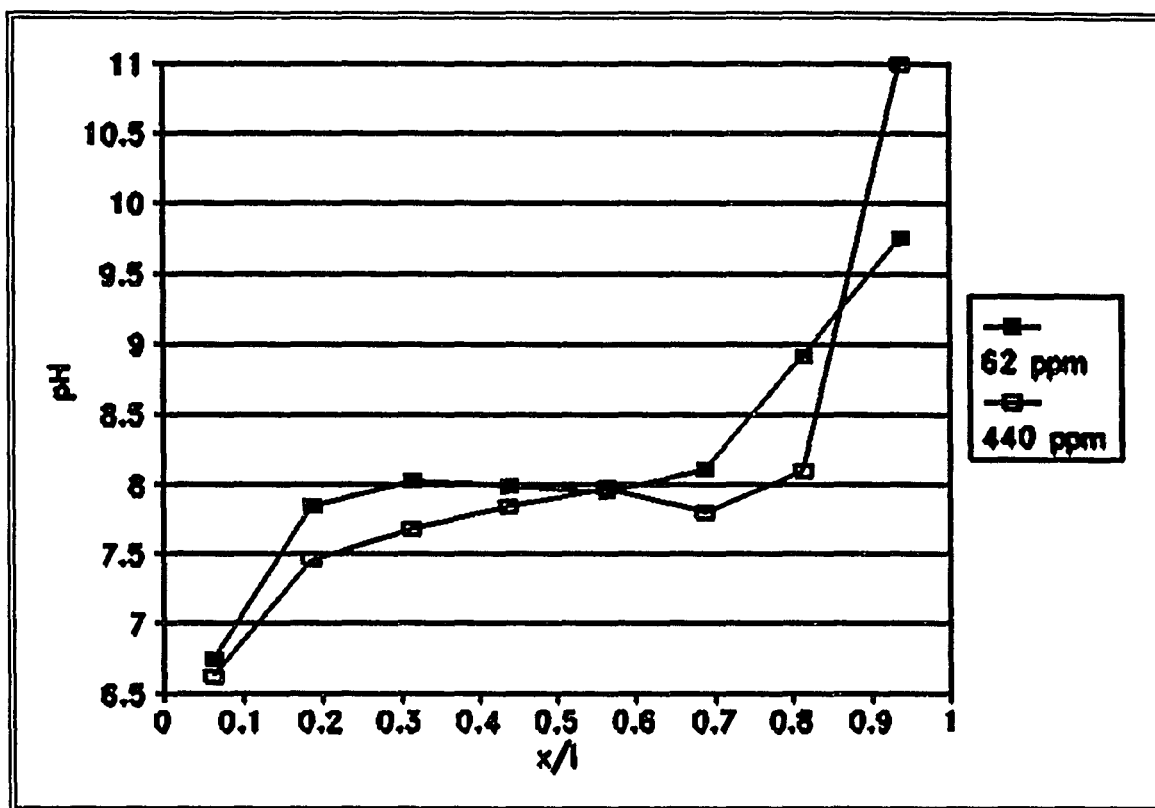
Figure 4.17 . The pH gradients developed after 12 hours of 1.5 mA electrical input with carbon electrodes and initial nitrate concentrations of 62 ppm and 440 ppm.

4.2 OPEN SYSTEM

The closed system experiments were utilized to study the electromigration of nitrate under an imposed electrical potential in a closed column. In the open system experiments, a preset constant hydraulic flow was input to the porous media.

The objectives of the open system experiments were:

1. To study the effect of hydraulic flow super-imposed on electro-migration.

2. To determine the limiting hydraulic velocity above which elecromigration effects were negated by hydraulic flow.

Six laboratory experiments were conducted in which the effects of an electrical potential were tested with four different hydraulic flow rates, two salt concentration levels, and two electrical current levels. In all experiments, coarse silica sand was used as an inert porous media and sodium nitrate as the salt in the interstitial solution. Test durations, current levels, hydraulic flow velocities, and the initial solute concentration in the experiments are presented in Table 4.2.

Table 4.2. Summary of the Open System Experiment Parameters

Test #	Current (mA)	Velocity (cm/hour)	Duration (hours)	Initial Con.(ppm)
1	3	9.5	12	85
2	3	17.3	12	85
3	3	32.3	12	85
4	3	70.3	12	85
5	6	17.3	12	85
6	3	17.3	12	170

4.2.1 Mass Balance

A mass balance calculation was made to determine the chemical recovery for each experiment. The mass balance calculation took into account the salt input with hydraulic flow, the salt output with hydraulic flow, the initial salt input to the soil column at the

beginning of the tests, and the amount of the salt present in the soil column at the end of the tests as follows:

$$S_i = S_p + S_{ih} \qquad (4.6)$$

where S_i is the amount of salt input during a test, S_p is the amount of salt initially present in the system, and S_{ih} is the amount of salt introduced with hydraulic flow. S_i was calculated as :

$$S_{ih} = \frac{C_o * t * V_x * A}{1000} \qquad (4.7)$$

where C_o is the initial solute concentration (the concentration of the solution in the Marriot Bottle) in mg/l, t is test duration in hours, V_x is the hydraulic flow velocity in cm/hr, and A is the cross sectional area of the column in cm^2.

The output amount of salt was calculated as :

$$S_o = S_R + S_{oh} \qquad (4.8)$$

where S_o is the output amount of salt in mg/l, S_R is the amount of salt present in the column at the end of a test, and S_{oh} is the amount of salt exiting the system with the hydraulic flow. S_{oh} was calculated as :

$$S_{oh} = \frac{C_{out}*t*v_x*A}{1000} \qquad (4.9)$$

where C_{out} is the measured outflow salt concentration.

The amount of salt present at the end of a test was calculated as :

$$S_R = \sum S_{Ri} = \sum \frac{V_i C_i}{1000} \qquad (4.10)$$

where S_R is the calculated total amount of sodium or nitrate present in the column at the end of a test (mg), S_{Ri} is the amount of sodium or nitrate in segment i (mg), C_i is the measured concentration in this segment (mg/l), and V_i is the volume of fluid in segment i calculated as:

$$V_i = L_i * A * n \qquad (4.11)$$

where L_i is the length of the segment (cm), and n is the porosity.

The percent recovery for each experiment was calculated as:

$$R = \frac{S_o}{S_i} * 100 \qquad (4.12)$$

Satisfactory mass balance results were obtained for all experiments. Results of the mass balance calculations are presented in Appendix A.

4.2.2 Chemical Gradients for NO_3^-, Na^+, and pH

Analysis of the interstitial solutions found a tendency for nitrate to move towards the anode with all test hydraulic flow velocity levels. Although the sand had a very high hydraulic conductivity and applied hydraulic flow was in the direction opposing the direction of NO_3^- migration, it is clear from test results that a nitrate concentration gradient was established as a direct response to the imposed electrical potential. Nitrate movement and accumulation appeared to be highly dependent on the applied hydraulic flow velocity. Results also showed that sodium did not respond to the imposed electrical potential even though the direction of the hydraulic flow was in the same direction as of Na^- migration. Only a slight increase in the Na^+ concentration was observed near the cathode for all the hydraulic flow velocity levels. The pH level varied from high values near the cathode to low values near the anode. The pH gradient appeared to be dependent on the rate of hydraulic flow.

4.2.2.1 NO_3^- Gradient

Figure 4.18 shows the relative concentration gradients for NO_3^- which were developed under the influence of an introduced electrical potential(current = 3 mA) and hydraulic potential (V_x=9.5 cm/hr.) for three different test durations (4 hrs., 8 hrs.,and 12 hrs.). The direction of the introduced hydraulic flow was from the anode to the cathode. Figure 4.18 shows relatively limited movement of nitrate towards the anode. The relative NO_3^- concentration dropped to 0.8 near the cathode after the 4 hour and 8 hour test durations, then to 0.75 after 12 hours. On the other hand, the relative
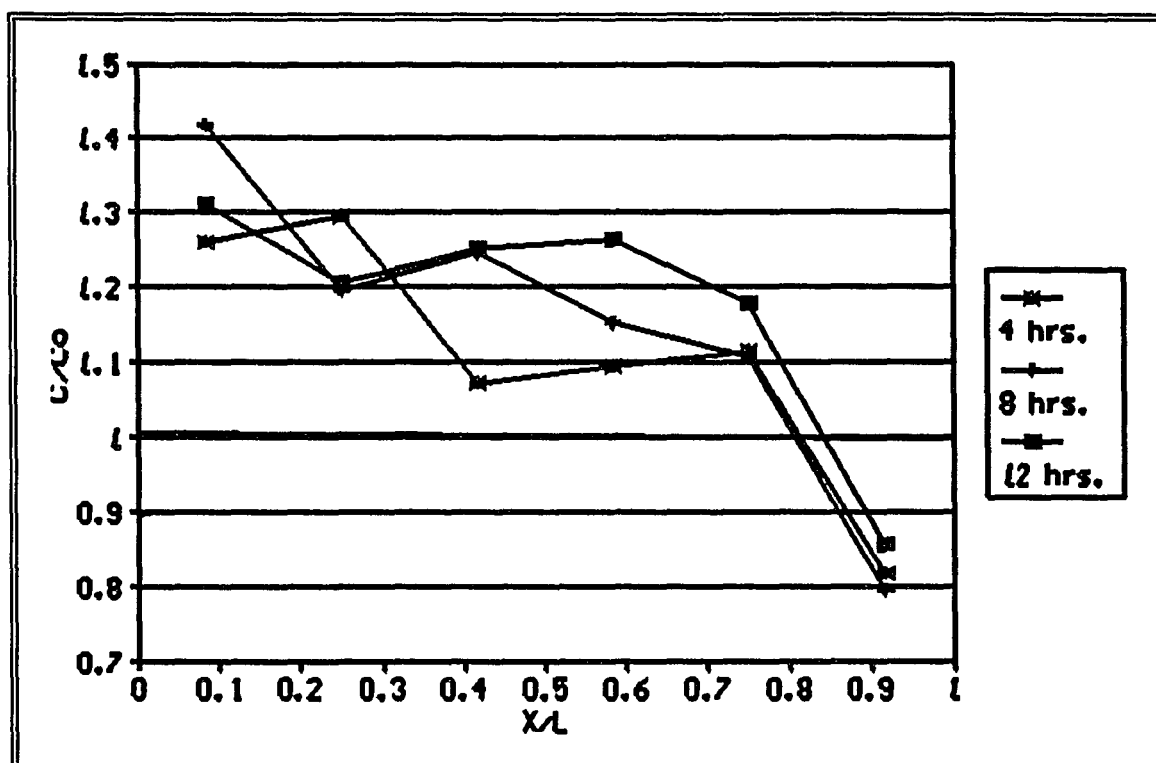
Figure 4.18 . Nitrate concentration (c/c₀) developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 9.5 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

concentration throughout the rest of the column was higher than the initial concentration (with the highest value at the anode end) for measurements made after all test durations. At a given test duration, NO_3^- concentration increased with the distance from the cathode. At a given location, the nitrate level appeared to continue to increase with time (except at the anode end). The relative nitrate concentration near the anode increased to 1.25 and 1.4 with the 4 and 8 hour test durations, respectively, then decreased to 1.3 with the 12 hour test duration. Salt was input continuously during the test. It appears from the results presented in Figure 4.17 that the amount of the salt introduced to the column

during the 12 hour test duration was so high that the electrical potential was no longer able to retain it against the hydraulic flow. As a result, some nitrate which had accumulated near the anode was lost and the nitrate concentration was lower after the 12 hour test than after an 8 hour test duration. Nitrate concentration at the cathode end was higher for the 12 than the 8 hour test duration.

The overall gradients of NO_3^- reflected the resistance to nitrate migration (electrical flow) caused by hydraulic flow. The results also indicated that at a relatively low hydraulic velocity, the electrical current overcame the hydraulic velocity and nitrate concentration in the column increased with time.

Figure 4.19 shows the relative concentration gradients for NO_3. which were established with a 32 cm/hour hydraulic flow velocity for three different test durations (4 hrs., 8 hrs., and 12 hrs.). A comparison with Figure 4.18 clearly shows the migration of nitrate towards the anode and the amount of NO_3^- held in the column depend on the hydraulic flow velocity. The NO_3^- concentration varied from 1.16 to 1.2 at the anode end to 0.85 to 0.95 at the cathode end of the column. Only a small difference in NO_3^- concentration between the cathode and anode ends was observed among the three test durations. Having nearly the same concentration gradients after all the time intervals indicates little additional nitrate was held in the column beyond 4 hours. The output concentrations for the 8 and 12 hours test durations were slightly less than the input concentration. At this hydraulic flow velocity it appears that the electrical potential was not able to retain additional nitrate after 4 hours.

Results shown in Figures 4.18 and 4.19 indicate a relationship of nitrate accumulation and migration to the hydraulic flow velocity. The lower the hydraulic velocity, the greater the amount of NO_3^- retained by the electrical potential.

The concentration gradients which were developed with 17 cm/hour and 72 cm/hour flows are shown in Appendix B (Figs. B1-B2). Mass balance calculations showed a relatively low percent NO_3^- recovery for the 8 and 12 hour test durations of the 17 cm/hour flow rate experiment (experiment # 2) and the 8 hour test duration for the 72 cm/hour experiment(experiment # 4). The concentration gradients in these figures differ from those shown in Figure 4.18. It hypothesized the difference is due to errors in analysis of interstitial solution concentration for these experiments.

The results shown in Figures 4.18 - 4.19 and Figures B1-B2 indicate the possibility of using an electrical potential in the presence of hydraulic flow to reduce the amount of nitrate leaving the system. The open system experiments were conducted with a coarse sand test media. Based on the previous results, the electro-kinetic process is expected to produce more favorable results with finer soils.

4.2.2.2 pH Gradient

Figure 4.20 illustrates the pH gradients developed under a 9.5 cm/hour hydraulic flow velocity with 3 mA electrical current for three different test durations. The pH
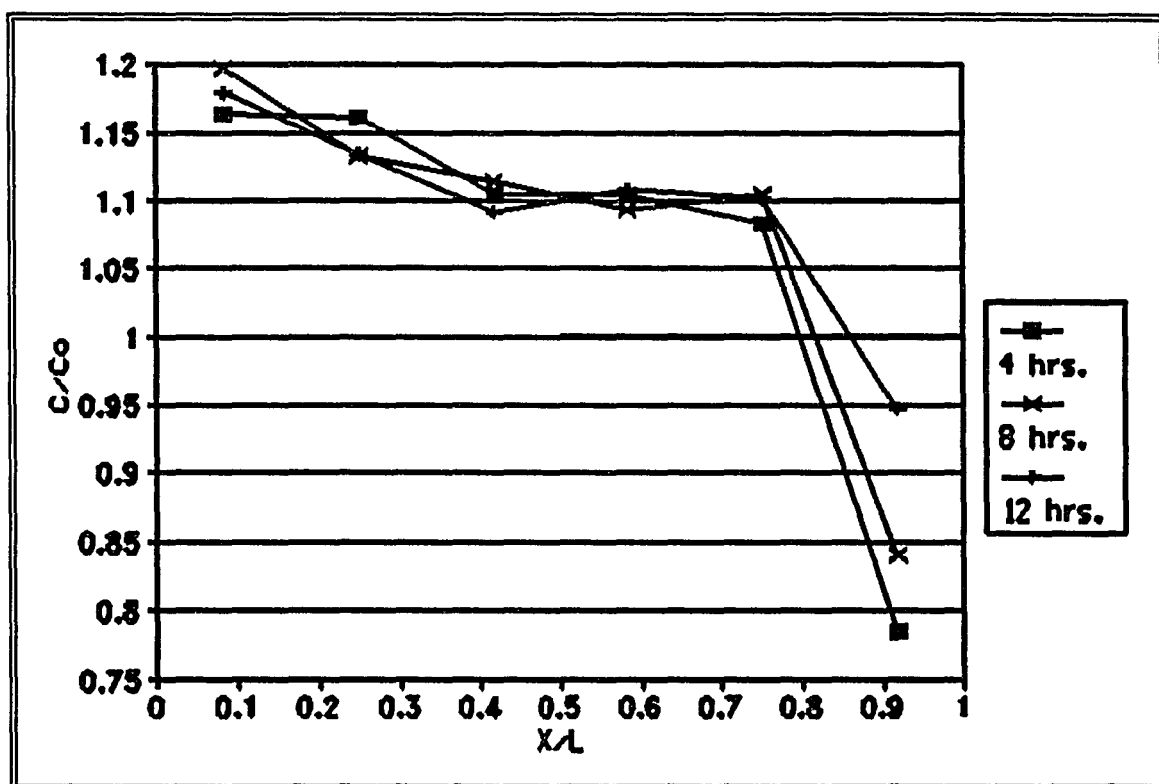
Figure 4.19 . Nitrate concentration (c/c₀) developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 32 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

gradients shown in Figure 4.20 show a higher pH value at the cathode end (pH = 9.5) and a lower pH value the anode end (pH = 3.5) for all the test durations. The difference in the pH values at the boundaries is believed to be a direct result of the electrolysis process by which H^+ and OH^- were generated at the anode and cathode respectively. The generated H^+ and OH^- appeared to be advancing to their respective opposite electrodes by both migration and diffusion. Results shown in Figure 4.20 indicate that, for this relatively low flow velocity, H^+ and OH^- were advancing at almost the same rate (the hydraulic flow seemed not to be dragging H^+ to the cathode).

