Soil Chemistry Effects and Flow Prediction in Remediation of Soils by Electric Fields

by

John Mason Dzenitis


Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 1996

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

This work addresses processes occurring during removal of contaminants from soils using electric fields, termed electroremediation. The technique uses an applied electric field to drive charged species by migration and the bulk solution by electroosmosis. These transport mechanisms, as well as those of diffusion and pressure-driven convection, are combined with equilibrium chemistry models in a numerical code that describes the multispecies electrochemical transport.

To enable prediction of varying electroosmotic flow, the dependencies of the soil surface potential are determined by electrophoresis measurements. To allow accurate description of the system chemistry, the effect of the soil on pore solution chemistry is explored by soil titrations and elemental analyses of the resulting solutions. Candidate chemical equilibrium models are developed from the data using acid/base, cation exchange, and aluminum reactions.

Numerical simulations are compared to laboratory experiments of electroremediation in kaolin clay with a sodium chloride background electrolyte. It is found that a soil chemistry model involving cation exchange and aluminum chemistry must be included to describe the process accurately. Varying electroosmotic flow is successfully predicted, but only until the development of a low ionic strength region in the medium. The insight gained allows the mechanisms of electroosmotic flow reversal and cessation to be positively identified.

As importantly, this investigation finds the low ionic strength region as a likely occurrence in many systems with or without significant soil chemistry. The region is shown to have several detrimental effects, including drastic reduction of charged contaminant migration rates in addition to cessation of electroosmotic flow. The understanding gleaned from this work points to electrode treatment approaches to avoid the condition and make the electroremediation technique more robust in practice.

Thesis Supervisor: Ronald F. Probst
Title: Ford Professor of Engineering
Acknowledgments

This work was supported in part by the Office of Science and Technology within the U.S. Department of Energy’s Office of Environmental Restoration and Waste Management, under the Contaminant Plumes Containment and Remediation Focus Area and the U.S. Environmental Protection Agency Northeast Hazardous Substance Research Center at New Jersey Institute of Technology, and by the John F. Hennessy Fellowship for Environmental Studies.

I thank my thesis advisor, Professor Ronald F. Probstin, for his guidance during this work. I cannot hope to match his intellect, but I do hope to have his level of energy throughout my career. Actually, I would like to have his level of energy at any point in my career. My gratitude also goes to the other members of my thesis committee, Profs. Aion A. Sonin and Lynn W. Gelhar and Dr. R. Edwin Hicks, for helping me improve this work. Dr. Hicks, in particular, has endured over three years of questioning.

The students, faculty, and staff of the Fluid Mechanics Laboratory helped me in this work and in my stay at MIT. My friend Richard Jacobs is foremost in my mind; our technical and personal discussions were always enlightening and enjoyable. Sebastian Tondorf got me started in the laboratory, and the mechanical contributions of Dick Fenner and the administrative efforts of Virginia Brambilla have kept me going. Other friends here and elsewhere were less involved with my work, but more involved in the rest of my life. I am lucky to know all of them.

My greatest appreciation and love go to my family. My parents and brothers have put up with me for some time, and my wife Beth has now entered into the fracas. I hope to show her my gratitude by making our life together more fun than anyone sees fit.
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Nomenclature

\[ a \quad \text{effective pore radius, m} \]
\[ A \quad \text{area, m}^2 \]
\[ Alk \quad \text{alkalinity, net charge concentration from strong bases, mol m}^{-3} = \text{mM} \]
\[ c \quad \text{concentration, mol m}^{-3} = \text{mM} \]
\[ d \quad \text{relative mobility parameter in steady-state analysis} \]
\[ D \quad \text{diffusion coefficient, m}^2 \text{ s}^{-1} \]
\[ E \quad \text{electric field, } E = -\nabla \phi, \text{ V m}^{-1} \]
\[ F \quad \text{Faraday's constant, 96,487 C mol}^{-1} \]
\[ g \quad \text{gravitational acceleration, m s}^{-2} \]
\[ i \quad \text{current density, A m}^{-2} \]
\[ I \quad \text{current, A} \]
\[ I \quad \text{ionic strength, } I = \frac{1}{2} \sum z_i^2 c_i, \text{ mol m}^{-3} = \text{mM} \]
\[ j \quad \text{dimensionless current in short-time analysis, } j = i/i_0 \]
\[ j \quad \text{interstitial species flux, mol s}^{-1} \text{ m}^{-2} \]
\[ k_e \quad \text{electroosmotic permeability, } k_e = -\varepsilon \eta \zeta / \tau^2, \text{ N V}^{-1} = \text{kg m}^{-1} \text{ s}^{-2} \text{ V}^{-1} \]
\[ k_h \quad \text{hydraulic permeability, N Pa}^{-1} = \text{m}^2 \]
\[ K \quad \text{equilibrium coefficient} \]
\[ l \quad \text{dimensionless length in steady-state analysis} \]
\[ L \quad \text{length or length of medium, m} \]
\[ L_s \quad \text{length of anode binary region in steady-state analysis, m} \]
\[ N_R \quad \text{number of reactions} \]
\[ N_s \quad \text{number of species} \]
\[ N_T \quad \text{number of total quantities} \]
\[ p \quad \text{total hydrostatic pressure, } \nabla p = \nabla p_s - \rho g, \text{ Pa} \]
\[ p_s \quad \text{static pressure, Pa} \]
\[ Pe_a \quad \text{anode region Peclet number in steady-state analysis, } Pe_a = uL/D_a \]
\[ Pe_c \quad \text{cathode region Peclet number in steady-state analysis, } Pe_c = -uL/D_c \]
\[ Q \quad \text{volumetric flow rate, m}^3 \text{ s}^{-1} \]
\[ R_i \quad \text{Riemann invariant in short-time analysis} \]
\[ R_i \quad \text{species generation rate, mol m}^{-3} \text{ s}^{-1} \]
\( R \) universal gas constant, 8.3143 J mol\(^{-1}\) K\(^{-1}\)

\( RT/F = 0.02569 \) V at 298 K

\( s_i \) dimensionless partial conductivity in short-time analysis

\( t \) time, s

\( T \) concentration of a chemical total quantity, mol m\(^3\)

\( u \) velocity, m s\(^{-1}\)

\( u_{30} \) characteristic velocity in short-time analysis, \( u_{30} = |Fz_i v_i E_0| \), m s\(^{-1}\)

\( U \) particle velocity in electrophoresis, m s\(^{-1}\)

\( v \) mobility, mol s kg\(^{-1}\)

\( V \) volume, m\(^3\)

\( x \) distance from anode end of medium, m

\( z \) charge number

\( \alpha \) ionization fraction

\( \alpha_{\text{tot}} \) total coefficient

\( \alpha_i \) relative mobility in short-time analysis, \( \alpha_i = -z_i v_i / (z_i v_s) \)

\( \varepsilon \) permittivity, 8.854 \( \cdot \) 10\(^{-12}\) C V\(^{-1}\) m\(^{-1}\) (vacuum), 6.93 \( \cdot \) 10\(^{-10}\) C V\(^{-1}\) m\(^{-1}\) (298 K water)

\( \phi \) electric potential, V

\( \eta \) dimensionless position in short-time analysis

\( \lambda \) Debye length, \( \lambda = \sqrt{(\varepsilon RT) / 2IF^2} \), m

\( \dot{\lambda} \) dimensionless propagation velocity in short-time analysis

\( \mu \) viscosity, kg m\(^{-1}\) s\(^{-1}\)

\( n \) stoichiometric coefficient

\( \rho \) density, kg m\(^3\)

\( \rho_e \) electric charge density, \( \rho_e = F \sum z_i c_i = -\varepsilon \nabla^2 \phi \), C m\(^{-3}\)

\( \sigma \) interstitial electrical conductivity, \( \sigma = F^2 \sum z_i^2 c_i v_i / \tau^2 + \sigma_s \), S m\(^{-1}\) = A V\(^{-1}\) m\(^{-1}\)

\( \sigma_i \) partial conductivity of species \( i \) in short-time analysis, S m\(^{-1}\) = A V\(^{-1}\) m\(^{-1}\)

\( \sigma_s \) surface conductivity, S m\(^{-1}\)

\( \tau \) dimensionless time in short-time analysis

\( \tau \) tortuosity, \( m_{\text{pore}} / m_{\text{medium}} \)

\( \zeta \) zeta-potential or surface potential, V
Subscripts

+  cation of binary electrolyte
-  anion of binary electrolyte
0  original or leading zone in short-time analysis
0  leading zone in short-time analysis
1  initial coion of 2 in short-time analysis
2  replacing ion in short-time analysis
3  initial counterion of 2 in short-time analysis
e  electroosmotic
h  hydraulic
i  initial
r  electrode reservoir
a  anode
c  cathode
m  measured or porous medium
Ec  constant potential in short-time analysis
t  terminating zone in short-time analysis
ic  constant current in short-time analysis
i  with reference to ith species
j  with reference to jth species
p  pore coordinates
s  surface
T  total

Superscripts

'  dimensionless
c  convection
d  diffusion
m  migration
1. Introduction

One of the major environmental problems in the United States today is the remediation of soils contaminated by past actions of both the government and private sectors. The slow dispersion of contaminants in soils, compared to the atmosphere and surface waters, presents both unique and difficult problems. The soil contaminants can prevail at poisonous levels for long periods of time, but an optimistic view is that this time can be used for remediation of the soil. Excavation followed by incineration or washing is the most established approach to soil cleanup. Innovative in situ methods have recently been gaining interest because of their avoidance of the cost of excavation, the dangers associated with exposing the contaminated soil to the atmosphere, and the possibilities of converting a ground pollution problem to an air pollution one.

One in situ method is bioremediation, wherein microbes are used to break down contaminants within the soil medium. Vapor extraction is an in situ air stripping process for volatile contaminants. Another approach is the “pump & treat” or “flushing” method, using source and sink wells to drive soil liquid with pressure differences. Of these three, only pump & treat would be applicable to heavy metal contaminants. All of these methods are ineffective in low hydraulic permeability soils such as clays because of the difficulty of moving fluids in such a medium.

Electroremediation is an innovative in situ approach that avoids the shortcomings of the methods above. In this method electrodes are inserted into the ground and a dc electric field applied. The field causes movement of contaminants to the electrode reservoirs by electroosmosis (for charged soil surfaces) and/or by migration (for charged contaminants) [Probstn 1994, Probstn and Hicks 1993]. Migration is effective for charged contaminants such as heavy metals; electroosmosis is most effective for uncharged contaminants that move with the bulk liquid, like soluble organic molecules. For example, electroosmosis can generate velocities on the order of $10^7$ m/s (10 mm/day) with a field of 25 V/m, while a pressure gradient on the order of 100 kPa/m (10 inch H$_2$O/inch) would be required to generate the same flow in tight soils. The same field strength will give migration velocities around $5 \times 10^7$ m/s (50 mm/day).