Figure 4.20 . pH gradients developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 9.5 cm/hr with carbon electrodes and initial pH level of 7.00.

Figure 4.21 shows the pH gradients which were established in experiment #3 (v_x = 32 cm/hour). Increasing the hydraulic flow velocity from 9.5 cm/hour (Fig. 4.20) to 32 cm/hour appeared to yield greater movement of H^+ to the cathode. Greater H^+ movement probably explains the resulting acidic environment along the length of the column (except at the cathode). The pH value was higher for the 4 and 8 hour test durations than after the 12 hour test. As the duration of the test increased, more H^+ and OH^- were generated by electrolysis at the anode and cathode respectively. According to
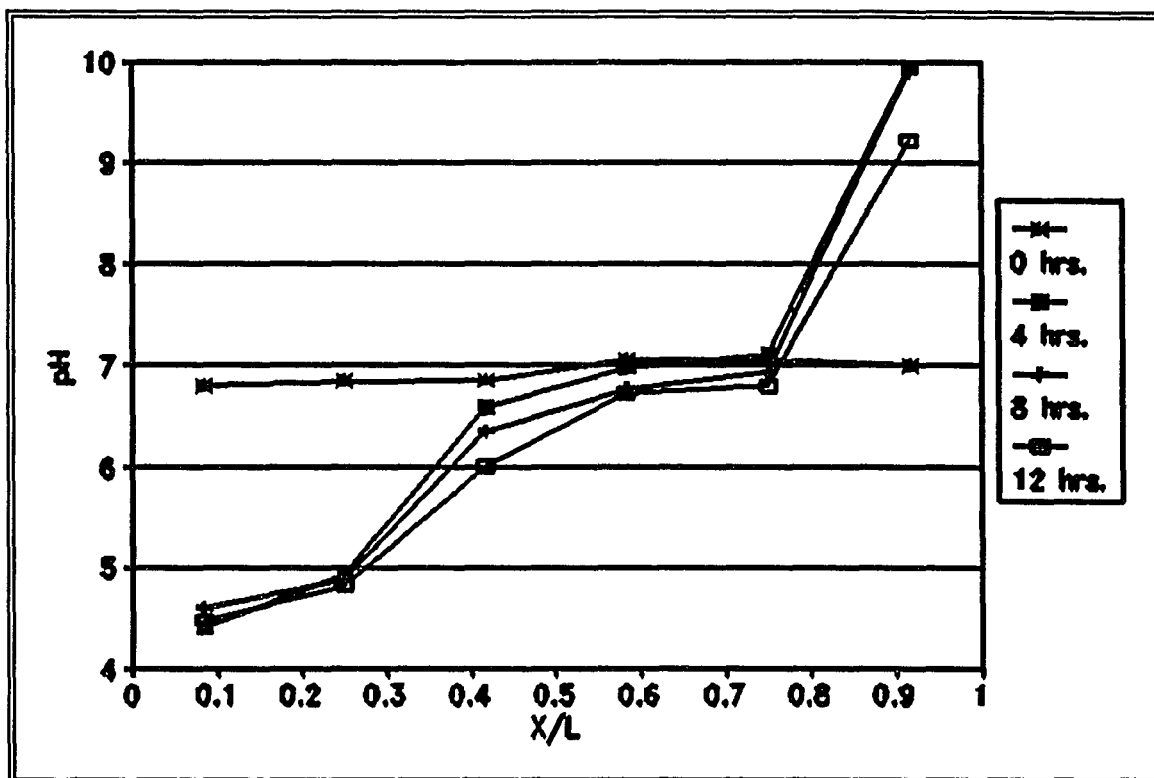
Figure 4.21 . pH gradients developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 32 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

Equations 2.1 and 2.2, twice as much H^+ as OH^- is generated for the same amount of electricity. The acidic front generated at the anode advanced towards the cathode much faster than OH^- until it appeared to reach the cathode after 12 hours test duration, neutralizing the basic condition and lowering the pH at the cathode.

pH gradients similar to those presented in Figures 4.20 and 4.21 are shown in Appendix B(Figs. B3-B4). The results presented in Figures 4.20 - 4.21 and Figures B3-B4 reveal the relationship of the pH gradient along the length of the specimen to the hydraulic flow velocity. The higher the velocity, the longer the distance that the acidic

environment extended along the column length.

4.2.2.3 Na$^+$ Gradient

Figure 4.22 shows the relative concentration gradients for Na$^+$ which were developed under the influence of an introduced electrical potential(current = 3 mA) and hydraulic potential (v_x = 9.5 cm/hour) for three different test durations. The direction of the hydraulic flow (from anode to cathode) was the same as Na$^+$ electromigration, but results revealed little tendency for Na$^+$ to move towards the cathode as a direct response to the imposed electrical potential. Almost no difference in the Na$^+$ concentration gradients was observed along the column between the cathode and anode, though a slight decrease and increase were observed at the anode and cathode respectively. The Na$^+$ concentration near the anode also seemed to be decreasing with time. The relative concentration at the cathode increased to 1.6 for the 4 hour test duration and then decreased to 1.4 and 1.18 for the 8 and 12 hour test durations, respectively. It could be concluded that the basic environment which was established near the cathode did not favor sodium solubility. As a result, Na$^-$ may have precipitated on the sand surface rather than remaining in solution. Also, salt was being continuously introduced to the system. Since Na$^+$ has a lower ionic mobility and transference number than the other ions (No$_3^-$, OH$^-$, and H$^+$), less current was carried by Na$^-$. As a result, Na$^-$ concentration near the cathode decreased with time The concentration gradients for Na$^+$ which were developed under 17 , 32, and 72 cm/hour hydraulic flow velocities are shown in Appendix B (Figs. B5-B7). All these figures show the same behavior for Na$^+$:
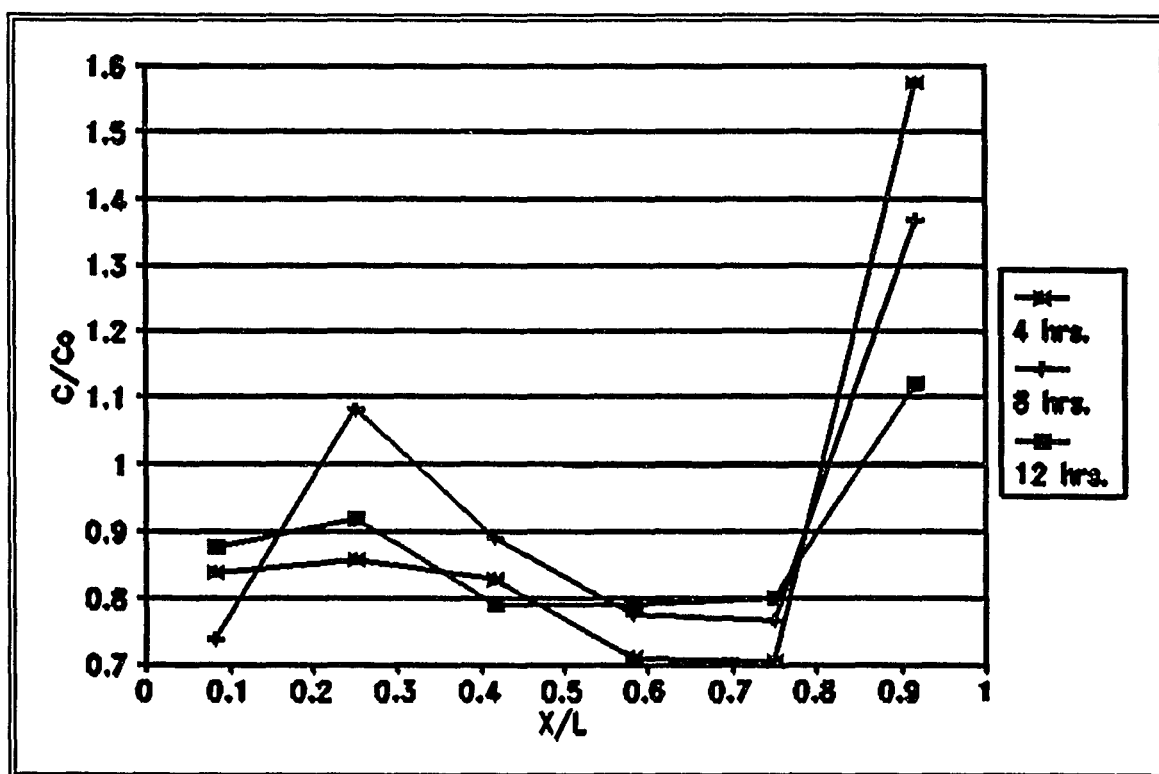
Figure 4.22 . Sodium concentration (c/c$_o$) developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 9.5 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

the Na$^+$ gradient was dependent on the hydraulic flow velocity. For the same test duration, the higher the hydraulic flow velocity, the lower the resulting Na$^+$ concentration near the cathode. Increasing the flow velocity resulted in a faster advance of H$^+$ towards the cathode and longer acidic environment over a greater length of the column. H$^+$ has very high ionic mobility that may have caused a decrease in the transference number of Na$^+$ near the cathode, resulting in a reduction in the contribution of Na$^+$ to the total effective conductivity .

4.2.3 Effect Of Variables

4.2.3.1 Hydraulic Flow Velocity

Figure 4.23 shows the NO_3^- gradients which were developed over 4 hours test duration with four different hydraulic flow velocity values(9.5 cm/hr., 17 cm/hr., 32 cm/hr, and 72 cm/hr.). The movement and accumulation of nitrate appears highly dependent on the hydraulic velocity. The lower the hydraulic velocity, the faster the movement of NO_{3-} and the higher the concentration near the anode after application of an electrical potential. The 9.5 cm/hour hydraulic velocity appeared to be low enough that the electrical potential was able to hold nitrate close to the anode. As the flow velocity increased to 17 cm/h, the hydraulic influence on NO_3^- movement increased. As a result, nitrate concentration dropped at the anode end and NO_{3-} appeared to be distributed over a longer column distance. Increasing the hydraulic velocity to 32 cm/h yielded a lower nitrate concentration gradient along the whole length of the specimen. As the hydraulic flow velocity was increased to 72 cm/hour, a slight increase in the nitrate concentration from the initial concentration ($C/C_o = 1.05$) was observed along the whole length of the column (except at the cathode).

It appears from these results that hydraulic flow was countering the migration of NO_{3-} towards the anode. For the same electrical potential, the greater the hydraulic velocity, the lower the ability of the electrical potential to hold nitrate. Based on the results shown in Figure 4.23, it appears there is a certain hydraulic flow velocity at which the electrical potential is equivalent to the introduced hydraulic potential and the
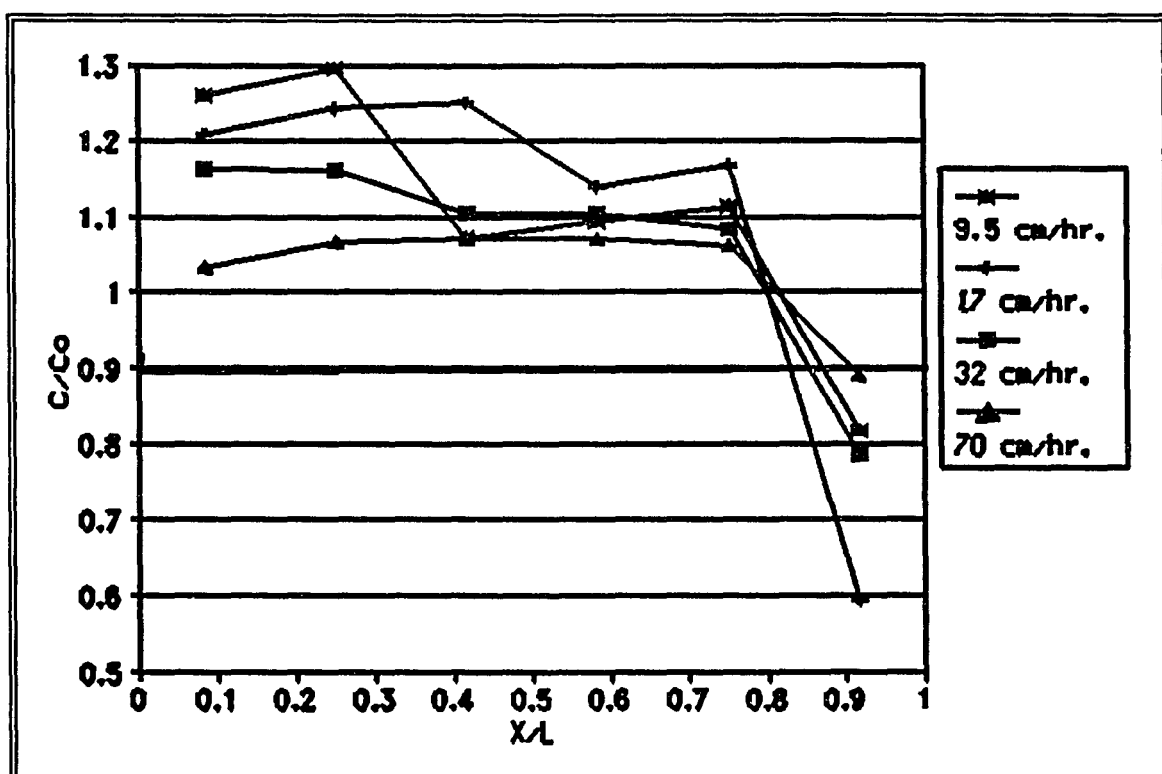
Figure 4.23 . Nitrate concentration (c/c$_o$) developed after 4 hrs. of 3 mA Dc current in the presence of different hydraulic flow velocity, 9.5, 17, 32, and 70 cm/hr, with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

initial condition of No$_3$. would be maintained along the whole length of the column.

Figure 4.24 shows the pH gradients which were developed under four different hydraulic flow velocities (9.5 cm/hr., 17 cm/hr, 32 cm/hr, and 72 cm/hr.). These results indicate the dependency of pH gradient along the length of the column to the hydraulic flow velocity. The pH at the anode increased with increased velocity level. The pH at the anode increased from 3.6 (with the 9.5 cm/h. flow velocity) to 4.4 and 6.2 with the 17 and 72 cm/h flow velocities, respectively. For given test duration, the amounts of H^+ and OH^- generated at the boundaries were the same for all velocity levels.
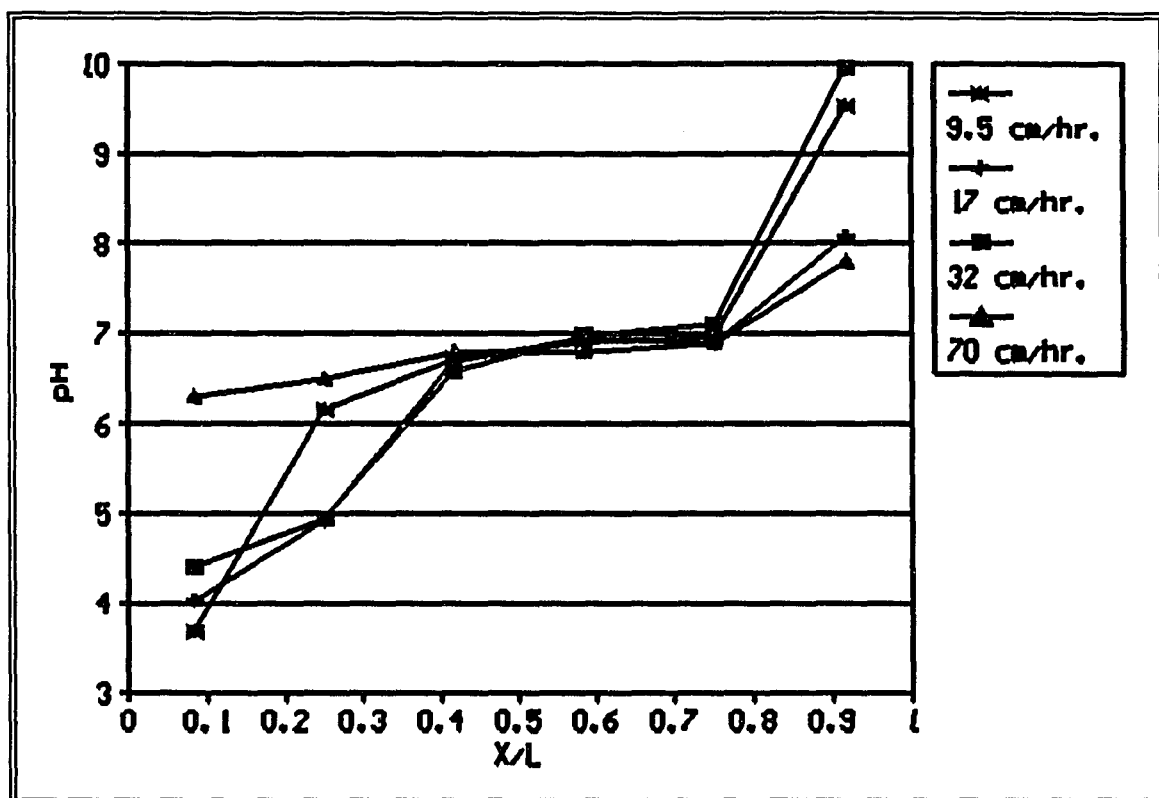
Figure 4.24   pH gradients developed after 4 hours of 3 mA electrical input in the presence of different hydraulic flow velocity, 9.5, 17, 32, and 70 cm/hr, with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

The generated H^+ and OH^- advance to their respective opposite electrodes by transport mechanisms which include migration caused by electrical gradient, pore fluid advection caused by hydraulic potential, and diffusion caused by generated chemical gradients. Since the introduced hydraulic flow was in the same direction as H^+ movement, the hydraulic flow appeared to be dragging H^+ toward the cathode. Increased movement with increased hydraulic velocity could explain the increase in pH at the anode.

The pH at the cathode was higher for both the 9.5 cm/hour and 17 cm/hour flow test than in the test with 72 cm/hour flow. As the hydraulic velocity increases, H^+ may

advance to the cathode faster. The acidic front generated at the anode seemed to be reaching the cathode in the 72 cm/hour velocity test, neutralizing the basic condition at the cathode and lowering the pH at the cathode.

The overall pH levels indicate acidic environment along a greater length of the column with higher velocity levels.

4.2.3.2 Current Level

Figure 4.25 shows the nitrate gradients which were developed under 17 cm/hour hydraulic flow for two different current level(3 mA and 6 mA). The higher nitrate gradient was obtained with the 3 mA current level, a result which did not agreed with expectation. The behavior of NO_3^- under the two current levels might be better understood by examining the pH gradients developed under both current levels (Fig. 4.26). Lower pH values were observed along the whole length of the column for the 6 mA test. These results indicated a much greater amount of H^+ was generated with the 6 mA so the transference number of H^+ was dominating. The H^+ generated at the anode advanced towards the cathode by transport mechanisms including migration caused by electrical gradient, pore fluid advection caused by the external hydraulic potential, and diffusion caused by generated chemical gradients. The mass transport of H^+ seemed to be countering the NO_3^- migration towards the anode. As a result, a lower NO_3^- concentration gradient was established for the 6 mA current level than with the 3 mA input.
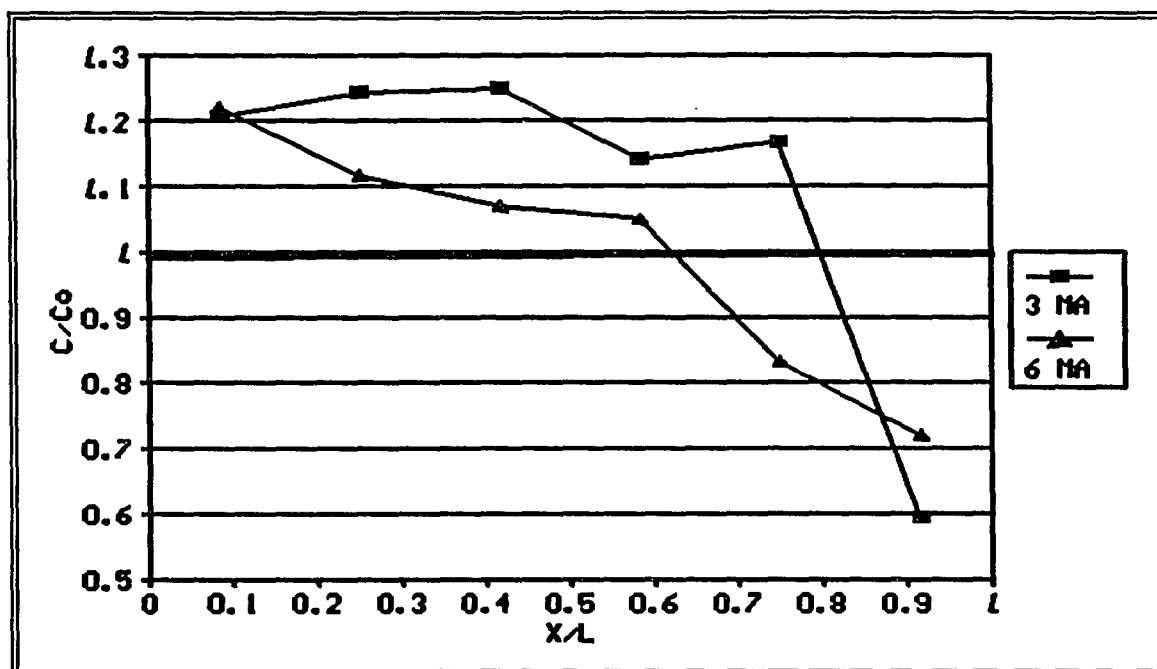
Figure 4.25 Nitrate concentration (c/c₀) developed after 4 hrs. of 3 mA and 6 mA DC current in the presence of hydraulic flow velocity of 17 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
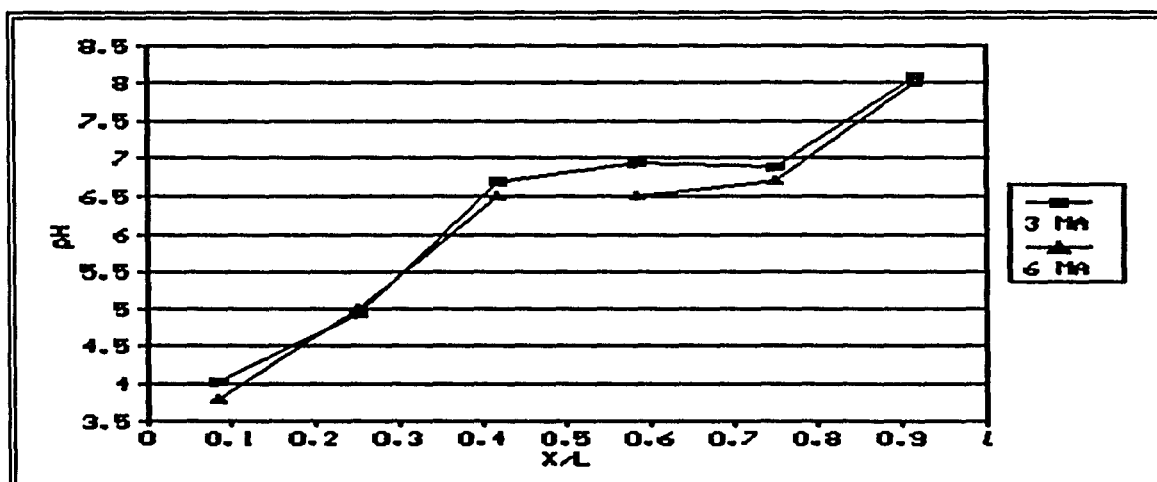
Figure 4.26 . The pH gradients developed after 4 hrs. of 3 mA and 6 mA DC current in the presence of hydraulic flow velocity of 17 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

4.2.3.3 Initial Concentration

The initial concentration of sodium nitrate solution seemed to have a direct effect on the movement of NO_3^- under an electrical potential. Figure 4.27 shows the NO_3^- gradients which were developed with a 3 mA current and 17 cm/hour hydraulic flow for two different initial concentrations of sodium nitrate (62 ppm and 130 ppm). It is clear from the figure that nitrate movement was greater in the 62 ppm initial concentration experiment (experiment # 6) than in the 130 ppm test. The difference in movement between the two experiments is attributed to the initial concentration of the solution, since the farther apart the ions, the lower the opportunity for the ions to be held back by ions of opposite charge. Increasing the initial concentration likely also resulted in an increase in opposing diffusion which acts against migration.

Figure 4.28 shows the pH gradients for two different initial sodium nitrate concentrations. The acidic front advance was greater for the 130 ppm experiment than in the 62 ppm test. The reduced response of NO_3^- to the imposed electrical current in the 130 ppm initial condition experiment may have allowed the acidic front, generated at the anode, to advance faster towards the cathode (less retardation from NO_3^-).
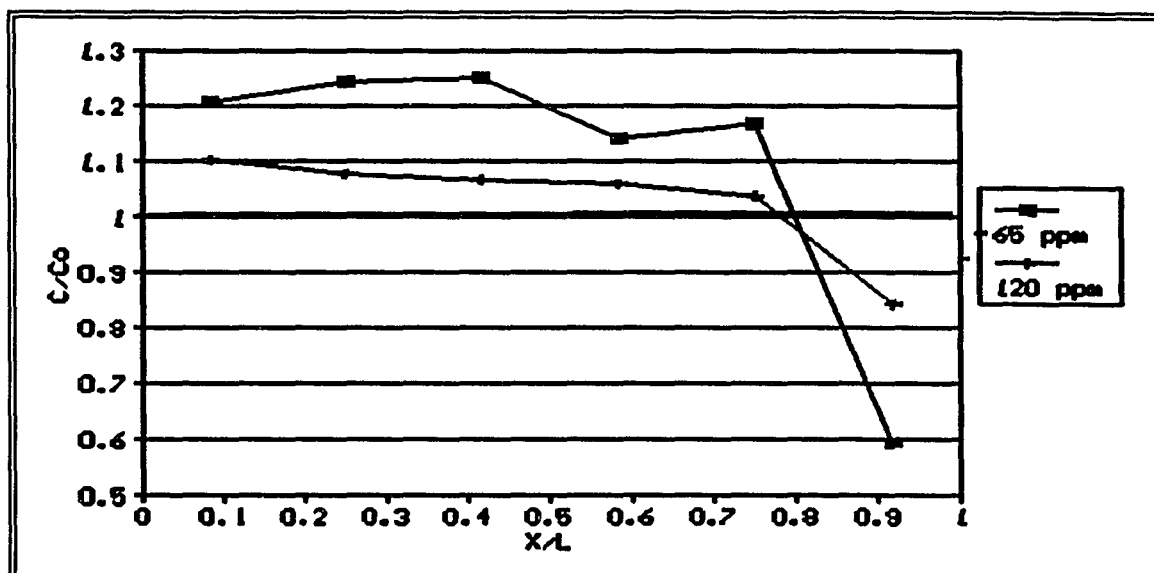
Figure 4.27 . Nitrate concentration (c/c_o) developed after 4 hrs. of 3 mA electrical input in the presence of a hydraulic flow velocity of 17 cm/hr with carbon electrodes and two initial sodium nitrate concentrations of 85 and 170 ppm.
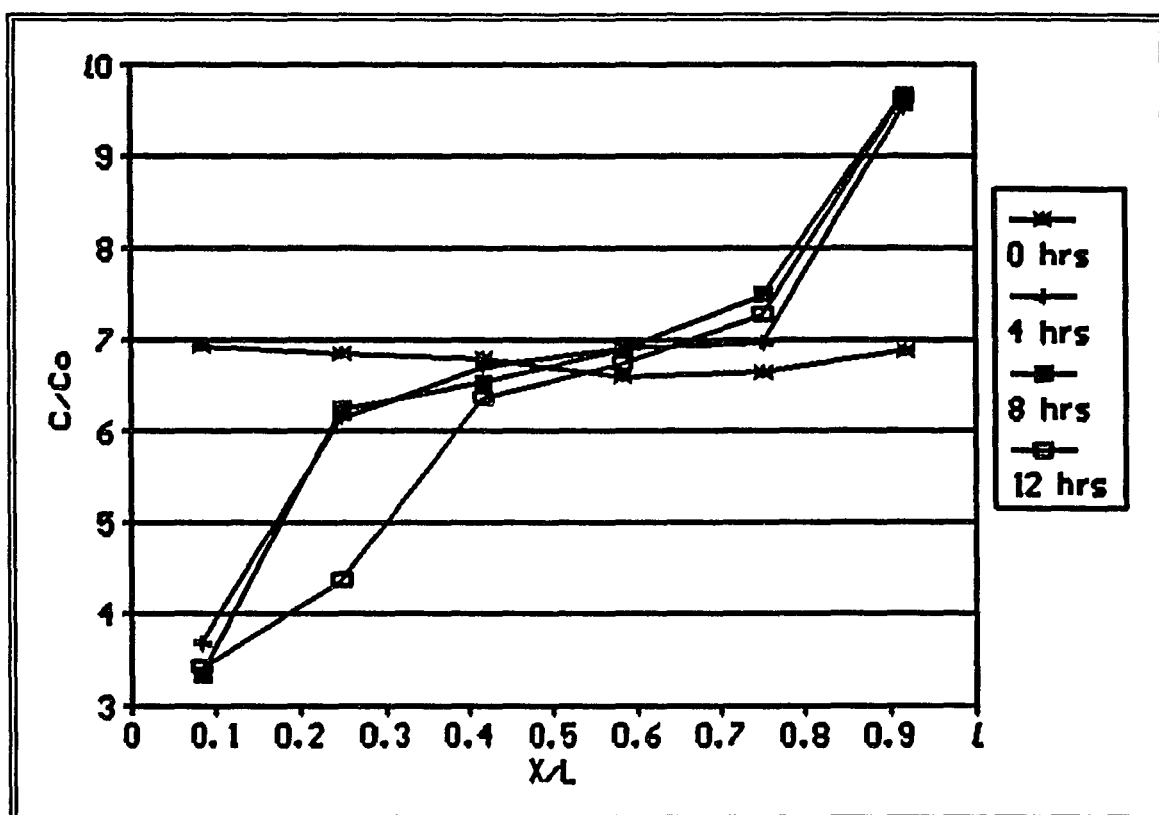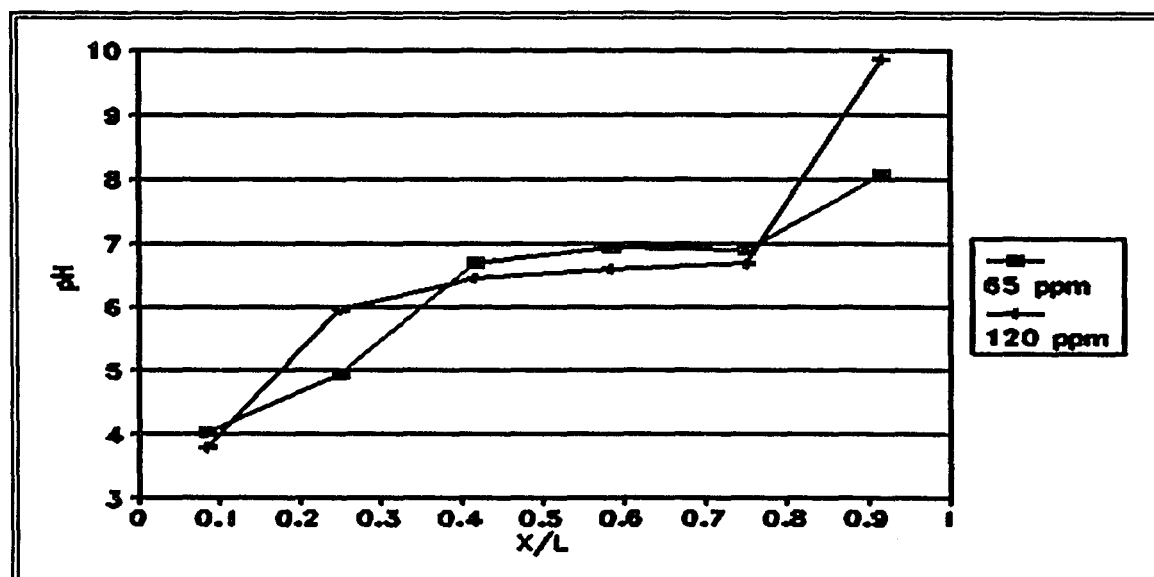

Figure 4.28 . The pH gradients developed after 4 hrs. of 3 mA electrical input in the presence of a hydraulic flow velocity of 17 cm/hr with carbon electrodes and initial sodium nitrate concentrations of 85 and 170 ppm.