The potential advantages of electroremediation have made it an active area of research in recent years, and the experimental work has been fairly plentiful. Laboratory experiments
on heavy metals (dominated by migration) include Runnels and Larson [1986], Hamed et al. [1991], Lindgren et al. [1992], Pamukcu and Wittle [1992], Acar and Alshawabkeh [1993], Hicks and Tondorf [1994], Acar et al. [1994], Acar et al. [1995], and Wong et al. [1996]. The work before 1994 is characterized by moving the metals but not necessarily removing them from the soil. Around this time the importance of the metal pH chemistry related to electrode reactions was fully recognized, and this led to more success in the latter works. The primary field work on metals has been performed by the Geokinetics company in The Netherlands [Lageman 1993]. There was mixed success depending on the chemical conditions in the soil, and the pH was identified as the key factor.

Organic laboratory experiments (dominated by electroosmosis) include Renaud and Probst [1987], Shapiro et al. [1989], Bruell et al. [1992], Acar et al. [1992], and Shapiro and Probst [1993]. High removal fractions were achieved in cases where electroosmotic flow was maintained to displace all of the liquid. However, in many cases the flow rate varied or ceased, and complete removal of the contaminant was not achieved. This problem has been recognized as involving electrode processes, and was addressed practically by Ho et al. [1995]. They placed “treatment zones” in the region between the electrodes so less total movement of the liquid was required. This approach was used in a successful field demonstration [Athmer and Ho 1995] by a consortium involving Monsanto, DuPont, General Electric, the Environmental Protection Agency, and the Department of Energy.

It can be seen from the comments above that the effects of chemical changes in the system have a great impact for both migration and electroosmosis in electroremediation. This was recognized by Shapiro et al. [1989] in their pioneering work modeling the detailed multispecies transport including effects of migration, convection, diffusion, and chemical reactions. Their model has been generalized and extended by Jacobs and Probst [1996]. Despite the detail of these models, the electroosmotic flow velocity is taken as being linearly proportional to the applied field. The constant of proportionality is based on matching a portion of the experimental flow, so the model is not predictive in terms of convective velocity. More significantly, the varying flow rates seen in experiments are not reproduced and the causes of flow cessation cannot be determined.

Eykholt was the first to include dependencies required to model varying electroosmotic flow [Eykholt 1992, Eykholt and Daniel 1994]. His model did show varying flow rate, and he was able to predict a change in the direction of electroosmotic flow when acid was added to the cathode reservoir. However, there was no quantitative agreement between his experiments and numerical simulations. It could not be determined whether this was a problem with the modeling approach or with the experiments themselves.
The main goal of this work is to determine the mechanisms of electroosmotic flow variation and cessation in electroremediation. In so doing, a fully predictive model of electroremediation must be created that includes no “free” parameters. This involves performing a wide variety of independent experiments to determine the physicochemical behavior of the medium, then incorporating this information in a detailed yet practical numerical transport model. The chemical effect of the soil has been traditionally overlooked, but it emerges here as an important factor in the system behavior. On a wider scale, the level of understanding of the chemical and electrode processes developed here will be useful for electroremediation work emphasizing migration as well as electroosmosis.

The next chapter, *Model*, begins by introducing the mass transport and chemical reaction framework of the multispecies electrochemical transport model used. This chapter also introduces a simple electrochemical transport example useful for later reference. *Experiments* details the independent measurements taken to determine parameters for the electroremediation model, as well as the electroremediation experiments that are used to test the simulations in *Applications of models to experiments*. In *Closing*, a discussion extending insight gained from the *Applications* chapter is given, followed by a summary of conclusions and recommendations for future work.
2. Model

In this chapter, the mathematical model used to describe the transport processes during electroremediation is presented in 2.1 Mass transport model and 2.2 Chemical reaction model. A fundamental case that captures much of the important behavior is examined in 2.3 Simple example. In that section, computational results are presented, followed by two analytical treatments that give a more physical understanding of the system’s behavior. The features and analyses of this simple case are used in later chapters.

2.1 Mass transport model

The basis of the electrochemical mass transport model used in this work was introduced by Shapiro et al. [1989]. The approach has proven successful in reproducing the experimental results of both organic and heavy metal contaminant removal [Shapiro and Probstein 1993, Jacobs et al. 1994, Hicks and Tondorf 1994]. Jacobs and Probstein [1996] generalized the earlier formulation to handle multidimensional domains and more complex chemical and physical species transformations. The outline presented here rests heavily on Jacobs [1995] and on the fundamental theory and details of other works [Probstein 1994, Shapiro 1990]; details are avoided here except when useful for later reference. The experiments and numerical simulations in this work are one-dimensional, but the transport equations are given in vector notation for completeness and cleanliness. The vectors below could be replaced with their x component, and the operator $\nabla$ replaced with $\frac{\partial}{\partial x}$.

2.1.1 Species conservation

The macroscopic mass conservation equation of a species $i$ can be written

$$\frac{\partial c_i}{\partial t} + \nabla \cdot j_i = R_i$$

where $c_i$ is the average molar concentration in terms of the liquid volume (mol m$^3$ = mM), $j_i$ is the interstitial flux (mol s$^{-1}$ m$^{-2}$) through the pore cross-sectional area, and $R_i$ is the species generation from chemical reactions and physical transformations (e.g., adsorption). Here the porosity $n$ (ratio of liquid to total medium volume) has been assumed to be
constant and drops out of the equation, although heterogeneous porosity could be easily included.

Equation 3.2 looks the same as a continuous medium equation, but particular care needs to be taken in the spatial scales. First, since the equation is macroscopic, any differential scale still needs to be large enough to represent the average medium well. Second, all species (including surface species, precipitates, et cetera) can be represented, but their concentrations must be defined in terms of the interstitial or pore dimension. Finally, \( c \) and \( R \) are expressed in terms of the interstitial dimension but the operator \( \nabla \) is expressed in terms of the total medium dimension. This means that the fluxes \( j \) must be expressed in such a way to convert the pore-scale driving force to a medium-scale driving force.

### 2.1.2 Species fluxes

The solutions here are assumed to be dilute, and the total flux \( j_i \) of a species \( i \) is a sum of independent contributions from migration, diffusion, and convection. The concentrations \( c_i \) are local “bulk” averages and the fluxes are written in terms of \( c_i \), so only an average movement is described. In particular, transport along the usually thin double layer at the solid-liquid boundary is neglected. Also neglected is the effect of hydrodynamic dispersion; this will be justified after the convection term is described.

#### 2.1.2.1 Diffusion flux

The flux from diffusion is given by Fick’s law

\[
j_i^d = -\frac{D_i}{\tau^2} \nabla c_i,
\]

where \( D_i \) is the molecular diffusion coefficient (m\(^2\) s\(^{-1}\)) and \( \tau \) is the tortuosity \((m_{\text{pore}}/m_{\text{medium}})\). The contribution from diffusion is often small compared to the convection and migration terms. The diffusion coefficients for some (e.g., adsorbed) species are zero.

The tortuosity is the average (meandering) distance that a particle travels relative to a direct (impossible) path through the medium. In this definition \( \tau \geq 1 \), although the term “tortuosity” also appears in literature [e.g., Bear 1972] as the inverse or the inverse-squared of the term here. It can be seen that the tortuosity achieves the conversion from pore-scale to medium-scale driving force mentioned above. In effect, one \( \tau \) each is used to modify the \( \nabla \) operators in Equations 3.2 and 2.2. For convenience in handling the equations, \( \tau^2 \) could be absorbed as a factor that decreases the molecular parameters \( (D_i, \nu_i, \text{ and } 1/\mu) \) which relate driving forces to fluxes.
2.1.2.2 Migration flux

The migration contribution to the flux is

\[ j^m = c_i \left(-Fz_i \frac{v_i}{\tau^2} \nabla \phi \right) \]  

2.3

where \( F \) is Faraday’s constant (96,487 C mol\(^{-1}\)), \( z_i \) is the charge number, \( v_i \) is the mobility (mol s kg\(^{-1}\)), and \( \phi \) is the electric potential (V). The term in parentheses is the migration velocity of a species. Since the electric field strength is \( E = -\nabla \phi \), a positively charged species moves in the direction of the field. Note also that uncharged species have zero charge number and adsorbed species have zero mobility, so neither move by migration.

2.1.2.3 Convection flux

The flux resulting from convection is

\[ j^c = c_i u_i \]  

2.4

where \( u_i = (u \text{ or } 0) \) and \( u \) is the average liquid velocity (m s\(^{-1}\)). The 0 condition is needed for species that do not move, such as solids. Equation 2.4 appears to be the simplest of the fluxes only because the velocity has not yet been defined. In most electrochemical systems, the bulk flow is determined by the standard equations of fluid mechanics, and convection is then decoupled from the electric field’s effects [Newman 1991]. In electroremediation, however, the electric field causes the convection and the two are intimately coupled in the mechanism of electroosmosis. Predicting electroosmotic flow during electroremediation is one focus of this work, so a more detailed look into the phenomena is undertaken.

Moving temporarily from the macroscale of the porous medium to the microscale of a pore, the momentum equation becomes

\[ 0 = -\nabla p_r + \mu \nabla^2 u + \rho g + (\varepsilon \nabla^2 \phi) \nabla \phi. \]  

2.5

where \( p_r \) is the static pressure (kg m\(^{-1}\) s\(^{-2}\)), \( \mu \) is the viscosity of the liquid (kg m\(^{-1}\) s\(^{-1}\)), \( \rho \) is its density (kg m\(^{-3}\)), \( g \) is the gravitational body force (kg m s\(^{-2}\)), and \( \varepsilon \) is the permittivity of the fluid (C V\(^{-1}\) m\(^{-1}\)). The body force per volume resulting from gravity is often incorporated into a total hydrostatic pressure as \( \nabla p = \nabla p_r - \rho g \). In addition to the usual gravitational body force, there is another resulting from a local charge density \( \rho_e = F \sum z_i c_i = -\varepsilon \nabla^2 \phi \) and the electric field \( E = -\nabla \phi \). The charge density results from the presence of a charged solid in a solution of ions, and the resulting field is typically large in magnitude but small in extent. The electric potential at the interface between the fixed solid and the mobile liquid is called the zeta-potential (\( \zeta \), in Volts), which is nondimensionalized as
\[ \zeta' = \frac{\zeta}{(RT/F)} \]  \hspace{1cm} 2.6

where the term in parenthesis is a combination of the gas constant, temperature, and Faraday's constant, with a value of 0.02569 V at 298.15 K. For most soils \(-4 \leq \zeta' \leq 1 \) [e.g., Hunter 1981]. Another important parameter is the Debye length \( \lambda'_D \) (m), which when nondimensionalized in terms of a characteristic distance \( a \) is

\[ \lambda' = \frac{1}{a} \left[ \frac{eRT}{2IF^2} \right]^{1/2}. \]  \hspace{1cm} 2.7

The ionic strength \( I \) has units of mol m\(^{-3} \) where the mole quantity is charge, and

\[ I = \frac{1}{2} \sum z^2 c_i. \]  \hspace{1cm} 2.8

For low potentials the Debye length is the scale of \( 1/e \) decay in the potential or field away from the interface [Probststein 1994]. A solution with ionic strength of 1 mM has a Debye length of 9.61 \( \cdot 10^{-9} \) m at 25°C; for a surface with a zeta-potential of -9.61 mV the field strength at the surface is then 1 \( \cdot 10^6 \) V m\(^{-1} \). It can be seen that the field's extent is small and its magnitude is large, as noted above.