4.3 Predicting the Hydraulic Velocity Below which the Electrical Effects can be Detected

One of the main goals of the open system experiments was to determine the hydraulic velocity below which the electrical effects could be obtained. Results previously discussed indicated that the ability of the electrical current to retain or concentrate nitrate around the anode was highly dependent on the hydraulic flow velocity. The ability of the electrical current to hold nitrate appeared to decrease with an increase in the hydraulic velocity.

It is clear from the results shown in Figure 2.23 that there is a hydraulic flow rate at which the electrical current is equivalent to the introduced hydraulic velocity. Above this point, the electrical current is overpowered by the hydraulic flow and is ineffective in retaining or moving nitrates.

To predict the point at which the hydraulic velocity and electrical current effects are equivalent, NO_3^- gradients developed in tests with different test duration and hydraulic velocity levels were redrawn with a new Y axis coordinate origin representing the initial concentration (C_o). The area under each curve was then calculated. This area represents the effect of the electrical current imposed on the hydraulic flow for given duration and given hydraulic velocity levels.

Figure 4.29 shows the relationship between the calculated area under the curve, developed for 3 mA electrical current tests, and hydraulic flow velocity for two different test durations (4 hours and 8 hours). The area under each curve, reflecting the change

in the NO_3^- concentration from the initial concentration, decreased with an increase in the hydraulic velocity level. Thus as the hydraulic flow increases, the ability of the electrical current to hold NO_3^- against the hydraulic flow decreases.

Several equations were tested to obtain an equation that best fit each set of data (power, exponentional, linear, and gaussian). A linear equation was found to best fit the data; the correlation coefficients for data from 4 and 8 hours duration tests were found to be 0.93 and 0.95 respectively. The intersection of each regression line with the X-axis determines the velocity level at which equilibrium of electromigration and hydraulic flow is predicted. These velocity levels were found to be 97.3 cm/hour and 105 cm/hour for the 4 and 8 hours tests duration, respectively(see Fig. 4.29).

Results shown in Figure 4.29 indicate that introducing a hydraulic flow with velocity of 97 cm/hour would exactly cancel the effects of an electrical current of 3 mA in a four hour test. Also, hydraulic flow with a velocity of 105 cm/hour would offset the effect of an electrical current of 3 mA in an 8 hour duration test . So, equivalent electrical current could

be used in place of hydraulic velocity in fields where shortage in water supplies are presented.

4.4 Model Results

The applicability of electro-kinetic methods to concentrating nitrate close to the anode for further removal was the main goal of this research. Also, prediction of the nitrate gradient developed under a specified electro-kinetic process as a function of
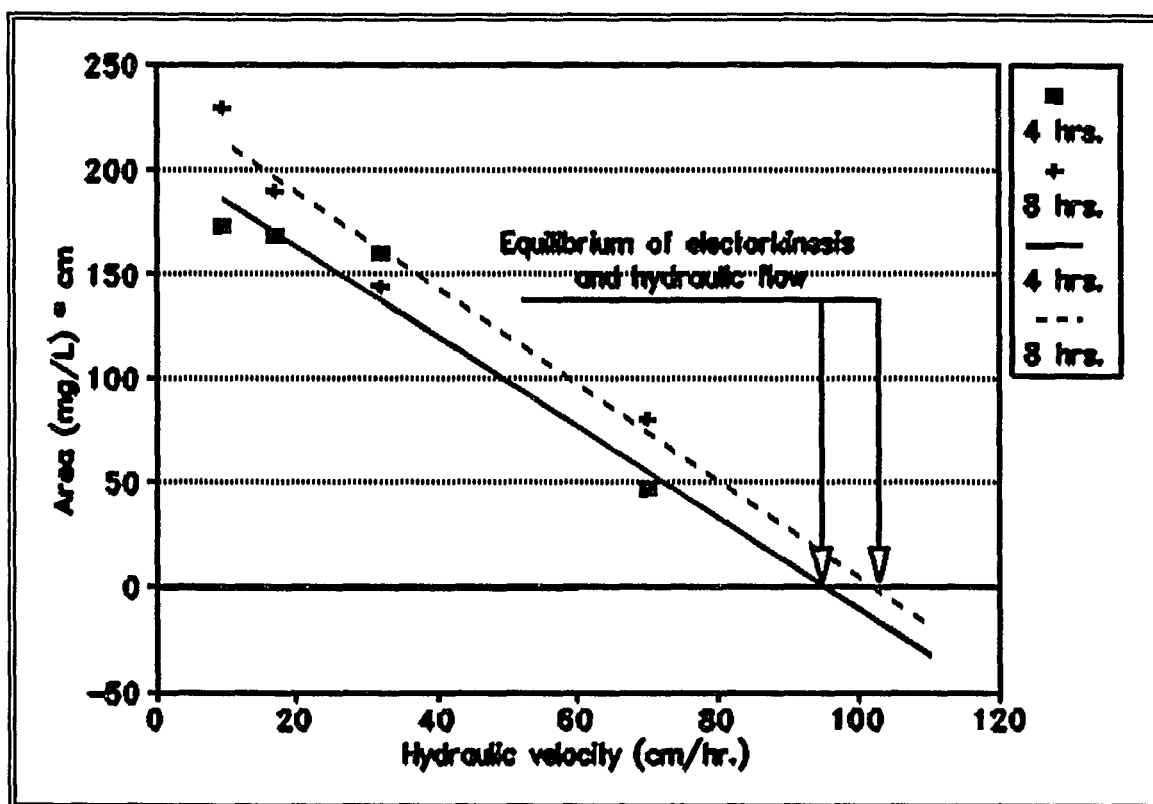
Figure 4.29 . The calculated area under the No$_3^-$ concentration curve vs. hydraulic flow velocity for 3 mA electrical current input and 4 and 8 hours test periods.

solution changes resulting from electrolysis was an additional relevant and interesting question in this research.

The results of the closed and open system, discussed previously, showed that the movement of NO$_3^-$ through the soil column was influenced by the movement of H$^+$ and OH$^-$ and vise versa. At the early stage of the experiment, NO$_3^-$ concentration was higher than both H$^+$ and OH$^-$ so that the transference number of No$_3^-$ was dominating. As a result, nitrate advanced towards the anode with almost no retardation, perhaps dragging OH$^-$ with it. As the duration of the tests increased, the amounts of H$^+$ and OH$^-$

generated at the boundaries increased. The fact that H^+ has a very high ionic mobility resulted in greater movement of H^+ towards the cathode with time (the transference number was increasing with time). As a result, NO_3^- movement was retarded by the advance of H^+ towards the cathode.

An inverse relationship with a high correlation coefficient was observed between the generated pH and NO_3^- gradients in both the closed and open systems. This relationship raised the possibility of using the pH gradient developed under an electro-kinetic process and regression equations relating pH and No_3^- to predict the nitrate gradient.

A one dimensional finite difference model (pH) was developed to predict the pH gradient developed during the electro-kinetic process. The model followed the theory developed by Acar et al (1991). Statistical software (Table curve) was used to determine the best regression equation relating the nitrate gradient to the corresponding pH gradient. The regression equations for the closed system and open system were found to be different.

4.4.1 Open system

The pH 1D model was used to simulate the movement of H^+ and OH^- during an open system electro-kinetic process. Model results for all open system experiments are summarized in Appendix C. Results of the model simulation then were used with a defined regression equation between pH and NO_3^- to predict the developed NO_3^-

concentration.

The regression equation that best fit the open system process was:

$$C/C_o = a + b\frac{\exp{(pH)}}{pH} + c \ln(t) \qquad (4.13)$$

where C/C_o is the relative concentration of NO_3^-, t is the test duration (hours) and, a, b, and c are the regression coefficients.

The regression analysis was performed on each individual experiment in order to determine the corresponding a,b, and c coefficients. Results of the regression analysis for the open system experiments are summarized in Table 4.3.

Table 4.3. Summary of the regression results for prediction of nitrate concentration in open system experiments

Test #	R^2	a	b	c
1	.84	1.07	-0.00027	.0065
2	.79	1.33	-.0011	-0.07
3	.94	1.12	-.00016	-.0017
4	.85	1.1	-.00084	0.039
5	.85	1.25	-.00146	0.0235
6	.93	.96	9.1e-6	0.06

Resuls of experiments #1,3 and 4 in which the hydraulic flow velocities were 9.5 cm/hour, 32 cm/hour, and 70 cm/hour, respectively, were lumped together to obtain one equation which include a velocity term. The equation that represents the three lumped experiments is:

$$C/C_o = a + b\,\frac{\exp(pH)}{pH} + c\,\ln(t) + d\,v_x \qquad (4.14)$$

where v_x is the hydraulic velocity in cm/hour.

The correlation coefficient for the lumped data equation was found to be 0.80. The a, b, c, and d parameters for the equation were 1.13, -0.00021, 0.032, and -0.00172, respectively.

Results of experiments # 2 and 5 were also lumped together (current= 3 mA, and 6 mA, respectively) in one equation after adding a current term. The equation which represented experiment 2 and 5 results in :

$$C/C_o = a + b\,\frac{\exp(pH)}{pH} + c\,\ln(t) + e\,C_u \qquad (4.15)$$

where C_u is the applied electrical current in mA.

The correlation coefficient for this equation was found to be 0.82. The a, b, c, and e coefficients were 1.18, -0.00014, -0.024, and 0.02, respectively.

Experimental and model results for a hydraulic flow velocity of 32.2 cm/hour (experiment # 3) are presented in Figures 4.30 a, b, c. A slight over-estimation of the pH was obtained with model simulation, as shown in the figures; this may be due the assumptions and limitations involved in developing the model (see chapter 2). Another factor which may account for over estimation of H^+ and OH^- is the input data (i.e., values for D_H, D_{OH}, α, R_H, and R_{OH}) which were chosen and calculated for a range found in the literature. Some of these parameters might have been higher than the actual experimental values. Some of the difference also may be due to inaccuracy in the measurement of pH.

However, there was overall agreement between the estimated and measured values. It is clear from the results that the numerical model simulated the behavior of H^+ and OH^- through the soil column quite accurately. Tables 4.4 and 4.5 show the results of paired t-tests for pH and NO_3^- respectively, which showed no significant difference between measured and simulated data at the 5 % level for pH and no significant difference between measured and simulated values in five of six tests for NO_3^-.

Figure 4.30 also shows a good match between the experimental NO_3^- gradient and the NO_3^- gradient computed with regression equations.

The difference between the two gradients did not exceed 5% at any point along the length. Differences between the experimental and the regression derived NO_3^- gradient may be due to:

1. Error introduced by analysis of NO_3^- concentration in the laboratory.

Table 4.4. Summary of paired t-test comparison of predicted with measured pH values for the six experiments.

Test #	n	Diff (pH_p-pH_e)	SD	t_{cal}	Significance
1	18	.159	.66	.24	ns
2	18	.154	.43	.36	ns
3	18	.174	.56	.31	ns
4	12	.1	.39	.26	ns
5	18	.03	.49	.065	ns
6	18	.152	.67	.23	ns

Table 4.5. Summary of paired t-test comparison of predicted with measured NO_3- values for the six experiments.

Test #	n	Diff (No_{3p}-No_{3e})	SD	t_{cal}	Significance
1	18	.05	.059	.97	ns
2	18	.001	.057	.024	ns
3	18	.003	.039	.08	ns
4	12	.05	.056	.74	ns
5	18	.114	.06	1.85	s
6	18	.006	.03	.2	ns
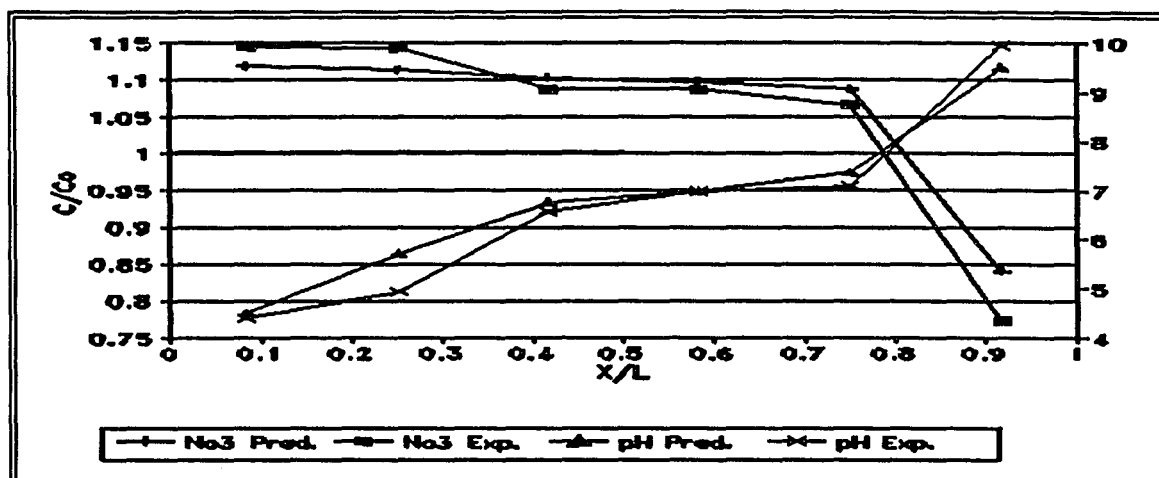
Figure 4.30a. Model and experimental results for NO_3^- and pH developed after 4 hrs. of 3 mA electrical input in the presence of v_x of 17 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
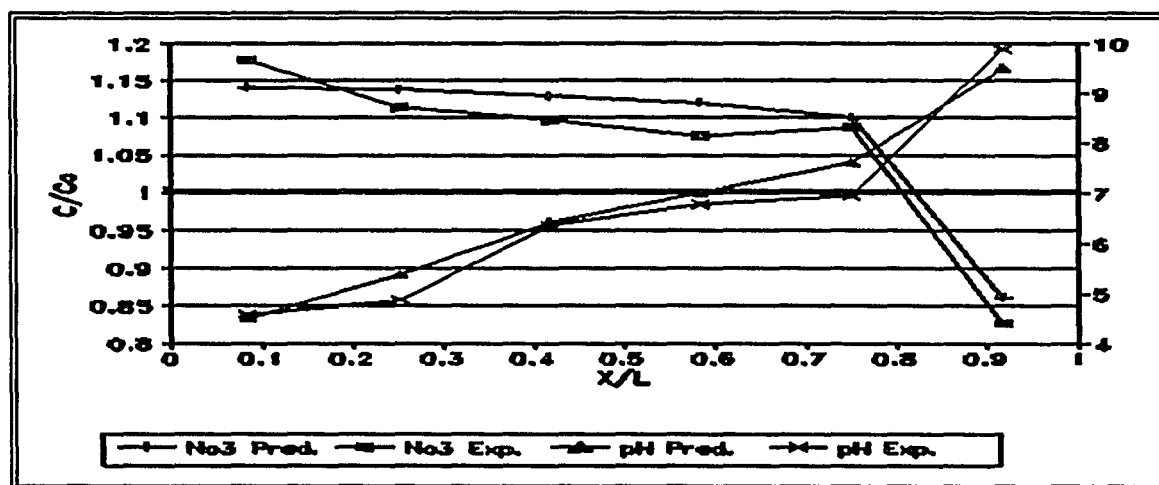
Figure 4.30b. Model and experimental results for NO_3^- and pH developed after 8 hrs. of 3 mA electrical input in the presence of v_x of 17 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
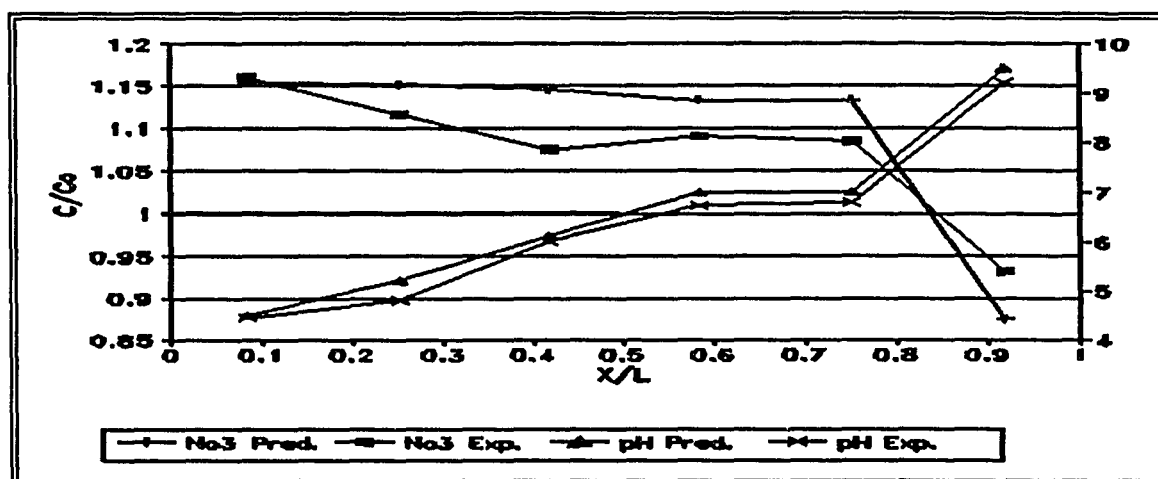
Figure 4.30c. Model and experimental results for NO_3^- and pH developed after 12 hrs. of 3 mA electrical input in the presence of v_x of 17 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

2. Differences between the predicted and experimental pH gradients discussed above.

Results shown in Figures 4.30 support the use of a finite difference model together with a derived regression equation to predict the spatial and temporal distribution of No_3^- developed under an electro-kinetic process in the presence of hydraulic flow.