Most derivations of electroosmosis are for a cylindrical capillary pore geometry with large length compared to radius, \( L/a >> 1 \), with assumptions about the magnitude of \( \lambda' \) or \( \zeta' \). For small Debye length and constant zeta-potential, pressure gradient, and electric field, Probststein [1994] shows that Equation 2.5 can be solved to give

\[ u_p = \frac{r^2 - a^2}{4\mu} \frac{dp}{dz} + \frac{e\zeta}{\mu} \frac{d\phi}{dz} \]  \hspace{1cm} 2.9

and integrated across the capillary to give an average velocity

\[ \overline{u_p} = -\frac{a^2}{8\mu} \frac{dp}{dz} + \frac{e\zeta}{\mu} \frac{d\phi}{dz}. \]  \hspace{1cm} 2.10

The subscript \( p \) is used to emphasize that this is a cylindrical pore velocity \( u_p \) in local coordinate \( r \) and not the macroscopic interstitial velocity in medium coordinates. Another analytical solution is possible without the small-Debye-length assumption if the surface potential is taken to be small [e.g., Rice and Whitehead 1965],

\[ \overline{u_p} = -\frac{a^2}{8\mu} \frac{dp}{dz} + \left[ 1 - 2\lambda \frac{I_1(1/\lambda')}{I_0(1/\lambda')} \right] \frac{e\zeta}{\mu} \frac{d\phi}{dz}. \]  \hspace{1cm} 2.11
where the \( I \) terms are modified Bessel functions of the first kind. The term in square brackets amounts to a nonzero-Debye-length attenuation of the maximum velocity that a given zeta-potential and field strength could induce. This attenuation factor is \((0.98, 0.81, 0.11)\) for \( \lambda' = (0.01, 0.1, 1) \), showing that the small-Debye-length assumption breaks down near 0.1. Although Equation 2.11 was derived for \( |\zeta'| \ll 1 \), comparisons with numerical solutions without that assumption [Gross and Osterle 1968] show that the results are good for \( |\zeta'| \leq 2 \).

Equations 2.9-2.11 were developed assuming all parameters and the two gradients are uniform in space, but in this work non-uniform conditions are common. It is well known in porous media flow [e.g., Bear 1972] that the pressure-driven term can be generalized to an isotropic medium with varying properties to give the macroscale interstitial velocity as

\[
\mathbf{u}_h = -\frac{k_A}{n\mu} \nabla p
\]

2.12

where \( k_A \) is the scalar hydraulic permeability \((\text{N Pa}^{-1} = \text{m}^2)\) and all of the terms may vary in space. The work of Anderson and Idol [1985] allows a similar extension to be made to the electric potential-driven term of Equation 2.10. They prove mathematically what many assume implicitly,

\[
\left\langle \mu \zeta \frac{d\phi}{dz} \right\rangle = \frac{\varepsilon}{\mu} \left\langle f \right\rangle \quad \text{where} \quad \left\langle f \right\rangle = \frac{1}{2L} \int_{-L}^{L} f(z)dz.
\]

2.13

This means that varying zeta-potential and electric field can be handled in a spatially-averaged sense. Making this average correspond to an elemental, three-dimensional volume of porous medium and assuming that it can be linearly combined with the pressure term gives

\[
\mathbf{u} = \mathbf{u}_h + \mathbf{u}_e = -\frac{k_A}{n\mu} \nabla p + \frac{\varepsilon \zeta}{\mu \tau_s} \nabla \phi = -\frac{k_A}{n\mu} \nabla p - \frac{k_e}{n\mu} \nabla \phi
\]

2.14

where the electroosmotic permeability \( k_e \) has units of \( \text{kg m}^{-2} \text{V}^{-1} \) or \( \text{N V}^{-1} \) and all terms may vary in space. Equation 2.14 is used by Jacobs and Probstein [1996] (with uniform \( k_A \)) and here (with varying \( k_A \)) to get the velocity needed in Equation 2.4. The flow is then based on the assumption of small Debye length. An extension of Anderson and Idol’s [1985] work to large Debye length has not been found, and in a strict sense corrections such as that in Equation 2.11 cannot be made on the medium scale.

In electroremediation work, \( k_e, \zeta, \) or its integral is typically taken to be constant, which leads to a prediction of flow that is a constant multiple of the applied electric potential. This behavior is seen in some experiments, but many others show flow that varies markedly and
in some cases stops altogether [Shapiro et al. 1989, Hamed et al. 1991, Jacobs et al. 1994, Acar et al. 1995]. Eykholt [1992] was the first to incorporate spatially varying zeta-potential in a framework similar to that of Shapiro et al. [1989] to explain the electroosmotic flow variation. His work was significant in showing the importance of local  ζ variations on the flow in a qualitative sense, but did not model the flow with an accuracy that could be called prediction. One goal here is to build from these past works to a level where varying electroosmotic flow can be predicted, with the object of enhancing contaminant removal in mind.

Justification for neglecting hydrodynamic dispersion as a first approximation can now be given. This dispersion results from a difference between the average solvent velocity and local velocities that species experience. Starting from uniform n, μ, k_s and ∇φ and incompressible flow (∇·u = 0), Equation 2.14 shows that ∇p is uniform if k_s is either uniform or varies perpendicularly to ∇p. If there is no applied pressure on the boundaries of the region, then ∇p = 0. Equation 2.9 then indicates that the velocity profile is flat (with slip at the solid-liquid interface). There is no difference between the average velocities and local velocities throughout the medium, so there is no dispersion mechanism. This is only a first approximation because variations in the electric field or zeta-potential will arise as the process evolves, causing pressure variations and associated velocity differences. This effect will still be small in the bench-top experiments, but on a field scale this and k_s heterogeneity effects could be significant.

2.1.3 Scalar fields

The fluxes have now all been specified in terms of the scalar fields c, φ, and p. Equations and boundary conditions for these fields must be specified to finish the description of the system.

2.1.3.1 Concentration distribution

The concentrations are tracked in time by integrating Equation 3.2 after the fluxes and reactions have been specified (see 2.2 Chemical reaction model as well). Typical boundary conditions would have no flux on the external domain; the concentrations at the internal boundaries (the electrode reservoirs) require some discussion.

It is assumed that an electrode reservoir has volume V_e, constant area in contact with the medium A_m, and is well-mixed so there is uniform concentration c_e. Integrating Equation 3.2 over the reservoir volume gives an ordinary differential equation for the reservoir mass of species i
\[
\frac{d}{dt} V_r c_{ir} = Q_{in} c_{i, in} - Q_{out} c_{i, out} - \int_{A_m} j_i \cdot dA + V_r R^b_i + \int_{A_n} \frac{V_e}{F} i \cdot dA
\]

where \( dA \) is defined to point out of the reservoir into the medium. The flux term of Equation 3.2 has become the first three terms on the right hand side. \( Q \) represents the volumetric flow of influx and efflux streams from external sources; usually \( Q_{in} = Q_{out} \) so \( V_r \) is constant. The \( j \) integral determines the mass of \( i \) entering or leaving the reservoir by the mechanisms of Section 2.1.2. For the convection term (Equation 2.4), the concentration \( c_{ir} \) is used if the flow is outward, and the concentration in the medium is used if the flow is inward. The last two terms are generation terms, which have been split into bulk reactions and electrochemical surface reactions. \( i \) is the current density and \( V_e \) is an electrochemical stoichiometric coefficient. This coefficient gives the moles of species \( i \) generated or destroyed per mole of charge in the electric circuit; for example, \( V_{e_i} = 1 \) for both \( H^+ \) and \( OH^- \) if water electrolysis is the only type of electrochemical reaction in the system.

\[
\frac{1}{2} H_2O = e^- + H^+ + \frac{1}{4} O_2 (g) \quad \text{(anode)}
\]

\[
H_2O + e^- = OH^- + \frac{1}{2} H_2(g) \quad \text{(cathode)}
\]

Electrochemical reactions are necessary if the charge carrier in the electrical domain is to be converted to a charge carrier in the chemical domain.

2.1.3.2 Electric potential distribution

The electric potential \( \phi \) is theoretically obtainable by solving Poisson’s equation

\[
\nabla^2 \phi = -\frac{\rho_e}{\varepsilon} = -\frac{F}{\varepsilon} \sum z_i c_i.
\]

However, the \( F/\varepsilon \) factor is so large that small errors in the concentrations would lead to large errors in the potential. This difficulty can be turned to an advantage by replacing Poisson’s equation with the electroneutrality condition [Newman 1991]

\[
\sum z_i c_i = 0.
\]

This is a good approximation everywhere except near charged solid surfaces as were treated in Section 2.1.2.3. It is emphasized that since Equation 2.17 was replaced with Equation 2.18, it is not true that \( \nabla^2 \phi = 0 \).

The electroneutrality condition is used in the following manner: The equation for total charge transport is found by multiplying Equation 3.2 by \( Fz_i \) and summing over all species plus a surface conductance \( \sigma_j \) to get
\[ F \frac{\partial}{\partial t} \left( \sum z_i c_i \right) + F \sum z_i \nabla \cdot j_i + \nabla \cdot (\sigma \nabla \phi) = F \sum z_i R_i. \]  

2.19

The electroneutrality condition makes the first term zero, and the right hand side is zero since charge is not created through chemical reactions. Substituting the flux terms found in Section 2.1.2, the convective contribution is zero because of electroneutrality, and

\[ -\nabla \cdot (\sigma \nabla \phi) = \nabla \cdot \left( F \sum z_i \frac{D_i}{\tau^2} \nabla c_i \right) \]  

2.20

where the Ohm’s law conductivity has been defined as

\[ \sigma = F^2 \sum z_i \frac{v_i}{\tau^2} c_i + \sigma_s. \]  

2.21

At a given time, all of the terms but \( \phi \) are known in Equation 2.20, and this can be solved with appropriate boundary conditions. Note that if the current density is defined as

\[ i = F \sum z_i j_i - \sigma_s \nabla \phi = F \sum \left( -z_i^2 F \frac{v_i}{\tau^2} c_i \nabla \phi - z_i \frac{D_i}{\tau^2} \nabla c_i \right) - \sigma_s \nabla \phi \]  

2.22

then the charge conservation equation is essentially being solved as

\[ \nabla \cdot i = 0. \]  

2.23

In one dimension, this means that the current density is constant throughout the medium.

The multidimensional boundary conditions would typically have no flux at the external boundaries of the domain and either \( i \) or \( \phi \) given on the electrode reservoir boundaries. In one dimension, these conditions are typically either constant current \( i \) or constant applied potential \( \Delta \phi \) across the medium. Another possibility that might be practical in the field would be constant power \( i \Delta \phi \).

2.1.3.3 Pressure distribution

Summing Equation 3.2 for all species including the solvent and assuming the liquid is incompressible gives

\[ \nabla \cdot u = 0 \]  

2.24

in analogy with Equation 2.23. Using Equation 2.14 with constant \( \mu \) and \( n \) gives

\[ -\nabla \cdot (k_s \nabla p) = \nabla \cdot (k_s \nabla \phi), \]  

2.25

in analogy with Equation 2.20, which can be solved for \( p \) after \( \phi \) is known.

The multidimensional boundary conditions would typically have no flux at the external boundaries of the domain and \( p \) given on the electrode reservoir boundaries as atmospheric
pressure; in one dimension this means the applied pressure difference $\Delta p$ is zero. These boundary conditions mean that any convective flow is the result of electroosmosis.
2.2 Chemical reaction model

The chemical reaction model is based on Morel and Hering [1993] and Jacobs [1995]. Chemical reactions and physical transformations (such as adsorption) given as

\[ aA + bB = cC + dD \]

can be written in the general form

\[ \sum_{i=1}^{N_s} \nu_{ji} S_i = 0 \]

where \( \nu_{ji} \) is the stoichiometric coefficient of species \( i \) in reaction \( j \) (positive for products), \( N_s \) is the number of species, and \( S \) is a placeholder for the name of the species. The extent of a reaction \( \xi_j \) can be defined to give

\[ \frac{\partial c_i}{\partial \xi_j} = \nu_{ji} \]

where \( c_i \) is the concentration of species \( i \). It is useful to define “total quantities”

\[ T_k = \sum_{i=1}^{N_s} \alpha_{ik} c_i \]

where the coefficients \( \alpha_{ik} \) are picked such that the total quantities are conserved through chemical reactions,

\[ \frac{\partial T_k}{\partial \xi_j} = \sum_{i=1}^{N_s} \alpha_{ik} \nu_{ji} = 0. \]

The number of species \( i \), total quantities \( k \), and chemical reactions \( j \) are related by \( N_s = N_T + N_r \). The formalism above allows great flexibility but is somewhat obscure; it will be seen in the examples below that identifying useful total quantities is not difficult in practice.

One great advantage of the total quantity approach is decoupling chemical reactions from the transport equations. This is important in numerical solutions because the small time scales for chemical reactions (e.g., complexation, \( 10^{-6} - 10^{-2} \) s [Morel and Hering 1993]) impose too small a time step in the overall simulation (e.g., \( 10^6 \) s). Eliminating the chemical reaction term from the transport takes care of this problem. Multiplying the transport expressions (Equation 3.2) by the total coefficients \( \alpha_{ik} \), summing over \( i \), and making use of Equation 2.29 gives
\[ \frac{\partial T_k}{\partial t} + \sum_{i=1}^{N_f} \alpha_{ik} \vec{v} \cdot \vec{j}_i = \sum_{i=1}^{N_f} \alpha_{ik} R_{ij} = \sum_{i=1}^{N_f} \alpha_{ik} \vec{v}_i \frac{d\xi_j}{dt} = 0. \]

These \( k = 1, \cdots, N_f \) equations are the actual transport equations that are integrated in time. The fluxes \( \vec{j}_i \) still depend on the individual species concentrations, so the \( c_i \)'s must be found. If the species are taken to be in chemical equilibrium, then the mass action laws are

\[ K_j = \prod_{i=1}^{N_f} c_i^{\alpha_{ik}} \]

where \( K_j \) is an equilibrium coefficient. The equilibrium coefficients do not need to be constant and may be defined, if necessary, to be functions of concentration, temperature, et cetera. In this approach the chemical reactions have, in effect, been divided into two groups: those that are fast enough to be considered in equilibrium compared to the transport time, and those that are so slow that they do not occur during the electroremediation process.

Two further chemical simplifications can be made to facilitate solving the transport equations. The first has already been alluded to: the solutions are assumed to be dilute, so the concentration of \( H_2O \) is constant (55.4 \( M \)) and does not need to be treated as a species. The second simplification is to make one total quantity the sum of the species charges by taking \( \alpha_{ii} = z_i \). This makes Equation 2.29 become

\[ T_i = \sum z_i c_i = 0, \]

true everywhere by the electroneutrality condition (Equation 2.18). The total quantity \( T_1 \) then does not need to be included in the transport equations, and electroneutrality is enforced through chemical equilibrium.

To give a concrete example of this framework, consider a system with \( NaCl \), a weak acid \( HA \), and a solid with surface sites \( X \) onto which the weak acid can adsorb. The concentrations of the eight species are represented by italics,

\[ \{ \{ H^+,OH^-,Na^+,Cl^-,HA,A^-,X,XHA \} \} = \{ H,OH,Na,Cl,HA,A,X,XHA \} \]

and five total equations can be written for these eight species

\[ T_1 = T_\ast = H - OH + Na - Cl - A \]
\[ T_2 = T_{Na} = Na \]
\[ T_3 = T_{Cl} = Cl \]
\[ T_4 = T_A = A + HA + XHA \]
\[ T_5 = T_X = X + XHA \]
This means that there must be \( N_s - N_T = N_r = 3 \) equilibrium equations, which could be represented by the mass action equations

\[
K_w = H \cdot OH \\
K_A = A \cdot H \cdot HA^{-1} \\
K_X = X \cdot I \cdot \cdots \cdot XHA^{-1}
\]

This is only one of several reasonable representations for this system, but it has significant advantage over most. Though there are eight species involved in the system, only three total quantity transport equations need to be tracked in time; \( T_1 \) is always zero and \( T_3 \) retains its initial distribution because the solid does not move.
2.3 Simple example

A simple example will illustrate important features of the changes that occur during electroremediation. Consider a system where a constant potential is applied to a medium containing a strong binary electrolyte (NaCl), the only bulk chemical reaction is dissociation of water, the electrode reactions produce $H^+$ and $OH^-$, and there is negligible electroosmotic flow. This situation is approached in systems with high background electrolyte concentration and either low soil surface potential or high hydraulic permeability.

To allow easy comparisons with experiments later, the medium’s length, porosity, and tortuosity are assumed to be 0.15 m, 0.54, and 1.65. For simplicity, the electrode reservoirs on either end of the medium are assumed to have negligible volume so all of the species reside within the medium. The average applied potential is 100 V m$^{-1}$.

After presenting the overall results below (2.3.1 Numerical simulation), two analytical treatments are pursued that give a more physical understanding of the system’s behavior (2.3.2 Short-time analysis, 2.3.3 Steady-state analysis).

2.3.1 Numerical simulation

A numerical implementation of the model described in Sections 2.1 and 2.2 was run for this simplified case. Figure 2.1 shows the progressing concentration distributions plotted as a function of $x' = x/L$, a dimensionless position from the anode end of the medium. Curves are shown for early times (up to $6 \times 10^3$ s = 1.7 hr) and at a later time ($4 \times 10^4$ s = 4.6 days) when the system is in an apparently steady state. The coupled motion of the species can be readily seen throughout the simulation. Sodium and chloride ions move to opposite electrodes under the influence of the applied field, decreasing the concentration at one end and increasing that at the other. Meanwhile, hydrogen and hydroxyl ions created in the electrode reactions from the current flow enter the medium and propagate inward. The medium remains electrically neutral, with $H^+$ or $OH^-$ making up any difference between Na$^+$ and Cl$^-$. At large times, the species have separated into two zones that are dominated by either HCl or NaOH. This acid/base behavior is also reflected in the pH distribution in Figure 2.2.
Figure 2.1: Concentration distributions for the NaCl simulation, showing short-time concentration shifts and linear profiles near steady state.

Figure 2.2: pH distribution for the NaCl simulation.
The increase in ionic strength near each electrode leads to higher conductivities and hence lower electric field strength in those areas, as shown in Figure 2.3. In fact, the conductivity increases everywhere except at one position near the center of the medium. As the electric field becomes larger here, Na\(^+\) and Cl\(^-\) are cleared from the region at greater rates, decreasing the conductivity and further increasing the local electric field strength in a positive feedback mechanism. Since the applied potential is constant in this case, the current density (Figure 2.4) represents the average conductivity of the medium. At first the average conductivity increases as H\(^+\) and OH\(^-\) move into the medium, but then the current drops as the low conductivity region begins to dominate. The drop in conductivity to a plateau is a feature of electroremediation experiments where the electrode reservoirs are not treated to control their chemical changes. The early increase in conductivity before the drop is a feature of systems where a faster ion replaces a slower one (e.g., H\(^+\) replaces Na\(^+\)), as will be discussed below. There is some numerical instability in the simulation when the large field strength forms, but this settles out as the system approaches steady state.

Figure 2.3: Electric field strength for the NaCl simulation at short times and near steady-state.
2.3.2 Short-time analysis

Figure 2.1 showed that at short times the system behaves as two independent zones. Each zone is initially a binary electrolyte and then has a new ion introduced from the electrode reaction; this replacing ion propagates inward while the concentration of the initial coion decreases and the initial counterion increases. With some approximations, this early behavior can be treated analytically in a method described by Denisov et al. [1996] and Baksikii et al. [1989]. The approach is to reduce the order of the transport equations by neglecting diffusion (appropriate at early times), eliminate the counterion concentration using electroneutrality, combine the two transport equations to make only one dependent on time, and solve this by the method of characteristics. The key steps are given below, then applied to this case. The references should be consulted for further detail.

Neglecting diffusion simplifies the convective diffusive equation for dilute species without reactions to

\[
\frac{\partial c_j}{\partial t} + u \cdot \nabla c_j = -z_j v_j F \nabla \cdot (c_j E) \tag{2.37}
\]
which is now first order in space. The current without diffusion is ohmic, \( i = \sigma E \).

Defining the species as 2 = replacing ion \((e.g., H^+)\), 1 = initial coion \((e.g., Na^+)\), and 3 = initial counterion \((e.g., Cl^-)\), the counterion equation is eliminated using electroneutrality so the conductivity can be written as

\[
\sigma = F^2 \sum z_i^2 v_i c_i = F^2 c_{10} z_1^2 v_1 \left[ 1 + \frac{-z_2 v_3}{z_1 v_1} \right] + F^2 c_{20} z_2^2 v_2 \left[ 1 + \frac{-z_3 v_3}{z_2 v_2} \right] = \sigma_1 + \sigma_2. \tag{2.38}
\]

The initial conductivity is defined in terms of the initial coion concentration

\[
\sigma_0 = F^2 c_{10} z_1^2 v_1 \left[ 1 + \frac{-z_2 v_3}{z_1 v_1} \right]. \tag{2.39}
\]

Dimensionless parameters are used in this one-dimensional analysis: \( s_j = \sigma_j / \sigma_0 \) are partial conductivities (essentially concentrations), \( \alpha_j = -z_j v_j / (z_3 v_3) \) are constant relative mobilities, \( j = i / i_0 \) is current, \( \eta = x / L \) is position, and \( \tau = \eta u_{30} / L \) is time where \( u_{30} = |Fz_3 v_3 E_0| \) is a characteristic velocity equal to the velocity of the counterion in the initial electric field. The presence of an external length scale \( L \) is arguably inappropriate since the equations are first order in \( x \) and only one spatial boundary condition can be applied. It turns out that space and time appear as the similarity variable \( \eta / \tau \) and so do not depend on \( L \).