4.4.2 Closed System

Model results for prediction of NO_3^- concentration for all the closed system experiments are summarized in Appendix C. Results of the model were used to develope a regression equation between pH and NO_3^- to predict NO_3^-.

The regression equation that best fit closed system test results was:

$$C/C_o = a + b \frac{\ln(pH)}{pH} \qquad (4.16)$$

where C/C_o is the relative concentration of NO_3^-, a and b are the regression coefficients.

The regression analysis was performed for each individual experiment to determine the corresponding a and b coefficients. Results of the regression analysis for the closed system experiments are summarized in Table 4.6.

The results of the pH model and NO_3^- regression prediction for Experiment # 5 are presented in Figure 4.31. There was a slight over-estimation of the pH with model simulation; this may be due the assumptions and limitations involved in developing the model (see chapter 2). Another factor which may have contributed to overestimation of H^+ and OH^- are the input values(i.e, values for D_H, D_{OH}, R_H, and R_{OH}) which were chosen from literature. Some of these parameters might have been higher than the actual experimental values. Some of the difference may also be due to inaccuracy in the measurement of pH.

However, there was overall agreement between the estimated and measured values. It is clear from the results that the numerical model simulated the behavior of H^+ and OH^- through the soil column quite adequately. There also was good consistancy between the experimental NO_3^- gradient and the NO_3^- gradient obtained from regression analysis. Differences between the experimental and the regression derived NO_3^- gradient may be due to:

Table 4.6. Summary of the regression analysis results for
prediction of nitrate concentration in closed system experiments.

Test #	R^2	a	b
1	0.74	-3.0	14.66
2	0.9	-3.9	18.0
3	0.8	-8.0	33.79
4	0.89	-10.6	43.00
5	0.94	-13.65	53.3
6	.97	-9.26	37.5
7	0.88	-7.07	31.15
8	0.9	-5.3	24.23
9	0.93	-19.67	77.83
10	0.98	-33.1	128.9
11	0.78	-13.66	56.2
12	0.64	-10.16	43.7
13	0.67	-13.8	56.6
14	0.71	-13.5	56.9
15	0.78	-5.29	23.7
16	0.97	-18.6	72.8
17	0.63	-8.0	33.49
18	0.94	-11.4	47.93
19	0.54	-1.95	11.39
20	0.78	10.89	46.5
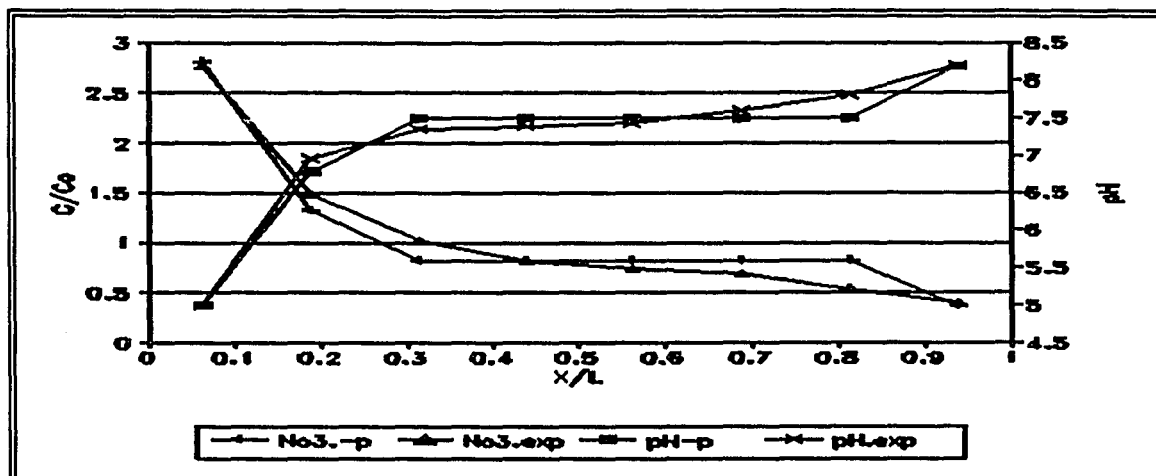
Figure 4.31. Model and experimental results for NO_3^- and pH gradients developed after 5 hours of 5 mA electrical input with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

1. Errors in analysis of NO_3^- concentration in the laboratory.

2. Differences between the predicted and experimental pH gradients discussed above.

Results shown in Figures 4.31 support the validity of using a finite difference and regression equation model to predict the spatial and temporal distribution of NO_3^- developed under an electro-kinetic process for closed system configurations.

CHAPTER FIVE

SUMMARY AND CONCLUSION

Chemicals applied to agricultural lands inevitably move below the root zone soil and may contaminate the underlying ground water reservoirs. Nitrate contamination of ground water is considered to be one of the more serious problems related to agricultural practices nationwide. Laboratory experiments utilizing closed and open system experiments were conducted in this study to test and evaluate the applicability of an electro-kinetic process to concentrate and retain nitrate close to the anode. In addition, a finite difference model was developed to predict the pH gradient developed during the electro--kinetic process. The model results were then used with a derived regression equation between pH and NO_3^- to predict the nitrate gradient developed during the electr-kinetic process.

The results of this research revealed the effectiveness of an electrokinetic method in concentrating and retaining nitrate close to the anode in saturated sandy soil. So, it is concluded that an electrokinetic method can be used as an in-situ remedial technique for reducing ground water contamination. Horizontal drainage tubing and parallel electrodes (with the anode near the drainage tube) could be used to concentrate nitrate near drain tubes for hydraulic removal. The electrokinetic process could also be used to retain nitrate in the root zone so that it could be utlized by the plant. Retaining nitrate in the root zone implies more efficient fertilizer use by the plant, thus reducing fertilizer

application.

Closed system experiment results yielded the following conclusions:

1- In the absence of hydraulic flow, the electro-kinetic process proved to be a very effective means for concentrating and retaining nitrate close to the anode.

2- The migration of NO_3^- towards the anode was directly dependent on the quantity of electricity applied (current*duration) with chemical movement and concentration occurring more rapidly as the quantity of applied electricity increased.

3- Under the same experimental conditions, substantial movement of NO_3^- was obtained using either the carbon or copper electrodes. On the other hand, less movement of NO_3^- was obtained using stainless steel electrodes.

4- A higher migration rate for nitrate was obtained with closer electrode spacing.

5- The basic environment developed by electrolysis did not favor Na^+ solubility. As a result, significant movement of Na^+ was observed only after long duration application of an electrical current (24 hrs.).

The results of the open system experiments revealed the following conclusions:

1- Relatively slow migration and accumulation of nitrate was obtained with all the hydraulic flow velocity levels.

2- The ability of an electrical potential to hold nitrate against the hydraulic potential was dependent on the hydraulic flow velocity. The higher the hydraulic velocity, the lower the capability of an electrical potential to retain nitrate.

3- The pH gradient developed during the electro-kinetic process was highly dependent on flow velocity. The higher the velocity level, the longer the acidic environment extended along the column length.

4- For this particular sandy, a hydraulic velocity of 100 cm/hour was predicted to be the limiting hydraulic velocity above which electromigration effects of 3 mA electrical input would be negated by hydraulic flow.

The following conclusions were obtained from both the closed and open system test results:

1- The initial concentration of nitrate had a direct effect on the performance of the electro-kinetic process. The lower the initial concentration, the more efficient the process and the faster the migration rate.

2- The pH model effectively predicted the pH gradients for both the closed and open system process.

3- The derived regression equations adequately represented the relationship between the pH and NO_3^- gradient developed during electro-kinetic processes for both the closed and open systems.

4- The technique of using the pH gradient abtained from a numerical model and the derived regression equation relating pH and No_3^- yielded good predictions of the NO_3^- gradient developed as a direct result of an imposed electrical potential.

5.1 Recommendations for Further Research

1- Evaluate the effectiveness of an electro-kinetic process to concentrating and retaining nitrate close to the anode in different soils.

2- Study nitrate mobility in response to an electrical potential with different degree of soil saturation.

3- Test the effect of using multiple anion and cation solutions on nitrate movement and concentration

APPENDIX A SUMMARY OF MASS BALANCE RESULTS.

Closed System Mass Balance Results

Test # 1

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.642857	1190	61.811898	295.5	15.349089
2	3.642857	1210	62.850753	163.5	8.4926431
3	3.642857	878	45.605753	202	10.49244
4	3.642857	551	28.620467	205	10.648268
5	3.642857	272	14.128434	148.5	7.7135016
6	3.642857	31.5	1.6361973	222	11.531295
7	3.642857	243	12.622093	320	16.621687

Total Amount Of Nitrate   227.2756
Total Amount Of Sodium   80.848924
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   104.91322 Sodium   R =   100.60406

test#2

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	4.083333	1100	64.045777	177.5	10.334659
2	4.083333	817	47.568545	255	14.846975
3	4.083333	905	52.692207	273	15.894997
4	4.083333	423	24.628512	297	17.29236
5	4.083333	35.6	2.0727542	243.5	14.177406
6	4.083333	14.5	0.8442398	321.5	18.718834

Total Amount Of Nitrate   191.85204
Total Amount Of Sodium   91.265232
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   88.561265 Sodium   R =   113.56555

Test# 3

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	68.6	2.9955956	44.6	1.9475738
2	3.0625	42.1	1.8384049	64.9	2.8340256
3	3.0625	33.2	1.4497635	91.7	4.0043166
4	3.0625	35.1	1.5327319	94.4	4.1222191
5	3.0625	30.1	1.314394	87.3	3.8121793
6	3.0625	26	1.135357	83.4	3.6418758
7	3.0625	5.72	0.2497785	86.5	3.7772452
8	3.0625	2.86	0.1248893	112.2	4.8995019

Total Amount Of Nitrate   7.645319
Total Amount Of Sodium   27.091364
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   3.5291735 Sodium   R =   33.711037

Test # 4

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.5	217	10.829559	19.9	0.9931254
2	3.5	99.3	4.9556459	40.4	2.0161943
3	3.5	61.7	3.0791879	70.2	3.5033872
4	3.5	63	3.1440654	83.1	4.147172
5	3.5	61	3.0442538	66.7	3.3287169
6	3.5	6.05	0.3019301	61.9	3.089169
7	3.5	0.6	0.0299435	40.2	2.0062132

Total Amount Of Nitrate   25.384585
Total Amount Of Sodium   19.083978
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   11.717838 Sodium R =   23.747077

Test # 5

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.5	222	11.079088	64.7	3.2289053
2	3.5	63.7	3.1789995	126.2	6.298112
3	3.5	59.7	2.9793763	97.4	4.8608249
4	3.5	36.9	1.841524	104.3	5.2051749
5	3.5	57.4	2.8645929	88.2	4.4016916
6	3.5	8.1	0.404237	76.5	3.8177937
7	3.5	1.77	0.0883333	48.6	2.4254219

Total Amount Of Nitrate   22.436151
Total Amount Of Sodium   30.237924
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   10.356804 Sodium R =   37.626449

Test # 6

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	207	9.039188	36.6	1.5982332
2	3.0625	111	4.8471008	34.5	1.5065313
3	3.0625	76.3	3.331836	63.6	2.7772578
4	3.0625	61	2.6637221	74.4	3.2488676
5	3.0625	55.2	2.4104501	82.2	3.5894747
6	3.0625	51.7	2.2576136	87.3	3.8121793
7	3.0625	39.8	1.7379695	94.5	4.1265858
8	3.0625	29.8	1.3012937	125.5	5.4802807

Total Amount Of Nitrate   18.549986
Total Amount Of Sodium   24.541177
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   8.5629022 Sodium R =   30.537723

Test # 7

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	144	6.2881308	89.6	3.9126147
2	3.0625	116	5.0654387	111	4.8471008
3	3.0625	88.5	3.8645804	102.8	4.4890267
4	3.0625	81.6	3.5632741	95.9	4.1877204
5	3.0625	71.4	3.1178649	91.5	3.9955831
6	3.0625	50.4	2.2008458	75.6	3.3012687
7	3.0625	29.2	1.2750932	90.6	3.9562823
8	3.0625	9.6	0.4192087	87.5	3.8209128

Total Amount Of Nitrate   19.506306
Total Amount Of Sodium   28.597895
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R = 9.0043512 Sodium R = 35.585684

Test # 8

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	173	7.5544905	68.7	2.9999624
2	3.0625	101	4.4104251	126.5	5.5239482
3	3.0625	88.5	3.8645804	105.9	4.6243962
4	3.0625	85.2	3.7204774	93.5	4.0829183
5	3.0625	83.5	3.6462425	87.2	3.8078125
6	3.0625	79.2	3.4584719	80.7	3.5239733
7	3.0625	41.1	1.7947373	77.4	3.3798703
8	3.0625	4.6	0.2008708	82.4	3.5982082

Total Amount Of Nitrate   21.095805
Total Amount Of Sodium   28.541127
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R = 9.7380839 Sodium R = 35.515045

Test # 9

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	379.8	16.584945	0.6	0.0262005
2	3.0625	41.5	1.8122044	5.25	0.2292548
3	3.0625	35.7	1.5589324	36	1.5720327
4	3.0625	27.3	1.1921248	121.95	5.3252608
5	3.0625	27.2	1.187758	51.3	2.2401466
6	3.0625	22.7	0.991254	46.95	2.0501926
7	3.0625	19.3	0.8427842	59.25	2.5873038
8	3.0625	5.45	0.2379883	140.85	6.1505779

Total Amount Of Nitrate   7.8230461
Total Amount Of Sodium   20.154769
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R = 3.6112145 Sodium R = 25.079512

Test # 10

Sec. #	Length	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	2.48	227.1	8.0306702	10.95	0.387212
2	2.48	39.9	1.4109368	15.5	0.5481083
3	2.48	17	0.601151	39.3	1.3897197
4	2.48	4.35	0.1538239	49.95	1.7663231
5	2.48	1.63	0.0576398	102.3	3.6175146

Total Amount Of Nitrate   10.254222
Total Amount Of Sodium   7.7088776
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   4.7334752 Sodium   R =   9.5925132

Test # 11

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	128	5.5894496	22	0.9606866
2	3.0625	76	3.3187357	38.17	1.6667913
3	3.0625	70.4	3.0741973	49.29	2.1523748
4	3.0625	65.6	2.8645929	46	2.0087085
5	3.0625	67.5	2.9475613	46.75	2.0414591
6	3.0625	39.5	1.7248692	45.5	1.9868747
7	3.0625	3.56	0.1554566	36.74	1.6043467
8	3.0625	4.63	0.2021809	66.75	2.9148106

Total Amount Of Nitrate   14.287594
Total Amount Of Sodium   14.375366
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   6.5953295 Sodium   R =   17.887933