The most important step is transforming the concentrations into Riemann invariants \( R \) in such a way that their time behavior is simplified. The proper combination is

\[
R_1 = \frac{s_1 + s_2}{\alpha_1} \quad R_2 = \frac{s_1 \alpha_2 + s_2 \alpha_1}{s_1 + s_2} \tag{2.40}
\]

and now the inverse transformations are

\[
s_{1,2} = \frac{\alpha_1 \alpha_2 R_1 (R_2 - \alpha_{1,2})}{R_2 (\alpha_1 - \alpha_2)} \quad \text{and} \quad c_{1,2} = s_{1,2} c_{10} \frac{z_1 (1 + \alpha_1)}{z_{1,2} (1 + \alpha_{1,2})}. \tag{2.41}
\]

The transport equations for \( R \) can be written

\[
\frac{\partial R_j}{\partial \tau_k} + \lambda_j (R) \frac{\partial R_j}{\partial \eta} = 0 \tag{2.42}
\]

where \( d \tau_c = j d \tau \) is the time change in a constant current domain. If the current is constant, then \( j = 1 \) and the times are the same; the applied field must change as the medium conductivity changes. On the other hand, if the applied field is constant, then \( j = j(\tau) \) and the constant current time is an expanded or contracted version of the actual time. For now the subscript \( ci \) is dropped, but it will be picked up later.
Equation 2.42 is a total differential when \( \lambda \) is the propagation velocity of a particular value of \( R \). The method of characteristics solution consists of tracking different values of \( R \) in space and time. It can be shown that \( \lambda \) is proportional to the convection velocity, so when this is zero \( R \) is immobile and keeps its initial value throughout the medium; the boundary condition on \( R \) is not involved in the solution. By solving the characteristic equation for \( R \), the behavior of the entire system is determined. Values of \( R \) propagate into the medium with different characteristic velocities depending on \( R \) and \( R \)

\[
\lambda = \frac{R^2}{\alpha_1 \alpha_2 R_1}.
\]

To keep the problem in a form with a simple analytical solution, simple boundary conditions are assumed. If the concentrations in the reservoirs are assumed to change suddenly at \( t = 0 \) and then remain constant, the characteristics will be linear. (This is only a rough approximation of the real situation, where concentrations gradually change as current flows. The appropriateness of this assumption will be addressed later.) The boundary conditions in \( c, s, \) and \( R \) become

\[
\begin{align*}
c_1(x \geq 0, t = 0) &= c_{i0} & s_1(\eta \geq 0, \tau = 0) &= 1 \\
c_2(x \geq 0, t = 0) &= 0 & s_2(\eta \geq 0, \tau = 0) &= 0 \\
c_1(x = 0, t > 0) &= c_{i1} & s_1(\eta = 0, \tau > 0) &= s_{i1} \\
c_2(x = 0, t > 0) &= c_{i2} & s_2(\eta = 0, \tau > 0) &= s_{i2} \\
R_1(\eta > 0, \tau \geq 0) &= 1/\alpha_1 & R_2(\eta \geq 0, \tau = 0) &= \alpha_2 \\
R_2(\eta = 0, \tau > 0) &= \frac{s_{i1} \alpha_2 + s_{i2} \alpha_1}{s_{i1} + s_{i2}}
\end{align*}
\]

where the \( t \) subscript refers to the terminating zone in space, which is the final condition. Substituting the terminating value of \( R \) into the inverse transformation for \( s \) demonstrates that the \( s \) boundary conditions are not unique, which is expected since there is now only one transport equation. One finds that

\[
s_{i2} = \frac{\alpha_2}{\alpha_1} (1 - s_{i1}).
\]

For the assumptions here \( (s_{i1}, s_{i2}) \) have maximum values of \( (1, \alpha_2/\alpha_1) \), and only one can be specified independently. The largest value of \( s \), is the best approximation in this case since Figure 2.1 shows large concentrations of replacing ions at the electrodes. From now on \( (s_{i1}, s_{i2}) = (0, \alpha_2/\alpha_1) \) and hence \( R_2(\eta = 0, \tau > 0) = \alpha_1 \).

Denisov et al. [1996] show that there are two types of solutions depending on the relative mobilities. For \( \alpha_2/\alpha_1 > 1 \) a composition shock wave forms with conditions independent of position and time on either side.
\[ s_1 = \begin{cases} 1, & \text{for } \alpha_1 \leq \eta/\tau \\ 0, & \text{for } 0 \leq \eta/\tau \leq \alpha_1 \end{cases} \]

\[ s_2 = \begin{cases} 0, & \text{for } \alpha_1 \leq \eta/\tau \\ \alpha_2/\alpha_1, & \text{for } 0 \leq \eta/\tau \leq \alpha_1 \end{cases} \]  \(2.46\)

The leading zone has the uniform initial composition and the terminating zone has a uniform composition free of coion. The discontinuity propagates with dimensionless velocity \(\alpha_1\) or dimensional velocity

\[ u_{th} = \alpha_1 u_{30} = u_{10} = u_{2i} = \frac{\alpha_1}{\alpha_2} u_{20} = \frac{E_i}{E_0} u_{20}. \]  \(2.47\)

This means that the shock velocity is the velocity of the coion in the initial field and that of the replacing ion in the terminating field. The terminating field is larger than the initial field because the replacing ion solution has a lower conductivity.

For \(\alpha_1/\alpha_2 < 1\) the changes propagate as diffuse waves of composition, giving three types of zones instead of the two above. The leading and terminating zones have the same composition as those before and after the shock in Equation 2.46. Since their velocities are different, though, there is an additional diffuse zone between them that grows in time.

\[ s_1 = \begin{cases} 1, & \text{for } \alpha_2 \leq \eta/\tau \\ \alpha_2 \left( \frac{\sqrt{\alpha_2 \eta/\tau} - \alpha_1}{(\alpha_2 - \alpha_1) \sqrt{\alpha_2 \eta/\tau}} \right), & \text{for } \alpha_2 \leq \eta/\tau \leq \alpha_2 \end{cases} \]

\[ s_2 = \begin{cases} 0, & \text{for } \alpha_2 \leq \eta/\tau \\ \frac{\alpha_2 (\alpha_2 - \sqrt{\alpha_2 \eta/\tau})}{(\alpha_2 - \alpha_1) \sqrt{\alpha_2 \eta/\tau}}, & \text{for } \alpha_2 \leq \eta/\tau \leq \alpha_2 \\ \alpha_1/\alpha_2, & \text{for } 0 \leq \eta/\tau \leq \alpha_2 \end{cases} \]  \(2.48\)

The leading zone propagates with dimensionless velocity \(\alpha_2\) or dimensional velocity \(u_i = \alpha_2 u_{30} = u_{20}\), which is the velocity of the replacing ion in the initial field. The terminating zone has dimensionless and dimensional velocities of \(\alpha_i^2/\alpha_2\) and

\[ u_i = \frac{\alpha_i^2}{\alpha_2} u_{30} = \frac{\alpha_2}{\alpha_2} u_{10} = \frac{E_i}{E_0} u_{10} = u_{i1} = \left( \frac{\alpha_1}{\alpha_2} \right)^2 u_i. \]  \(2.49\)

The terminating zone velocity is the velocity of the coion in the terminating field, which is smaller than the initial field. The diffuse zone between the leading and terminating zones has varying composition and electric field. In dimensional variables the concentration of the replacing ion in the diffuse zone is

\[ c_2 = c_{10} \frac{z_1 (1 + \alpha_1) \alpha_2}{z_2 (1 + \alpha_2) (\alpha_2 - \alpha_1)} \left( \sqrt{u_{20} t/\chi} - 1 \right). \]  \(2.50\)

In the example case of H\(^+\) and OH\(^-\) entering a medium of NaCl, the two electrode regions both have behavior of the second (diffuse) type above since \(\alpha_{a1}/\alpha_{a2} = 0.66/4.6 = 0.14\).
for H⁺ and Na⁺ and \( \alpha_1/\alpha_2 = 1.5/3.9 = 0.39 \) for O²⁻ and Cl⁻. Diffuse (versus shock) wave behavior is apparent in the concentration distributions of Figure 2.1.

Before comparing the results above to the numerical simulation, the adjusted time scale must be calculated since the simulation was run for constant applied potential instead of current. The current through the medium in this case is found by integrating the conductivity across five different zones (the initial zone plus diffuse and terminating zones propagating in from each electrode),

\[
j = \frac{i}{i_0} = \frac{\sigma_0 E_0}{\sigma_0 E_0} = \left[ \int_0^1 \frac{1}{d\eta} \right]^{-1} = \left[ 1 - \frac{t_{Ec}}{3L} \left( u_{a20} \left[ 1 - \left( \frac{\alpha_{cl}}{\alpha_{c2}} \right)^3 \right] + u_{c20} \left[ 1 - \left( \frac{\alpha_{c1}}{\alpha_{c2}} \right)^3 \right] \right) \right]^{-1}. \tag{2.51}
\]

The cubed terms are generally small compared to unity, so the equation that relates the constant-current and constant-potential times is

\[
t_{uc} = \int_0^{t_{Ec}} j(t') \, dt' = 3t_{mic} \ln \left( 1 - \frac{t_{Ec}}{3t_{mic}} \right)^{-1} \tag{2.52}
\]

where \( t_{mic} = L/(u_{a20} + u_{c20}) \) is the characteristic time for the replacing ion fronts to meet.

Equation 2.51 shows that the current increases with constant-potential time, which is confirmed in the early-time behavior of Figure 2.4. Because of this, conditions at a given constant-potential time correspond to those at a larger constant-current time. For this example, \( t_{mic} = 7200 \) s and

\[
t_{Ec} = (2000, 4000, 6000) \quad \leftrightarrow \quad t_{uc} = (2099, 4424, 7029). \tag{2.53}
\]

The final adjustment is to note that the tortuous medium simulated in Section 2.3.1 effectively reduces the mobilities \( \nu_j \), so a tortuosity of 1.65 then reduces the characteristic velocities \( u_j \) by a factor of 0.37.

The concentration profiles from this analysis are compared to those of the numerical simulation in Figure 2.5. The results are good considering the relative simplicity of the short-time analysis—essentially algebraic after the derivation is complete—compared to the full numerical simulation. It can be seen that the agreement for H⁺ is better than that for OH⁻; this is a result of the restrictions on the replacing ion concentration in the terminating zone, as specified by Equation 2.45. Since the actual replacing ion boundary concentrations are larger than those allowed by the theory’s assumptions, larger \( \alpha_2/\alpha_1 \) gives better agreement.
Figure 2.5: Theoretical and numerical short-time concentration distributions for the NaCl separation.

The short-time analysis gives a fair prediction of the concentration distributions, conductivity changes, and time and location of the meeting of the replacing ion fronts. Once the fronts meet, the assumption that the two electrodes do not interact with each other is violated. Also, as time progresses and the electric field becomes small in some regions, diffusion can no longer be neglected with respect to migration and a different approach is needed.

2.3.3 Steady-state analysis

Figure 2.1 demonstrates that at long times the species separate into two steady-state zones that are each composed mainly of two ions. Where two ions dominate the mixture’s electrochemical behavior, binary electrolyte analysis can be used to simplify the description of the system’s behavior [Newman 1991, Probstein 1994]. In this case, the convective diffusive equations for dilute species without reactions

\[
\frac{\partial c_i}{\partial t} + u \cdot \nabla c_j = -z_j v_j F \nabla \cdot (c_j \mathbf{E}) + D_j \nabla^2 c_j
\]

are combined with the electroneutrality equation to eliminate the electric field \( \mathbf{E} \) and yield
$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = D \nabla^2 c,$$

where the cation and anion have been combined to give an effective diffusion coefficient and reduced ion concentration,

$$D = \frac{z_+ v_+ D_+ - z_- v_- D_-}{v_+ - v_-} \quad \text{and} \quad c = \frac{c_+}{v_+} = \frac{c_-}{v_-}.$$

The $v$ terms are stoichiometric coefficients in the conceptual dissociation of a compound into a binary electrolyte

$$A_{v_+} B_{v_-} = v_+ A^{v_+} + v_- B^{v_-}.$$

The procedure here is to determine the steady-state concentration distributions in two separate binary zones to one common unknown, then match the current in both zones to determine this unknown. This completely determines the current and the distributions of species, electric potential, and field. The current in the binary solution is given by

$$\frac{i}{F} = \left( z_+^2 v_+ v_+ + z_-^2 v_- v_- \right) F c E - (D_+ - D_-) \nabla c.$$

To find the concentration distributions the steady-state, one-dimensional version of Equation 2.55 is integrated. Using boundary conditions $c(x = 0) = c_r$ at the reservoir and $c(x = L_r) = 0$ at the end of the binary zone results in

$$c = c_r e^{\frac{M_c}{D}} \left( 1 - \frac{x}{L_r} \right) = c_r e^{Pe} \left( 1 - \frac{x'}{l} \right)$$

where $L$ is the length of the medium, $x' = x/L$ is a dimensionless distance, $l = L_r/L$ is the distance to the end of the binary electrolyte zone ($0 \leq l \leq 1$), and $Pe = uL/D$ is a Peclet number based on the binary diffusion coefficient and the length of the medium. When the convective velocity is zero, the concentration profile is linear. A necessary term will be the derivative of the concentration at the boundary between the reservoir and the medium,

$$\left. \frac{dc}{dx} \right|_{x=0} = -\frac{c_r Pe}{L} e^{Pe} \left( \frac{1}{Pe l} - 1 \right).$$

At this point, $c_r$ and $l$ are unknown. A mass balance from the initial condition is used to find $c_r$ as follows: Integrating Equation 2.59 gives the amount of material in the medium

$$\int_0^L c \, dx = c_r L \left[ e^{Pe} - Pe l - 1 \right].$$
The small Pe behavior of Equation 2.61 can be examined by taking the Taylor expansion as \( Pe l \rightarrow \varepsilon \) and discarding terms of order greater than one in \( \varepsilon \), giving

\[
\lim_{Pe l \rightarrow \varepsilon} \int_{0}^{l} c \, dx = c_r L l \left( \frac{1}{2} + \frac{\varepsilon}{6} + \cdots \right). \tag{2.62}
\]

This gives a quantitative measure of when convection can be neglected. When the Peclet number is small, the linear concentration profile leads to an integrated concentration with the area of a triangle, \( (height)(base)(1/2) \).

The total number of moles \( N_r \) is known from the initial conditions and subsequent chemical addition or removal, if any. This is equal to the moles in the reservoir plus that in the medium, Equation 2.61, and leads to

\[
c_r = \left( \frac{N_r}{LA_r n} \right) \left[ \frac{V_r}{LA_r n} + l \left( \frac{e^{Pe l} - Pe l - 1}{(Pe l)^2} \right) \right]^{-1} = c_r \left[ l_r + l \left( \frac{e^{Pe l} - Pe l - 1}{(Pe l)^2} \right) \right]^{-1}. \tag{2.63}
\]

Here a total concentration and a dimensionless reservoir length have been defined in terms of the void volume in the medium. Since the normalizing volume does not include the reservoirs, \( c_r \) will be greater than the actual initial concentration if the reservoirs start out containing electrolyte.

Equations 2.59, 2.60, and 2.63 were developed for a binary zone near the anode with \( 0 \leq x \leq L \), and could bear the subscript \( a \). The analysis can be transformed to represent another binary zone near the cathode \( L \leq x \leq L \) and given the subscript \( c \), and the corresponding equations are

\[
c_c = c_c e^{Pe_c (1-x)} \left( 1 - \frac{1 - x'}{1 - L} \right) \tag{2.64}
\]

\[
\frac{dc_c}{dx} \bigg|_{x=L} = \frac{c_c Pe_c}{L} e^{Pe_c (1-l)} \left[ 1 - \frac{1}{Pe_c (1-l)} \right] \tag{2.65}
\]

\[
c_c = c_c \left[ l_c + (1 - L) \left( \frac{e^{Pe_c (1-l)} - Pe_c (1-l) - 1}{[Pe_c (1-l)]^2} \right) \right]^{-1} \tag{2.66}
\]

where \( Pe_c = -uL/D_c \) and \( D_c \) is defined as in Equation 2.56. The anode and cathode zone Peclet numbers are of different sign if they are not zero.

Assuming that only the cation participates in the anode electrochemical reaction, the flux of the nonreactive anion is zero. This fact can be used to eliminate the electric field from the
one-dimensional version of Equation 2.58, then simplified with $v_{a+}z_{a+} + v_{a-}z_{a-} = 0$ and the Nernst-Einstein relation $D_j = v_j RT$, to give

$$\frac{i}{F} = v_{a+} \left( \frac{z_{a+} D_{a+} - z_{a-} D_{a-}}{D_{a-}} \right) u c_a - v_{a-} (z_{a+} - z_{a-}) D_{a+} \frac{dc_a}{dx}.$$  \hspace{1cm} 2.67

Transformed to the cathode binary zone, the current must be the same,

$$\frac{i}{F} = -v_{c+} \left( \frac{z_{c+} D_{c+} - z_{c-} D_{c-}}{D_{c+}} \right) u c_c + v_{c-} (z_{c+} - z_{c-}) D_{c-} \frac{dc_c}{dx}.$$  \hspace{1cm} 2.68

With the concentration equations given above, these expressions can be equated and solved (at least numerically) to give the unknown length of the binary region, $l$. Once this is found the current can be calculated, as can the concentration and electric field distributions. Figure 2.6 shows the steady-state concentration profiles for a separation of a 10 mM NaCl solution when the reservoir volumes are negligible and nonreactive species do not leave or enter the system. The solution without convective flow matches the long-time behavior of the numerical simulation above (Figure 2.1). Convective velocities larger than those shown (either Peclet number greater than two, approximately) give impossible solutions with negative currents. This means that a steady-state of the type assumed here does not

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![Image](image_url)

**Figure 2.6:** Theoretical steady-state concentration distributions for the NaCl separation, including near-limiting velocities.
exist, since a negative current corresponds to a different type of electrode reaction than was assumed. Note that the boundary condition that nonreactive species do not leave the system is rather artificial if there is convective flow; this means that deionized water is being introduced at one end, which is reasonable, and being removed at the other end, which is not reasonable. However, the Peclet number limit keeps the velocities small enough that the concentration errors are likely to be small.

Note that there has been no mention of the applied potential; the current and electric field are independent of it. In fact, this analysis corresponds directly to the well known electrochemical phenomena of limiting current. Instead of the classic case of an electrode where a reactive species is destroyed ("plates out") with concentration approaching zero, the electroremediation case has a jump at \( l \) where two reactive species are destroyed by combining with each other. In a limiting current situation, the current has reached a maximum value independent of further increases in the applied potential. In order to pass a higher current, other processes not described above (such as decomposition of the electrode) must take place. The electric field is relatively small everywhere except near the jump, where \( E \to \infty \) as \( x' \to l \), giving behavior such as that seen in Figure 2.3.

The development above describes a wide range of situations, but a simpler case can demonstrate the behavior of the system more easily. An analytical solution is possible in the case of no convective flow. With the further assumption of infinitesimal reservoir volumes, one finds

\[
I = \left[ 1 + \frac{1}{\sqrt{d}} \right]^{-1}\quad \text{where} \quad d = \frac{v_{a-}(z_{a+} - z_{a-})D_{a+}c_{aT}}{v_{c+}(z_{c+} - z_{c-})D_{c-}c_{cT}},
\]

\[
i = FD_{a+}(z_{a+} - z_{a-}) \frac{2c_{aT}}{Li^2},
\]

\[
E = \frac{RT}{-z_a FL} \frac{1}{(l - x')} \quad \text{for} \quad 0 \leq x' < l.
\]

The limiting current is proportional to the initial ionic concentration and inversely proportional to the medium length. If nonreactive species are not added to or removed from the system,

\[
d = \frac{v_{i-}(z_{a+} - z_{a-})D_{a+}}{v_{i+}(z_{c+} - z_{c-})D_{c-}},
\]

where subscript \( i \) refers to the initial electrolyte, and the jump position depends only on the species' properties. For example, a symmetric electrolyte separated by \( H^+ \) and \( OH^- \) has
l = 0.57, and one separated by Fe²⁺ and OH⁻ has l = 0.31. If the initial solution is 10 mM NaCl and the medium length is 0.15 m, then the resulting current density from H⁺ and OH⁻ is i = 0.74 A m⁻². For comparison, the initial current in a field of 100 V m⁻¹ would be 12.6 A m⁻². A tortuous medium such as that simulated in Section 2.3.1 effectively reduces the diffusion coefficients, and a tortuosity of 1.65 then reduces these currents by a factor of 0.37. The theoretical limiting current from the analysis above (0.28 A m⁻²) does not match the long-time simulation value shown in Figure 2.2 (0.55 A m⁻²) because finite grid spacing limits the minimum conductivity.

The jump position will move right if: nonreactive cations are removed from the system, nonreactive anions are added, the cathode reservoir volume increases, or the anode reservoir volume decreases. Opposite conditions would cause a move to the left. Under these conditions a jump will still exist even if l → 0 or l → 1, and there could be large changes very close to the reservoir interface.

In showing the conditions for steady state, this analysis also indicates what conditions would prevent steady state. Most importantly, this state depends on the replacing ions reacting with each other at the jump position l. If one or both of these replacing ions are nonreactive, there will not be a steady state of this type. As was mentioned before, large convective velocities in either direction can also make this type of steady state impossible.
3. Experiments

This chapter is divided into three sections: Transport property experiments, Chemical property experiments, and Electroremediation experiments. Discussion is limited to how the experimental data were obtained and presentation of the results themselves. The topics of modeling these results are held until the next chapter.

3.1 Transport property experiments

The parameters introduced in the mass transport model need to be determined before predictions about the electroremediation process can be made. In this work, the solvent properties (density, viscosity, permittivity) are taken to be those of pure water, and the solute properties (diffusion coefficient, mobility) are taken to be those of the infinitely dilute species in water. However, since the medium transport properties (porosity, tortuosity, hydraulic permeability, surface conductivity, surface potential) will depend strongly on the specific soil and local conditions in the medium, these transport properties need to be determined separately. The transport properties are research areas in themselves, but the approach here is to merely determine the behavior to the extent necessary for first-order model predictions.

3.1.1 Porosity

The porosity \( n \) is the ratio of the void volume to the total volume at a point in the medium. In the case of a saturated medium such as that here, the void volume is the liquid volume. Porosity depends on soil type, degree of saturation, pore liquid composition, mechanical matrix stress, and consolidation history of the soil [Mitchell 1976]. The apparatus represented schematically in Figure 3.1 was used to make measurements of porosity; the heart of this apparatus is used for hydraulic permeability, tortuosity, and electroremediation experiments as well. This approach allowed variation of most parameters while keeping others, such as applied stress distribution, as close as possible to the conditions of the electroremediation experiments.