Test # 12

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	122	5.3274441	67.9	2.9650283
2	3.0625	74.4	3.2488676	52.8	2.305648
3	3.0625	69.9	3.0523635	52.4	2.2881809
4	3.0625	71.4	3.1178649	50.5	2.2052125
5	3.0625	69.9	3.0523635	46.4	2.0261755
6	3.0625	71.3	3.1134981	49.8	2.1746452
7	3.0625	57.2	2.4977853	44.7	1.9519406
8	3.0625	32.2	1.4060959	54.6	2.3842496

Total Amount Of Nitrate   19.488839
Total Amount Of Sodium   15.336052
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   8.9962882 Sodium   R =   19.08336

Test # 13

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	122	5.3274441	34	1.4846976
2	3.0625	90.4	3.9475488	40.8	1.7816371
3	3.0625	83	3.6244087	50	2.1833788
4	3.0625	57	2.4890518	48.4	2.1135106
5	3.0625	9.1	0.3973749	38.2	1.6681014
6	3.0625	3.64	0.15895	29.8	1.3012937
7	3.0625	3.3	0.144103	32.7	1.4279297
8	3.0625	24.3	1.0611221	79.1	3.4541052

Total Amount Of Nitrate   11.822559
Total Amount Of Sodium   13.929956
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   5.4574391 Sodium R =   17.333689

Test # 14

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	133	5.8077875	6.82	0.2978129
2	3.0625	83.5	3.6462425	5.39	0.2353682
3	3.0625	3.37	0.1471597	4.4	0.1921373
4	3.0625	3.7	0.16157	6.8	0.2969395
5	3.0625	3	0.1310027	6.6	0.288206
6	3.0625	2.8	0.1222692	9.13	0.398685
7	3.0625	2.6	0.1135357	44	1.9213733
8	3.0625	4.8	0.2096044	268.4	11.720377

Total Amount Of Nitrate   4.5313843
Total Amount Of Sodium   15.053086
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   2.0917428 Sodium R =   18.731252

Test # 15

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	190	8.2968393	20.5	0.8951853
2	3.0625	89	3.8864142	45.4	1.9825079
3	3.0625	85	3.7117439	46.7	2.0392758
4	3.0625	92.9	4.0567177	51	2.2270463
5	3.0625	62	2.7073897	42.8	1.8689722
6	3.0625	32	1.3973624	37.4	1.6331673
7	3.0625	5.1	0.2227046	27.5	1.2008583
8	3.0625	6.4	0.2794725	62.6	2.7335902

Total Amount Of Nitrate   16.261805
Total Amount Of Sodium   13.685418
Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   7.5066497 Sodium R =   17.029399

Test # 16

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	513.7	22.432033	18.6	0.8122169
2	3.0625	137	5.9824578	9.2	0.4017417
3	3.0625	15.5	0.6768474	33.6	1.4672305
4	3.0625	3.8	0.1659368	26.9	1.1746578
5	3.0625	3.7	0.16157	21.1	0.9213858
6	3.0625	3.7	0.16157	23.5	1.026188
7	3.0625	2.8	0.1222692	22.5	0.9825204
8	3.0625	3.2	0.1397362	77.5	3.3842371

Total Amount Of Nitrate   7.4103875
Total Amount Of Sodium   9.3579613
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   3.4207262 Sodium   R =   11.644544

Test # 17

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	4.083333	240	13.973624	22.2	1.2925602
2	4.083333	120.8	7.0333907	31.1	1.8107488
3	4.083333	81.9	4.7684992	43.1	2.50943
4	4.083333	10.7	0.6229907	30.9	1.7991041
5	4.083333	2.88	0.1676835	16.6	0.966509
6	4.083333	3.3	0.1921373	15.1	0.8791738
7	4.083333	2.7	0.1572033	25.9	1.5079869
8	4.083333	4.6	0.2678278	89.9	5.2342867

Total Amount Of Nitrate   13.209733
Total Amount Of Sodium   14.707239
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   6.0977754 Sodium   R =   18.300898
         Sodium   R =   18.300898

Test # 18

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	134.9	5.8907559	31	1.3536948
2	3.0625	74	3.2314006	47.7	2.0829433
3	3.0625	77.9	3.4017041	45	1.9650409
4	3.0625	54.4	2.3755161	65.6	2.8645929
5	3.0625	61.5	2.6855559	39.6	1.729236
6	3.0625	56	2.4453842	35.3	1.5414654
7	3.0625	6.8	0.2969395	31.1	1.3580616
8	3.0625	0.53	0.0231438	77.8	3.3973373

Total Amount Of Nitrate   14.459644
Total Amount Of Sodium   14.938677
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   6.67475 Sodium   R =   18.588888

Test # 19

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	3.0625	434.7	18.982295	75.4	3.2925352
2	3.0625	558.1	24.370874	162.1	7.0785139
3	3.0625	507.5	22.161294	164	7.1614823
4	3.0625	532.3	23.24425	163.8	7.1527488
5	3.0625	512.5	22.379632	177.6	7.7553613
6	3.0625	371.3	16.213771	166.2	7.257551
7	3.0625	484.9	21.174407	172.9	7.5501237
8	3.0625	165.6	7.2313504	167	7.292485

Total Amount Of Nitrate   136.77558
Total Amount Of Sodium   51.248266
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   63.137293 Sodium R =   63.770589

Test # 20

Sec. #	Sec.Leng	NO3 (ppm)	NO3 (mg)	Na (ppm)	Na (mg)
1	2.8	171.6	6.8510682	8	0.3193971
2	2.8	90.7	3.6211648	10.6	0.4232012
3	2.8	61.5	2.4553654	15.5	0.6188319
4	2.8	12.8	0.5110354	4.9	0.1956307
5	2.8	3.9	0.1557061	67.9	2.7108831

Total Amount Of Nitrate   13.59434
Total Amount Of Sodium   4.267944
 Initial Nitrate   216.632
Initial Sodium   80.363482
Nitrate R =   6.2753149 Sodium R =   5.3108003

The Beaker Experiment Results

Treatmen	pH	NO3	Na
Solution	6.55	65	21.3
X-Sol.	8.07	72	60.3
X-Blank	8.12	7.2	37.9

Mass Balance Calculations For Nitrate
(Open System)

Test #1

Hour	Sin	Sit	Sout	Sd	R %
4	36.38	77.49	73.33	38.21	98
8	38.21	77.49	71.82	40	97
12	40	77.49	73.84	40.37	97

Test #2

Hour	Sin	Sit	Sout	Sd	R %
4	18.25	147.79	142.66	39.64	97
8	39.64	147.79	129.5	39.66	89
12	37.66	147.79	132.23	37.82	92

Test #3

Hour	Sin	Sit	Sout	Sd	R %
4	38.85	269.9	235.2	39.71	89
8	39.71	269.9	274.62	40.11	101
12	40.11	269.9	271.62	41.55	101

Test #4

Hour	Sin	Sit	Sout	Sd	R %
4	40.08	608.9	587.4	38.62	96
8	38.62	608.9	606.1	40.78	99

Test #5

Hour	Sin	Sit	Sout	Sd	R %
4	43.36	158.8	133.14	42.78	87
8	42.78	158.8	129.42	38.95	84
12	38.95	158.8	121.62	41.99	83

Test #6

Hour	Sin	Sit	Sout	Sd	R %
4	75.25	299.84	275.13	75	93
8	75	299.84	277.17	78.33	95
12	78.33	299.84	297.35	78.47	99

Mass Balance Calculations For Sodium
(Open System)

Test #1

Hour	Sin	Sit	Sout	Sd	R %
4	12.33	322.8	24.82	12.96	107
8	12.96	22.8	29.3	12.52	116
12	12.52	22.8	24.49	11.82	103

Test #2

Hour	Sin	Sit	Sout	Sd	R %
4	13.56	52.41	38.09	16.58	83
8	16.58	52.41	58.05	14.31	105
12	14.31	52.41	48.57	13.93	94

Test #3

Hour	Sin	Sit	Sout	Sd	R %
4	12.95	88.41	82.25	14.39	95
8	14.39	88.41	74.54	13.53	86
12	13.53	88.41	87.4	14.04	99.5

Test #4

Hour	Sin	Sit	Sout	Sd	R %
4	14.18	187.4	190.6	13.82	101
8	13.82	187.4	196	12.6	103

Test #5

Hour	Sin	Sit	Sout	Sd	R %
4	10.9	39.92	41.1	10.64	101
8	10.64	39.92	42.2	10.7	105
12	10.7	39.92	42.68	10.82	105

Test #6

Hour	Sin	Sit	Sout	Sd	R %
4	24.67	97.5	126.7	25.89	125
8	25.89	97.5	145.7	27.94	140
12	27.94	97.5	98.89	27.03	100

APPENDIX B SUMMARY OF THE EXPERIMENTAL RESULTS.

Closed System Test Results

test #1

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.85714	0.071429	4.95	1190	295.5
5.57143	0.214286	3.75	1210	163.5
9.28571	0.357143	8.3	878	202
13	0.5	8.5	551	205
16.7143	0.642857	8.7	272	148.5
20.4286	0.785714	9.1	31.5	222
24.1429	0.928571	9.3	243	320

test #2

Distance	X/L	pH	No3 (ppm	Na (ppm)
2.08333	0.083333	4.84	1100	177.5
6.25	0.25	4.09	817	255
10.4167	0.416667	5.45	905	273
14.5833	0.583333	7.77	423	297
18.75	0.75	10.21	35.6	243.5
22.9167	0.916667	10.84	14.5	321.5

test #3

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	5.75	68.6	44.6
4.6875	0.1875	7.48	42.1	64.9
7.8125	0.3125	7.91	33.2	91.7
10.9375	0.4375	8.06	35.1	94.4
14.0625	0.5625	8.06	30.1	87.3
17.1875	0.6875	8.01	26	83.4
20.3125	0.8125	8.15	5.72	86.5
23.4	0.936	8.81	2.86	112.2

test #4

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	5.05	217	19.9
4.6875	0.1875	7.7	99.3	40.4
7.8125	0.3125	7.75	61.7	70.2
10.9375	0.4375	7.5	63	83.1
14.0625	0.5625	7.68	61	66.7
17.1875	0.6875	8.01	6.05	61.9
23.4	0.936	8.55	0.6	40.2

test #5

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	5	222	64.7
4.6875	0.1875	7.1	63.7	126.2
7.8125	0.3125	7.4	59.7	97.4
10.9375	0.4375	7.2	36.9	104.3
14.0625	0.5625	7.6	57.4	88.2
17.1875	0.6875	7.7	8.1	76.5
20.3125	0.8125	8	1.77	48.6

test #6

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	5	207	36.6
4.6875	0.1875	6.96	111	34.5
7.8125	0.3125	7.36	76.3	63.6
10.9375	0.4375	7.39	61	74.4
14.0625	0.5625	7.43	55.2	82.2
17.1875	0.6875	7.6	51.7	87.3
20.13	0.8052	7.8	39.8	94.5
23.4	0.936	8.2	29.8	125.5

test #7

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	5.88	144	89.6
4.6875	0.1875	7.51	116	111
7.8125	0.3125	7.83	88.5	102.8
10.9375	0.4375	7.87	81.6	95.9
14.0625	0.5625	8.28	71.4	91.5
17.1875	0.6875	8.4	50.4	75.6
20.3125	0.8125	9.08	29.2	90.6
23.4375	0.9375	9.24	9.6	87.5

test #8

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	5.1	173	68.7
4.6875	0.1875	7.71	101	126.5
7.8125	0.3125	7.9	88.5	105.9
10.9375	0.4375	7.9	85.2	93.5
14.0625	0.5625	7.95	83.5	87.2
17.1875	0.6875	7.95	79.2	80.7
20.31	0.8124	9.21	44.1	77.4
23.4	0.936	9.4	4.6	82.4

test #9

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	5.19	379.8	0.6
4.6875	0.1875	7.33	41.5	5.25
7.8125	0.3125	7.72	35.7	36
10.9375	0.4375	8.22	27.3	121.95
14.0625	0.5625	8.25	27.2	51.3
17.1875	0.6875	8.24	22.7	46.95
20.31	0.8124	8.2	19.3	59.3
23.4	0.936	8.9	5.45	140.85

test #10

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.3	0.1	6.61	227.1	10.95
3.9	0.3	7.72	39.9	15.5
6.06667	0.466667	8.12	17	39.3
8.23333	0.633333	8.1	4.35	49.9
10.4	0.8	8.229	1.63	102.3

test #11

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	6.88	128	22
4.6875	0.1875	7.86	76	38.17
7.8125	0.3125	7.93	70.4	49.29
10.9375	0.4375	7.87	65.6	46
14.0625	0.5625	8.11	67.5	46.75
17.1875	0.6875	8.12	39.5	45.5
20.3125	0.8125	8.19	3.6	36.74
23.4	0.936	9.21	4.63	66.75

test #12

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	7.89	122	67.9
4.6875	0.1875	7.91	74.4	52.8
7.8125	0.3125	8.12	69.9	52.4
10.9375	0.4375	8.22	71.4	50.5
14.0625	0.5625	8.13	69.9	46.4
17.1875	0.6875	8.22	71.3	49.8
20.3125	0.8125	8.27	57.2	44.7
23.4375	0.9375	9.21	32.2	54.6

test #13

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	6.42	122	34
4.6875	0.1875	7.69	90.4	40.8
7.8125	0.3125	8.03	83	50
10.9375	0.4375	7.99	57	48.4
14.0625	0.5625	8.22	9.1	38.2
17.1875	0.6875	8.24	3.64	29.8
20.3125	0.8125	8.25	3.3	32.7
23.4375	0.9375	9.29	2.43	79.1

test #14

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	4.7	233	6.82
4.6875	0.1875	6.3	83.5	5.39
7.8125	0.3125	7.1	3.37	4.4
10.9375	0.4375	8.2	3.7	6.8
14.0625	0.5625	8.9	3	6.6
17.1875	0.6875	9.52	2.8	9.13
20.3125	0.8125	9.76	2.6	44
23.4375	0.9375	11.83	4.3	268.4

test #15

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	4.41	190	20.5
4.6875	0.1875	7.76	89	45.4
7.8125	0.3125	7.82	85	46.7
10.9375	0.4375	7.82	92.9	51
14.0625	0.5625	7.85	62	42.8
17.1875	0.6875	8	32	37.4
20.3125	0.8125	8	5.1	27.5
23.4	0.936	10.8	6.4	62.6

test #16

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	4.1	513.7	18.6
4.6875	0.1875	7.36	137	9.2
7.8125	0.3125	8.14	15.5	33.6
10.9375	0.4375	7.99	3.8	26.9
14.0625	0.5625	7.78	3.7	21.1
17.1875	0.6875	7.82	3.7	23.5
20.3125	0.8125	8.32	2.8	22.5
23.4375	0.9375	8.53	3.2	77.5

test #17

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	5.13	240	22.2
4.6875	0.1875	8.01	120.8	31.1
7.8125	0.3125	8.02	81.9	43.1
10.9375	0.4375	8.05	10.7	30.9
14.0625	0.5625	8	2.88	16.6
17.1875	0.6875	7.98	2.3	16.6
20.3125	0.8125	8.07	2.7	16.6
23.4	0.936	10.98	4.6	89.9

test #18

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.5625	0.0625	6.74	134.9	31
4.6875	0.1875	7.85	74	47.7
7.8125	0.3125	8.03	77.9	45
10.9375	0.4375	7.99	54.4	65.6
14.0625	0.5625	7.95	61.5	39.6
17.1875	0.6875	8.11	56	35.3
20.3125	0.8125	8.91	6.8	31.1
23.4375	0.9375	9.75	0.53	77.8

test #19

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.56	0.0624	6.62	434.7	75.4
4.6875	0.1875	7.46	558.1	162.1
7.8125	0.3125	7.68	507.5	164
10.9375	0.4375	7.85	532.3	163.8
14.0625	0.5625	7.97	512.5	166.24
17.1875	0.6875	7.8	371.3	172.96
20.3	0.812	8.1	484.9	172.9
23.425	0.937	11	165.6	167

test #20

Distance	X/L	pH	No3 (ppm	Na (ppm)
1.4	0.1	7.05	171.6	8
4.2	0.3	7.97	90.7	10.6
7	0.5	7.96	61.5	15.5
9.8	0.7	8.57	12.8	4.9
12.6	0.9	10.26	3.9	67.92