The soil mixture was contained in a clear PVC tube (Excelon R4000, Ain Plastics, Norwood MA) with an inner diameter of 54 mm. The ends of the soil were held by filter paper against a stainless steel screen that acted as a mechanical support and "passive
Figure 3.1: Apparatus for determination of tortuosity, porosity, and hydraulic permeability.

electrode.” On one end the screen was supported by a fixed, = 3 mm thick, stainless steel plate that had been repeatedly drilled to make most of the area open; on the other end the screen rested against a similarly drilled piston head and rod made of Delrin (Ain Plastics, Norwood MA). This rod passed through a lubricated seal to a pneumatic actuator connected to a regulated pressurized gas supply. By this means the applied unaxial stress on the soil could be varied and measured. The average porosity could be determined by the position of the piston, and a porosity distribution could be determined at the end of a test by sectioning and weighing the soil before and after drying. Electrode reservoirs on either side of the soil held a liquid solution that was the same as that initially mixed with the soil.

The clay used for these and subsequent experiments was an acid (H+) form of a nearly pure kaolin (Albion Sperse 100, Albion Kaolin Co., Hephzibah GA). A barely-liquid soil mixture was made by gradually stirring the dry clay into the aqueous solution until a solid:mass ratio of 1:1 was reached. The test cell was prepared by capping the fixed (nonpiston) end, positioning the cell vertically, and filling it with solution. The soil mixture was then poured into the solution in the cell, and the piston end was added and filled with solution before laying the cell back down horizontally. To produce a more uniform medium, the stress on the soil was increased gradually by ≈ 9 kPa increments at 30 minute intervals. Faster consolidations caused the medium to be significantly tighter near the piston than it was elsewhere in the medium. It should be noted that the soil medium undergoes plastic deformations and the consolidation process is highly irreversible.
For the electroremediation experiments, the loading and consolidating procedure was repeated three times to build up the total soil length; roughly 300 g of soil mixture was added for each section. While developing the consolidation procedure, destructive porosity distribution tests were made to see how uniform the consolidated soils were. An example of these results are shown in Figure 3.2, where porosity for several clay sections is plotted versus nondimensionalized distance from the piston. It can be seen that the porosity within a loading section varies measurably, but the average porosity (≈ 0.54) is nearly the same for the three loading sections. In terms of mass transport and the continuity equation, these porosity variations have only a small effect on the species velocities. However, other parameters (such as hydraulic permeability) have a strong dependence on porosity, so those variations could be large.

To examine the effect of pore chemistry and applied stress on porosity, single-load tests were done in three different pore solutions (10 mM NaCl, 100 mM HCl, and 100 mM NaOH). The average porosity for soils made with these three pore solutions is plotted versus applied stress in Figure 3.3. The NaCl and HCl solutions give essentially the same values, but the NaOH solution produces a clay with an appreciably lower porosity at a given stress. The pore solutions interact chemically with the clay particles and change their surface properties, which in turn affect the medium's mechanical properties. The mechanisms for this [van Olphen 1963] will not be pursued in detail in this work.

![Figure 3.2: Porosity distribution for a clay column built from three loadings.](image-url)
Figure 3.3: Porosity versus applied stress showing effects of pore liquid composition.

All of the clay mixtures are more sensitive at low stresses. This, in fact, illuminates the motivation for using the piston in the first place. It was found during early testing that unstressed clay mixtures sometimes cracked and formed large voids during electroremediation tests. These major nonuniformities were responses of sensitive clay to chemical and stress changes. An actual soil will be under some initial mechanical stress and so less sensitive to these changes, so the electroremediation tests were run with constant applied stress (= 80 kPa). This tended to maintain uniform and constant transport properties even though chemical and mechanical changes were occurring within the medium. From the test of Figure 3.2, \( n = 0.54 \) was chosen for the electroremediation simulations.

3.1.2 Tortuosity

Tortuosity is a measure of the indirect path that a particle must take moving through a porous medium, as was discussed in the mass transport model. The tortuosity can be most easily determined by electrical measurements in the medium. It can be shown from the developments in the model chapter that when the surface conductivity is negligible (true except for low ionic strengths) and there are no concentration gradients,
\[ \tau^2 = \frac{\Delta \phi A_r n \sigma_p}{I_m L} \]  

where \( \Delta \phi \) is the applied voltage, \( A_r \) is the medium area perpendicular to the flow, \( \sigma_p \) is the pore solution conductivity (S m\(^{-1} \)), \( I_m \) is the measured current (A), and \( L \) is the medium length. The tortuosity can be found by an ac field method [Shapiro 1990, Nadler and Frankel 1980] or from the initial medium conductivity in an electroremediation experiment, both in an apparatus such as Figure 3.1. For the consolidated kaolin soils to be simulated, \( \tau = 1.65 \).

### 3.1.3 Hydraulic permeability

In the mass transport model, it was shown that the convective interstitial velocity depends on the hydraulic permeability \( k_h \) as

\[ u = -\frac{k_h}{n\mu} \nabla p - \frac{k_r}{n\mu} \nabla \phi. \]  

In one dimension with uniform properties and no electric potential difference, this can be rearranged to give the hydraulic permeability as

\[ k_h = \frac{\mu L m}{\rho A_r \Delta p} \]  

where \( \Delta p \) is the applied pressure (Pa) and \( m \) is the resulting mass flow rate (kg s\(^{-1} \)). If the potential difference is not zero across an electrokinetically active medium, then another term would appear involving \( k_r \).

The apparatus shown in Figure 3.1 and already described for the porosity measurements was used to measure the hydraulic permeability. The electrodes across the clay were connected electrically to minimize any potential that might arise across the medium. Hydraulic permeability results are shown in Figure 3.4 for the same conditions given in Figure 3.3. The values vary over nearly two orders of magnitude. Within a solution, the hydraulic permeability is a strong function of porosity, but less so as the porosity decreases. Between the solutions, the permeabilities are not the same for a given porosity, which indicates that there are qualitative particle packing differences for each solution. The NaCl and HCl values converge at the lower porosities. Again, the NaOH solution is significantly different than the other two, although it is possible that NaCl and HCl would converge to it at lower porosities.
Figure 3.4: Hydraulic permeability versus porosity showing effects of pore liquid composition.

For now the hydraulic permeability is taken to be a constant $4.3 \times 10^{-16}$ m$^2$. It is apparent from Figure 3.4 that this will be a poor assumption as the chemical properties change, and the topic will arise again below.

3.1.4 Surface conductivity

The surface conductivity $\sigma_s$ introduced in the transport model is needed because the charge transport in the Debye layer was neglected. Although neglecting the double layer is an appropriate assumption for moderate-to-high ionic strength, it is less so as the ionic strength and conductivity decrease in the bulk solution. The resulting high electric field strength would constrain the simulation time steps to be impractically small. Including constant surface conductivity is a first approximation to mitigate this effect. For simulations of the clay experiments, the value measured by Shapiro [1990] for the same clay will be used ($1.3 \times 10^{-3}$ S m$^{-1}$). This is $1/100$ of the conductivity of a 10 mM solution of NaCl. The surface conductivity is negligible except in low conductivity regions.
3.1.5 Surface potential

Within the resolution of this work, the surface potential is the same as the zeta-potential (ζ-potential), which is the electric potential at the "surface of shear" of a charged solid-liquid interface [e.g., Hunter 1981, Probstein 1994]. It was shown in the transport model that the zeta-potential is needed in order to determine the local value of the electroosmotic permeability

\[ k_e = -\frac{e n \zeta}{\varepsilon} \]  \hspace{1cm} 3.4

It is well known that the zeta-potential of some materials such as kaolin clay is highly pH-dependent, and the simulation of the simple example presented earlier showed that large pH variations tend to occur during electroremediation. In order to predict the electroosmotic flow, it was necessary to describe how zeta-potential varied with solution chemistry for the particular clay used here.

The zeta-potential of a material can be inferred through a variety of methods, including streaming potential and electrophoresis measurements. Streaming potential measurements are made by forcing a flow through a porous medium and measuring the induced electric potential. This approach has advantages in that it can closely resemble the medium of interest in terms of solid concentration and heterogeneity, but there are disadvantages including long preparation and measurement times for each data point. Electrophoresis involves measuring the velocity of particles in a dilute hydrosol (sol) under the influence of an applied electric field, and has advantages and disadvantages opposite those above. Since the soil of interest was a pure kaolin clay, electrophoresis was used to allow easier variation of the solution chemistry. The zeta-potential is calculated from electrophoresis measurements by the Helmholtz-Smoluchowski equation [Probstein 1994]

\[ \zeta = \frac{\mu U}{\varepsilon E} \]  \hspace{1cm} 3.5

where \( U \) is the measured speed of the particle (m s\(^{-1}\)), \( \varepsilon \) is the permittivity of the liquid (6.93-10\(^{-10}\) C V\(^{-1}\) m\(^{-1}\)), and \( E \) is the applied electric field strength (V m\(^{-1}\)), yielding \( \zeta \) (V). This equation applies to a uniformly-charged particle of any shape if the Debye length \( \lambda_d \) is small compared to the surface's radii of curvature [Fair and Anderson 1989]. The Debye lengths are small for the solutions used here, but kaolinite particles are not uniformly charged [van Olphen 1963]. The Helmholtz-Smoluchowski equation is used in spite of this, with the argument that the averaged \( \zeta \) from using Equation 3.5 will be similar to the averaged \( \zeta \) needed in Equation 3.4, so the correction ultimately cancels.
The sols were prepared by adding approximately 0.03 g of clay to 100 g of solution while stirring. Since NaCl was used as the representative soil background electrolyte in the electroremediation experiments, HCl and NaOH were used to vary the pH of the solutions. Selective interactions with cations and ionic strength are known to be important, so sodium concentration (added as NaCl) was used as another parameter. The closed flasks were swirled every 12 hours to allow sedimented clay to sample the solution composition. Measurements were taken after one and six days, which are on the time scale of the electroremediation experiments. pH measurements were made with a Ross Sure-Flow 8172 pH electrode (Orion, Boston MA). Zeta-potential measurements were taken with a micro-electrophoresis device (Zeta-Meter 3.0+, Zeta-Meter Inc., Long Island NY) in which individual clay particles are tracked as they move under the influence of an applied field.

The measured zeta-potential is plotted versus pH in Figure 3.5 for sols with different total Na+ concentrations after 1 and 6 days in solution. With the exception of two points, time made little difference in the pH or zeta-potential. For pH < 6, ζ is positive and ranges up to ~ 10 mV, and the three sodium concentrations fall on the same curve. For pH > 6, ζ is negative and ranges as low as -45 mV. There is an effect of higher sodium concentration decreasing ζ from approximately -40 to -22 mV at a pH of 12.