Open System Test Results

Test # 1

X	X/L	0 hours			4 hours			8 hours			12 hours		
		Na	No3	pH	Na	No3	pH	Na	No3	pH	Na	No3	pH
2.5	0	20.9	60.3	6.94	17.5	71.8	3.68	15.4	80.8	3.33	18.3	74.7	3.42
7.5	0.2	20.7	59.1	6.85	17.9	73.8	6.15	22.6	68.2	6.25	19.2	68.7	4.36
12.5	0.4	20.9	58.5	6.8	17.3	61.1	6.72	18.6	71	6.54	16.5	71.3	6.37
17.5	0.6	20.7	59.8	6.6	14.8	62.4	6.91	16.2	65.7	6.9	16.5	72	6.75
22.5	0.8	20.7	60.6	6.65	14.7	63.5	6.97	16	63.1	7.5	16.7	67.1	7.29
27.5	1	20.9	57.4	6.89	32.9	46.5	9.52	28.6	45.3	9.66	23.4	48.8	9.63
out fl		12.5	55.3	6.8	19.7	58.2	7.5	23.2	57	8.3	19.4	58.6	8.51

Test # 2

X	X/L	0 hours			4 hours			8 hours			12 hours		
		Na	No3	pH	Na	No3	pH	Na	No3	pH	Na	No3	pH
2.5	0	23	68.2	6.78	21.9	74.9	4.03	21.8	68.4	4.37	22.1	70.4	4.36
7.5	0.2	23	65.2	6.6	22.4	77.1	4.93	20.7	66.8	5.23	21.3	65.6	5.1
12.5	0.4	23	62.8	6.8	25.4	77.5	6.69	21.4	65.7	6.56	20.6	64.4	6.56
17.5	0.6	23	54	6.78	25.5	70.7	6.94	17.4	65.8	6.74	20	65.6	6.78
22.5	0.8	23	63	6.79	22.2	72.4	6.89	16.1	66.6	6.9	20.4	67.1	7
27.5	1	23	61.2	6.9	37.3	36.8	8.07	32	44.9	8.03	26.6	44.8	8.28
out f		19.8	65.9	7.7	16.6	62.9	7.4	25.3	57.1	7.6	21.4	58.3	7.77

Test # 3

X	X/L				4 hours			8 hours			12 hours		
		Na	No3	pH	Na	No3	pH	Na	No3	pH	Na	No3	pH
2.5	0	22.2	64.1	6.8	19.5	72.1	4.4	21.2	74.2	4.59	21.9	73.1	4.47
7.5	0.2	22.2	64.2	6.84	21.1	72	4.94	21.4	70.2	4.88	21.6	70.3	4.82
12.5	0.4	22.2	63.2	6.85	21.4	68.5	6.58	20.3	69.1	6.35	22.2	67.7	6.01
17.5	0.6	22.2	62.6	7.05	19.9	68.5	6.98	20.4	67.8	6.77	22.5	68.7	6.73
22.5	0.8	22.2	63.5	7.05	26.7	67.2	7.1	21.5	68.5	6.94	20.7	68.3	6.8
27.5	1	22.2	65.9	7	32	48.7	9.94	24.5	52.1	9.9	25.4	58.7	9.21
out fl		23.4	64.3	7	19.2	54.9	8.97	17.4	64.1	7.57	20.4	63.4	7.5

Test # 4

X	X/L	0 hours			4 hours			8 hours		
		Na	No3	pH	Na	No3	pH	Na	No3	pH
2.5	0	20.9	66.7	6.9	20	64	6.3	20.2	70	5.2
7.5	0.2	20.9	64.7	6.8	21	66.1	6.5	21	69.3	6.57
12.5	0.4	20.9	64.5	6.9	19.9	66.4	6.8	18.9	66.5	6.59
17.5	0.6	20.9	65.1	7	21.1	66.4	6.8	18.9	67.7	6.8
22.5	0.8	20.9	65.8	7.1	21	65.8	6.9	20.6	67.1	6.9
27.5	1	20.9	67.1	7	27.7	55.2	7.8	21.7	59.8	7.4
o. flo		20.1	65.3	6.6	18.5	57	7.5	21.7	65	6.8

Test # 5

X	X/L	0 hours			4 hours			8hours			12 hours		
		Na	No3	pH	Na	No3	pH	Na	No3	pH	Na	No3	pH
2.5	0	18	74	6.4	15	85.4	3.8	14.1	78.3	3.9	16.6	81.4	3.9
7.5	0.2	18	70.2	6.8	16.5	78.1	5	15.7	75.5	5.1	16.6	74.9	4.6
12.5	0.4	18	66.6	6.9	16	74.8	6.5	16.3	73	6.7	17.3	75.1	6.6
17.5	0.6	18	67.5	7	20	73.4	6.5	18.6	72.8	6.98	17.3	73.8	6.9
22.5	0.8	18	69.1	7.2	20	58.2	6.7	20	62.1	7.04	18.1	70.2	7.1
27.5	1	18	67.9	7.4	20	50.4	8	22.2	34.8	8.2	20.6	45.5	8.1
o. flo		17.6	50.1	7.3	17.9	58.7	8	18.4	45.6	7.8	18.6	42.9	7.8

Test # 6

X	X/L	0 hours			4 hours			8 hours			12 hours		
		Na	No3	pH	Na	No3	pH	Na	No3	pH	Na	No3	pH
2.5	0	42.5	108	7.1	42.2	132	3.79	41.2	135	3.82	41.8	137	3.78
7.5	0.2	42.5	121	7.05	40.2	130	5.95	46.7	131	6.24	41.1	136	4.36
12.5	0.4	42.5	122	7.2	40.6	128	6.46	43.9	130	6.89	45.2	133	6.74
17.5	0.6	42.5	122	7.2	39.2	127	6.6	49.5	130	7.27	45.4	134	7
22.5	0.8	42.5	121	7.07	42.5	125	6.69	45.8	128	8.1	42.1	136	7.4
27.5	1	43	127	7.1	44.1	101	9.86	47.4	114	10	46.5	109	10.1
o. flo		41.5	128	7.1	55.2	121	7.77	63.5	122	8.91	43.1	131	8.95
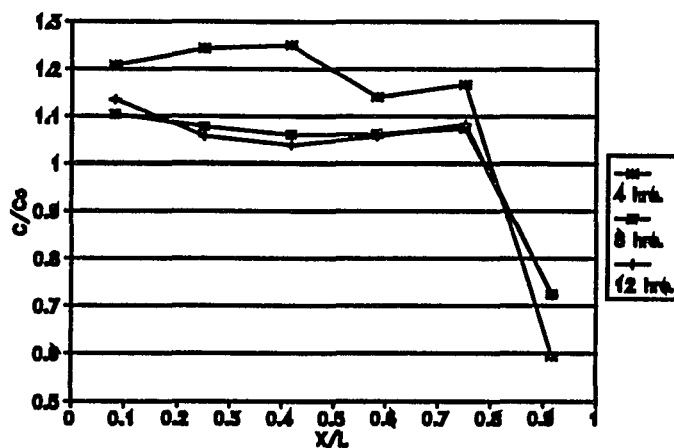
Figure B.1. Nitrate concentration (C/C_o) developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 17 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
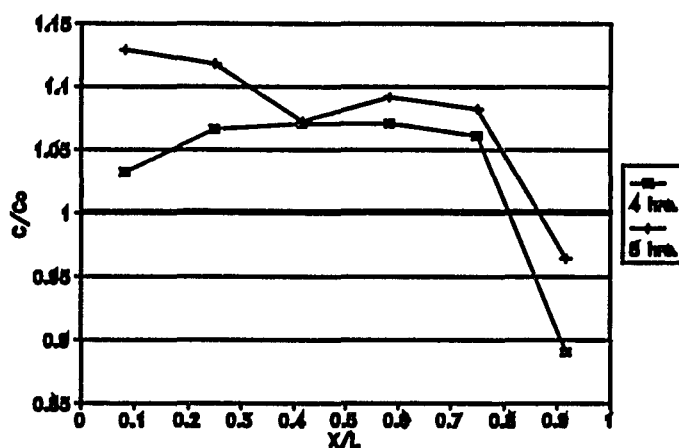
Figure B.2. Nitrate concentration (C/C_o) developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 70 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
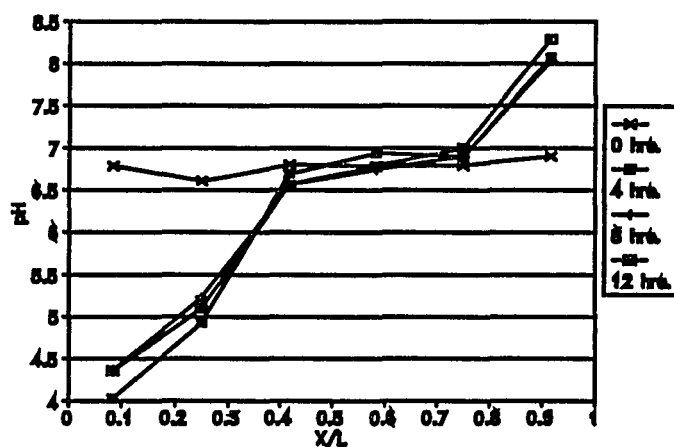
Figure B.3. The pH gradients developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 17 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
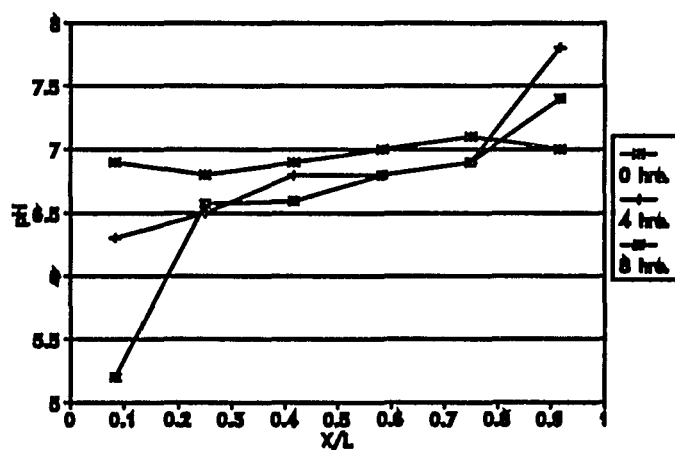
Figure B.4. The pH gradients developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 70 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
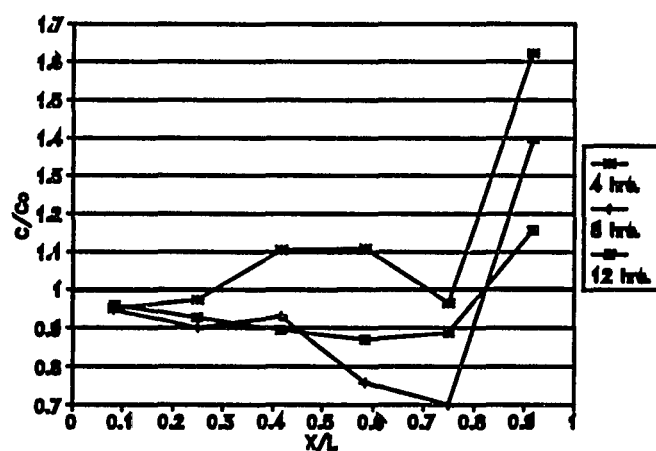
Figure B.5. Sodium concentration (C/C$_o$) developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 17 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
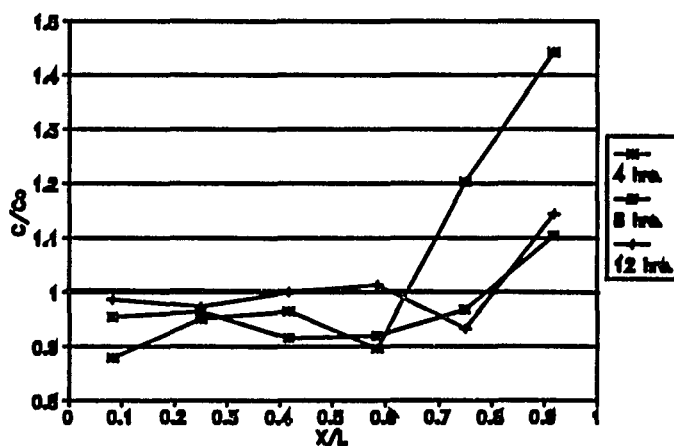
Figure B.6. Sodium concentration (C/C$_o$) developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 32 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.
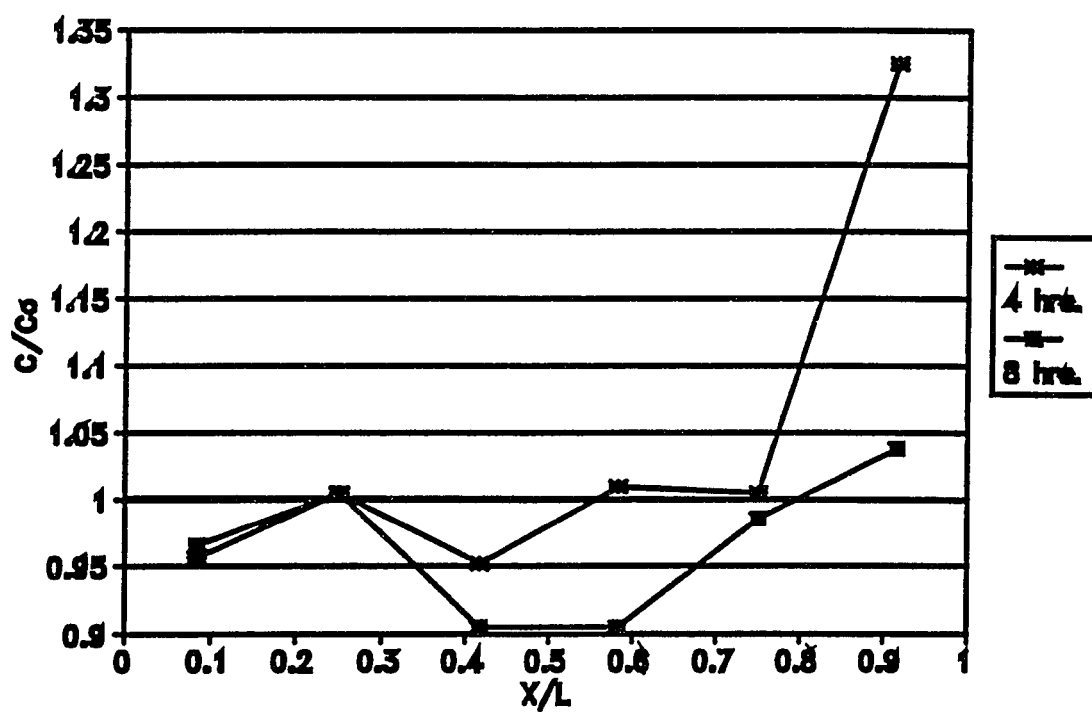
Figure B.7. Sodium concentration (C/C$_o$) developed after 4, 8, and 12 hours of 3 mA electrical input in the presence of hydraulic flow velocity of 70 cm/hr with carbon electrodes and initial sodium nitrate concentration of 85 ppm.

APPENDIX C SUMMARY OF THE pH MODEL AND STATISTICAL

RESULTS

Closed System Prediction

Test #1

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.857	0	4.95	4.95	1190	1.919	1.737
5.571	0.167	3.75	5.2	1210	1.952	1.648
9.286	0.333	8.3	7.49	878	1.416	0.941
13	0.5	8.5	7.49	551	0.889	0.941
16.71	0.667	8.7	8.3	272	0.439	0.738
20.43	0.833	9.1	8.6	31.5	0.051	0.668
24.14	1	9.3	9.3	243	0.392	0.515

Test #2

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
2.083	0.083	4.84	4.84	1100	2.391	1.965
6.25	0.25	4.09	5.2	817	1.776	1.807
10.42	0.417	5.45	5.301	905	1.967	1.763
14.58	0.583	7.77	7.452	423	0.92	0.952
18.75	0.75	10.21	9.232	35.6	0.077	0.434
22.92	0.917	10.84	10.84	14.5	0.032	0.057

Test #3

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	5.75	5.75	68.6	2.144	2.279
4.688	0.188	7.48	7.259	42.1	1.316	1.227
7.813	0.313	7.91	7.495	33.2	1.038	1.081
10.94	0.438	8.06	7.495	35.1	1.097	1.081
14.06	0.563	8.06	7.495	30.1	0.941	1.081
17.19	0.688	8.01	7.495	26	0.813	1.081
20.31	0.813	8.15	7.573	5.72	0.179	1.033
23.44	0.938	8.81	8.81	2.86	0.089	0.345

Test #4

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	5.05	5.05	217	3.1	3.189
4.688	0.188	7.7	6.826	99.3	1.419	1.5
7.813	0.313	7.75	7.495	61.7	0.881	0.956
10.94	0.438	7.5	7.495	63	0.9	0.956
14.06	0.563	7.68	7.495	61	0.871	0.956
17.19	0.688	8.01	7.495	6.05	0.086	0.956
23.4	0.936	8.55	8.55	0.6	0.009	0.192

Test #5

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	5	5	222	3.581	3.507
4.688	0.188	7.1	6.79	63.7	1.027	1.386
7.813	0.313	7.4	7.495	59.7	0.963	0.674
10.94	0.438	7.2	7.495	36.9	0.595	0.674
14.06	0.563	7.6	7.495	57.4	0.926	0.674
17.19	0.688	7.7	8.214	8.1	0.131	0.015
20.31	0.813	10.2	10.15	1.77	0.029	0

Test #6

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	5	5	207	2.76	2.811
4.688	0.188	6.96	6.786	111	1.48	1.322
7.813	0.313	7.36	7.495	76.3	1.017	0.818
10.94	0.438	7.39	7.495	61	0.813	0.818
14.06	0.563	7.43	7.495	55.2	0.736	0.818
17.19	0.688	7.6	7.495	51.7	0.689	0.818
20.31	0.813	7.8	7.495	39.8	0.531	0.818
23.44	0.938	8.2	8.19	29.8	0.397	0.369

Test #7

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	5.88	5.88	144	2.057	2.315
4.688	0.188	7.51	7.31	116	1.657	1.407
7.813	0.313	7.83	7.495	88.5	1.264	1.301
10.94	0.438	7.87	7.495	81.6	1.166	1.301
14.06	0.563	8.28	7.495	71.4	1.02	1.301
17.19	0.688	8.4	7.495	50.4	0.72	1.301
20.31	0.813	9.08	7.679	29.2	0.417	1.199
23.44	0.938	9.24	9.24	9.6	0.137	0.426

Test #8

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	5.1	5.1	173	2.276	2.44
4.688	0.188	7.71	6.865	101	1.329	1.499
7.813	0.313	7.9	7.495	88.5	1.164	1.212
10.94	0.438	7.9	7.495	85.2	1.121	1.212
14.06	0.563	7.95	7.495	83.5	1.099	1.212
17.19	0.688	7.95	7.495	79.2	1.042	1.212
20.31	0.813	9.21	7.741	41.1	0.541	1.106
23.44	0.938	9.4	9.4	4.6	0.061	0.476

Test #9

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	5.19	5.19	379.8	5.426	5.025
4.688	0.188	7.33	7.02	41.5	0.593	1.936
7.813	0.313	7.72	7.99	35.7	0.51	0.574
10.94	0.438	8.22	7.99	27.3	0.39	0.574
14.06	0.563	8.25	7.99	27.2	0.389	0.574
17.19	0.688	8.24	7.99	22.7	0.324	0.574
20.31	0.813	8.2	7.99	19.3	0.276	0.574
23.44	0.938	8.9	8.9	5.45	0.078	0

Test #10

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.3	0.1	6.61	6.611	227.1	3.785	3.727
3.8	0.292	7.99	7.77	39.9	0.665	0.913
6.3	0.485	8.15	7.99	17	0.283	0.427
8.8	0.677	8.1	8.26	4.35	0.073	0
11.3	0.869	9.6	9.6	1.63	0.027	0

Test #11

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	6.88	6.879	128	2.133	2.095
4.688	0.188	7.86	8	76	1.267	0.948
7.813	0.313	7.93	8	70.4	1.173	0.948
10.94	0.438	7.87	8	65.6	1.093	0.948
14.06	0.563	8.11	8	67.5	1.125	0.948
17.19	0.688	8.12	8	39.5	0.658	0.948
20.31	0.813	8.19	8	3.56	0.059	0.948
23.44	0.938	9.21	9.21	4.63	0.077	0

Test #12

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	7.89	7.886	122	1.743	1.284
4.688	0.188	7.91	8	74.4	1.063	1.199
7.813	0.313	8.12	8	69.9	0.999	1.199
10.94	0.438	8.22	8	71.4	1.02	1.199
14.06	0.563	8.13	8	69.9	0.999	1.199
17.19	0.688	8.22	8	71.3	1.019	1.199
20.31	0.813	8.27	8	57.2	0.817	1.199
23.44	0.938	9.21	9.21	32.2	0.46	0.375

Test #13

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	6.42	6.42	122	2.44	2.593
4.688	0.188	7.69	7.787	90.4	1.808	1.118
7.813	0.313	8.03	8	83	1.66	0.912
10.94	0.438	7.99	8	57	1.14	0.912
14.06	0.563	8.22	8	9.1	0.182	0.912
17.19	0.688	8.24	8	3.64	0.073	0.912
20.31	0.813	8.25	8.089	3.3	0.066	0.828
23.44	0.938	9.29	9.29	24.3	0.486	0

Test #14

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	4.7	4.7	133	4.156	4.235
4.688	0.188	6.3	5.922	83.5	2.609	2.59
7.813	0.313	7.1	7.244	3.37	0.105	1.054
10.94	0.438	8.2	7.926	3.7	0.116	0.362
14.06	0.563	8.9	8.096	3	0.094	0.199
17.19	0.688	9.52	8.978	2.8	0.088	0
20.31	0.813	9.76	10.47	2.6	0.081	0
23.44	0.938	11.83	11.83	42.8	1.338	0

Test #15

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	4.41	4.41	190	2.714	2.685
4.688	0.188	7.76	6.281	89	1.271	1.643
7.813	0.313	7.82	7.838	85	1.214	0.936
10.94	0.438	7.82	8	92.9	1.327	0.87
14.06	0.563	7.85	8	62	0.886	0.87
17.19	0.688	8.1	8	32	0.457	0.87
20.31	0.813	7.9	8.686	5.1	0.073	0.608
23.44	0.938	10.8	10.61	6.4	0.091	0

Test #16

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	4.1	4.19	513.7	6.421	6.293
4.688	0.188	7.36	5.7	137	1.713	3.629
7.813	0.313	8.14	7.29	15.5	0.194	1.238
10.94	0.438	7.99	7.99	3.8	0.048	0.335
14.06	0.563	7.78	7.99	3.7	0.046	0.335
17.19	0.688	7.82	7.99	3.7	0.046	0.335
20.31	0.813	8.32	8.1	2.8	0.035	0.201

Test #17

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	5.13	5.13	240	3.2	2.674
4.688	0.188	8.01	6.622	120.8	1.611	1.561
7.813	0.313	8.02	7.832	81.9	1.092	0.801
10.94	0.438	7.97	8	10.7	0.143	0.705
14.06	0.563	8	8	2.88	0.038	0.705
17.19	0.688	7.98	8	2.3	0.031	0.705
20.31	0.813	8.07	8	2.7	0.036	0.705
23.44	0.938	10.98	10.98	46.8	0.624	0

Test #18

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	6.74	6.745	134.9	2.248	2.164
4.688	0.188	7.85	7.816	74	1.233	1.209
7.813	0.313	8.03	8	77.9	1.298	1.058
10.94	0.438	7.99	8	54.4	0.907	1.058
14.06	0.563	7.95	8	61.5	1.025	1.058
17.19	0.688	8.11	8	56	0.933	1.058
20.31	0.813	8.91	8.349	6.8	0.113	0.783
23.44	0.938	9.75	9.75	0.53	0.009	0

Test #19

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.563	0.063	6.62	6.62	434.7	0.988	1.302
4.688	0.188	7.46	7.42	558.1	1.268	1.127
7.813	0.313	7.68	7.5	507.5	1.153	1.11
10.94	0.438	7.85	7.5	532.3	1.21	1.11
14.06	0.563	7.97	7.5	512.5	1.165	1.11
17.19	0.688	7.72	7.82	371.3	0.844	1.046
20.31	0.813	8.1	9.365	484.9	1.102	0.771
23.44	0.938	11	11.01	165.6	0.376	0.532

Test #20

distan	X/L	pH exp	pH Pre	C (NO3	C/Co	C/Co P
1.4	0.1	7.05	7.051	171.6	2.451	1.991
4.2	0.3	7.97	7.886	90.7	1.296	1.287
7	0.5	7.96	8	61.5	0.879	1.197
9.8	0.7	8.57	8.778	12.8	0.183	0.617
12.6	0.9	10.26	10.26	3.9	0.056	0

Open System Predictions

Test #1

		0 hour		4 hour					8 hour					12 hour				
X	X/L	pH init	Co	pH exp	pH Pred	C (NO3)	Co	C/Co Pr	pH exp	pH Pred	C o	C/Co	C/Co Pr	pH exp	pH Pred	C o	C/Co	C/Co Pr
2.1	0.08	6.94	60.3	3.68	3.45002	71.8	1.2	1.12367	3.33	3.45002	80.8	1.15429	1.14585	3.42	3.45002	75	1.2661	1.15882
6.3	0.25	6.9	59.1	6.15	5.05601	73.8	1.3	1.12103	6.25	4.70162	68.2	0.97429	1.1442	4.36	4.51802	69	1.16441	1.15756
10	0.42	6.8	58.5	6.72	6.6163	61.1	1	1.10864	6.54	6.15566	71	1.01429	1.13661	6.37	5.82931	71	1.20847	1.15234
15	0.58	6.8	59.8	6.91	6.99005	62.4	1.1	1.10153	6.9	7	65.7	0.93857	1.12348	6.75	7	72	1.22034	1.13646
19	0.75	6.8	60.6	6.37	7.40435	53.5	1.1	1.08983	7.5	7.65983	63.1	0.90143	1.10196	7.29	7	67	1.13729	1.13646
23	0.92	6.9	57.4	9.52	9.59999	46.5	0.8	0.81427	9.66	9.59999	45.3	0.64714	0.83645	9.63	9.59999	49	0.82712	0.84543

Test #2

		0 hour		4 hour					8 hour					12 hour				
X	X/L	pH init	Co	pH exp	pH Pred	C (NO3)	C/Co	C/Co Pr	pH exp	pH Pred	C (N	C/Co	C/Co Pr	pH exp	pH Pred	C	C/Co	C/Co Pr
2.1	0.08	6.9	68.2	4.03	4.30103	74.9	1.2	1.19566	4.37	4.30103	68.4	1.08571	1.17903	4.36	4.30103	70	1.17746	1.1693
6.3	0.25	6.9	65.2	4.93	5.72148	77.1	1.2	1.16093	5.23	5.38312	66.8	1.06032	1.15744	5.1	5.20871	65	1.0381	1.15293
10	0.42	6.9	62.8	5.69	6.84394	77.5	1.2	1.066	6.56	6.55326	65.7	1.04286	1.08486	5.56	6.29478	64	1.02222	1.0391
15	0.58	6.9	64.9	6.94	7	70.7	1.1	1.04223	6.74	6.97344	65.8	1.04444	1.02991	6.78	6.92133	66	1.04127	1.02831
19	0.75	6.9	63	6.89	7.01989	72.4	1.1	1.03893	6.9	7.04486	66.6	1.05714	1.01805	7	7.06821	67	1.06508	1.00425
23	0.92	6.9	61.2	8.07	8.09968	36.8	0.6	0.71272	8.03	8.09968	44.9	0.7127	0.69608	8.28	8.09968	45	0.71111	0.68535

Test #3

		0 hour		4 hour					8 hour					12 hour				
X	X/L	pH init	Co	pH exp	pH Pred	C (NO3)	C/Co	C/Co Pr	pH exp	pH Pred	C (N	C/Co	C/Co Pr	pH exp	pH Pred	C	C/Co	C/Co Pr
2.1	0.08	6.81	64.1	4.4	4.59	72.2	1.1	1.11832	4.59	4.59	71.4	1.13333	1.1405	4.59	4.59	73	1.16032	1.15347
4.2	0.17	6.85	64.2	4.94	5.70813	72	1.1	1.11406	4.88	5.38055	70.2	1.11429	1.138	4.82	5.21793	70	1.11587	1.15166
8.3	0.33	6.85	63.2	6.58	6.76175	68.5	1.1	1.10224	6.35	6.40313	69.1	1.09683	1.12989	6.01	6.12709	68	1.0746	1.14592
13	0.5	7.05	62.6	6.98	6.98769	68.5	1.1	1.09764	6.77	7	67.8	1.07619	1.03368	6.73	7	68	1.09048	1.13251
17	0.67	7.05	63.5	7.1	7.36391	67.2	1.1	1.08725	6.94	7.60696	68.5	1.0873	1.10031	6.8	7	68	1.08413	1.13251
21	0.83	7.05	65.9	9.94	9.5	48.7	0.8	0.83983	9.9	9.5	52.1	0.82698	0.86201	9.21	9.5	59	0.93175	0.87498

Test #4

		0 hour		4 hour					8 hour				
X	X/L	pH init	Co	pH exp	pH Pred	C (NO3)	C/Co	C/Co Pr	pH exp	pH Pred	C (N	C/Co	C/Co Pr
2.1	0.08	6.9	66.7	3.8	5.75007	54	1	1.02739	5.2	5.75007	70.5	0	1.04957
6.3	0.25	6.8	64.7	6.5	6.54365	66.1	1	1.0194	6.5	6.31561	69.3	1.11429	1.04456
10	0.42	6.9	64.5	6.8	6.94407	66.4	1.1	1.01221	6.6	6.81789	66.5	1.09683	1.03698
15	0.58	7	65.1	6.8	7	66.4	1.1	1.01096	6.8	6.97632	67.7	1.07619	1.03368
19	0.75	7.1	65.8	6.9	7.00964	65.8	1	1.01074	6.9	7.02205	67.1	1.0873	1.03263
23	0.92	7.2	67.1	7.8	7.79934	55.2	0.9	0.98277	7.4	7.79934	59.2	0.82698	1.00495

Test #5

		0 hour		4 hour					8 hour					12 hour				
X	X/L	pH init	Co	pH exp	pH Pred	C (NO3)	C/Co	C/Co Pr	pH exp	pH Pred	C (N	C/Co	C/Co Pr	pH exp	pH Pred	C	C/Co	C/Co Pr
2.1	0.08	6.8	74	3.8	3.8	85.4	1.2	1.26002	3.9	3.8	78.3	1.11857	1.24339	3.9	3.8	81	1.16286	1.23366
6.3	0.25	6.8	70.2	5	5.23581	78.1	1.1	1.23855	5.1	4.88874	75.5	1.07857	1.23018	4.6	4.71192	75	1.07	1.22367
10	0.42	6.9	67	5.5	6.62481	74.8	1.1	1.1537	5.76	6.17361	73	1.04286	1.17811	6.6	5.85615	75	1.07286	1.18796
15	0.58	7	68	6.5	6.9859	73.4	1	1.10454	6.98	6.92076	72.8	1.04	1.09813	6.9	6.78771	74	1.05429	1.10733
19	0.75	7.2	69	5.7	7.01989	58.2	0.8	1.09893	7.04	7.04486	62.1	0.88714	1.07805	7.1	7	70	1.00286	1.07537
23	0.92	7.4	68	8	8	50.4	0.7	0.81959	8.2	8.2	34.8	0.49714	0.70395	8.1	8.2	46	0.65	0.69422

Test #6

		0 hour		4 hour					8 hour					12 hour				
X	X/L	pH init	Co	pH exp	pH Pred	C (NO3)	C/Co	C/Co Pr	pH exp	pH Pred	C (N	C/Co	C/Co Pr	pH exp	pH Pred	C	C/Co	C/Co Pr
2.1	0.08	7	120	3.79	3.8	132.3	1.1	1.04277	3.82	3.8	135	1.1082	1.08436	3.78	3.8	137	1.19967	1.10869
6.3	0.25	7	121	5.95	5.20181	129.5	1.1	1.04153	6.24	4.85589	131	1.07623	1.0836	4.36	4.68055	136	1.11721	1.10811
10	0.42	7	122	6.46	6.58348	128.1	1.1	1.0366	6.89	6.11549	130	1.06311	1.08065	6.74	5.79493	133	1.09344	1.11561
15	0.58	7	122	6.6	6.98218	127.3	1	1.03337	7.27	7	130	1.06557	1.07479	7	7	134	1.1	1.09912
19	0.75	7	121	6.69	7.7043	124.5	1	1.023	8.1	8.01832	128	1.04918	1.05714	7.4	7	136	1.11721	1.09912
23	0.92	7	122	9.86	10	101.1	0.8	0.84274	10	10	114	0.93525	0.88433	10.12	10	109	0.89098	0.90365

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