This potential versus pH behavior is typical of other reactive surfaces such as iron oxide [Dzombak and Morel 1990], and kaolinite itself has been studied extensively. Figure 3.6 shows the streaming potential results of Lorenz [1969] and the electrophoresis results of Williams and Williams [1978] for kaolinite clay treated to produce a sodium form. These values and those of Figure 3.5 do not match precisely because the materials were different despite being based on the same mineral, but the overall trend and ranges are similar. When viewed in light of the pH changes that can be developed from electrolysis, it can be seen that spatially-varying ζ is needed to describe the local contributions of electroosmosis in Equation 3.2. Also, the pH and ionic strength dependence of the surface charge is likely to be a factor in the mechanical property changes seen in the sections above.
Figure 3.5: Measured zeta-potential versus pH (H-kaolinite).

Figure 3.6: Literature values of zeta-potential versus pH (Na-kaolinites).
3.2 Chemical property experiments

The chemical properties of the entire system are important because they determine the species that are present, the electric field distribution, and the soil surface charge. In other words, chemistry determines what is present and how it moves, which is the crux of the problem. In this work, well-characterized species such as the contaminant and background electrolyte are taken to be governed by their standard chemical equilibrium reactions and constants found in the literature. The soil medium, however, is a more complicated issue.

It is difficult to describe the soil chemistry for several reasons: total composition varies, surface composition varies, surface reactions are complicated by electrostatic effects, and chemical equilibrium typically does not prevail. Tackling the medium at a detailed level for use in describing the overall electroremediation process is hopeless, and because of this the issue of soil chemistry has traditionally been avoided in electroremediation work. It will be seen, however, that soil chemistry cannot be neglected in general if quantitative predictions of electroremediation are desired. The goal of this section is to test the chemical behavior of the kaolin soil in a manner useful for electroremediation.

In examining the pH behavior in 3.1.5 Surface potential, it was found that adding even a small amount of clay would affect a solution’s pH. This was one clear indication that the soil will participate in the system’s chemical reactions. The proper way to explore the soil’s chemical behavior for electroremediation is not an established fact, but turns out to be rather natural: acid-base titration. The reason for this can be most easily seen in the chemical changes in the simple example simulation. By separating the background electrolyte, migration creates mixtures of different alkalinity and ionic strength throughout the medium.

Alkalinity has several interpretations [Morel and Hering 1993], but can be viewed here as the (possibly negative) net amount of strong base in solution

\[
Alk = [\text{OH}^-] - [\text{H}^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \text{[net charge from other weak acids]}
\]

\[
= [\text{Na}^+] - [\text{Cl}^-] + \text{[net charge from other strong bases]}
\]

\[
= \text{[positive charge from strong bases]} - \text{[negative charge from strong acids]}
\]

In the case of a "blank" solution with negligible weak acids and bases,

\[
Alk = [\text{OH}^-] - [\text{H}^+] = 10^{-(11-pH)} - 10^{-(pH-3)} \text{ (equiv m}^3 = \text{mM)}.
\]

If the system initially includes only H\(^+\), OH\(^-\), Na\(^+\), and Cl\(^-\), then the system is initially determined if alkalinity and ionic strength are given because electroneutrality and water equilibrium are always assumed to hold. The titrations were performed from
$-100 \leq Alk_i \leq 100 \text{ mM}$ using NaOH for positive Alk, and HCl for negative values. Instead of trying to completely cover the two-dimensional alkalinity/ionic strength space, two extremes were taken:

- constant initial ionic strength titration with NaCl added as necessary to make $I_i = 100 \text{ mM}$
- minimum initial ionic strength titration with no NaCl added so $I_i = |Alk_i|$.

In making the soil mixtures, a compromise was struck between reproducing the electroremediation test conditions and having a workable mixture. A solid:liquid mass ratio of 1.5:1 was selected for the initial pH experiments because the resulting slurry could still be stirred but was close to the in situ concentration of 2.2:1. For each titration point, 45 g of the dry kaolin clay were gradually stirred into 30 g of solution described above. To prevent carbon dioxide from dissolving into the samples, nitrogen gas was used to displace the air over the sample jars before they were sealed, although the CO$_2$ effect would probably have been small.

### 3.2.1 pH results

After 24 hours, the pH of each slurry was measured with the pH electrode, which was kept moving in the slurry until the reading stabilized. The results are shown in Figure 3.7 as pH versus initial liquid alkalinity $Alk_i$. The pH curve for the initial blank solution is also

![Figure 3.7: Experimental titration of kaolin clay for two ionic strength paths.](image)
plotted for reference. The relative flatness of the experimental curves represents buffering, which is a resistance to pH change. The clay shows some buffering to acid and more pronounced buffering to base, which is expected because this particular clay is in acid (H⁺) cation form. The acidic nature of the clay is seen as well in the fact that with no added alkalinity, the initial pH is less than 7. The shape of the curve also gives an indication of the amount of reactive material that the clay provides: Moving away from $\text{Alk} = 0$ in either direction, the buffering is exhausted when the slope of the clay curve matches that of the blank.

Ionic strength had little effect on the titration curve. This an unexpected result in some ways because surface chemistry models include ionic strength dependence, and simple ion exchange models would include dependence on sodium concentration (as will be discussed below). On the other hand, the relative insensitivity to background electrolyte compared to H⁺ is common and is the same sort of behavior seen in 3.1.5 Surface potential. There is some deviation between the two curves for small positive alkalinities in Figure 3.7, and the differences could be attributed to higher Na⁺ concentration displacing more H⁺ from the clay surface. The difference is small on the overall scale, however, and the ionic strength dependence will be neglected from now on.

It should be noted that taking pH measurements in the presence of charged material can affect the reading [Bolt et al. 1978], but this effect should be minimized by the type of electrode that was used.

### 3.2.2 Elemental analysis results

In the titrations done for elemental analysis, a slightly lower solid:liquid mass ratio (1:2:1) was used to make it easier to get liquid for the analysis, and only the constant ionic strength titration was done. The mixtures were prepared as before, and 24 hours later pore liquid samples were separated from the mixtures by centrifuging in tubes with internal membranes (Ultrafree-Cl 30,000 NMWL or 0.45 μm, Millipore Inc., Bedford MA). The pore solutions were analyzed for Na, Cl, Al, Ca, Fe, K, and Mg using inductively coupled plasma (ICP) spectroscopy in a Perkin-Elmer Plasma 40 (Norwalk CT). Since Cl cannot be detected with this device, its concentration was inferred from precipitation with Ag as

$$\text{Ag}^+ + \text{NO}_3^- + \text{Cl}^- = \text{AgCl(s)} + n\text{NO}_3^-.$$  

In retrospect, since kaolinite is an aluminosilicate, Si should have been added to the elements analyzed. The clay behavior can be modeled without it, but greater insight might have been possible if Si had been included.
The preparation procedure was as follows: The pore liquid was diluted with distilled water if necessary to reduce the concentrations for the ICP. 1.0 mL of this sample was placed in a 14 mL disposable plastic test tube, 0.2 mL of concentrated (73 %) HNO₃ was added and mixed, 2.0 mL of Ag reagent (usually 100 mM AgNO₃) was added, and distilled water was added to make a volume of 10.0 mL before mixing well again. This results in a solution with 2 % HNO₃. The white AgCl precipitate was removed by centrifuging the tube for > 10 minutes, then approximately 8 mL of clarified liquid was carefully pipetted to a new test tube. Various metal standards (VWR Inc., Boston MA) diluted to the appropriate concentrations were used for calibrating the ICP, and a 2 % HNO₃ solution was used as the blank.

The element analysis results for Na and Cl are plotted as change in pore liquid concentration versus initial liquid alkalinity in Figure 3.8. The major trend seen is consumption of Na⁺ in the positive alkalinity range. This mechanism can explain the buffering to base (NaOH) seen in Figure 3.7, as will be discussed in the applications chapter. There may also be a trend of consuming Cl⁻ in negative alkalinity and releasing Cl⁻ in positive alkalinity. These actions would produce buffering to acid and base. However, the Cl⁻ data is questionable because it has variations equal to its magnitude, perhaps a result of the indirect procedure used to determine its concentration. The variations of both concentrations near zero alkalinity may not be significant. In this range, [NaCl] = 100 mM and the accuracy of the entire procedure is probably not better than 5 %.

The results for Al, Ca, Fe, K, and Mg are shown as changes in pore liquid concentration multiplied by the ion charge in Figure 3.9. Presenting the data in this way weights the elements according to their charge contribution. (This is not strictly true, however, since Al will be in the Al(OH)₄⁻ form at high pH.) None of these species were present in the liquid initially, and the measured changes are only positive as expected. The greatest effect is from Al release at both negative and positive alkalinites. In addition, Ca and Mg are released in similar amounts in negative alkalinity. There is no change in Fe or K concentration. All of these measured clay element responses match the pH results; they are changes that buffer the system pH to both base and acid addition.
Figure 3.8: Change in ion concentration (Na, Cl) in titration showing Na consumption by the clay.

Figure 3.9: Change in ion charge concentration (Al, Ca, Fe, K, Mg) in titration showing Al, Ca, Mg release from the clay.
3.3 Electroremediation experiments

The apparatus for electroremediation experiments is shown in Figure 3.10. Most of the setup is the same as that shown in Figure 3.1 and described in 3.1 Transport property experiments. The main difference in this case is that a dc field is applied across the clay via graphite rods (Middlesex Gases & Technology Inc., Everett MA) embedded in “active” carbon fiberboard electrodes (Fiber Materials Inc., Biddeford ME). This causes migration of the charged species and electroosmotic flow of the bulk liquid.

Another difference is the addition of a recirculation system for the anode reservoir for one experiment where chemicals were added to the reservoir. Larger external reservoirs were used because more “chemical capacitance” was desired, and recirculation was necessary to keep the volume well mixed. The flow through the reservoir is caused by gravity at a constant head, so the flow is steady. A small centrifugal pump with a magnetic drive and polypropylene wetted surfaces (March AC2CPMD, Cole Parmer Inc., Niles IL) returned the flow to the feed tank. It was desired to have zero applied pressure difference across the cell, so a test was done with no soil in the system to find the cathode level that would match the pressures at both ends; this level was used for the electroremediation experiment. Since there is no applied pressure across the cell, all of the measured flow results from electroosmosis.

The instrumentation for measurement of applied voltage, uniaxial stress, current, and tank mass is the same as in 3.1 Transport property experiments. The probes in the soil are new to these experiments. The probe body is 3.18 mm (1/8 inch) OD hollow stainless steel tubing. A wire is silver-soldered to the outside of this tube for voltage measurements. A

Figure 3.10: Apparatus for electroremediation experiments, indicating measurement of current, voltage, pressure, mass, and stress.
solid state pressure transducer (Micro Switch 26PCCFA1D, Powell Electronics, Westborough MA) is sealed to the outside end the probe, and a #100 porous stainless steel stone is driven into the soil end of the probe. The porous stone keeps the soil from moving into the probe, and assures that the pore liquid hydrostatic pressure is measured without mechanical stress contributions from the soil. The internal volume of the transducer was filled with a degassed dimethylpolysiloxane liquid (10,000 cs. Dow Corning 200, George Mann & Co., Providence RI) and the probe tube with degassed water to prevent volume changes with pressure variations. Otherwise, a drop in pressure in the soil could cause gas expansion in the probe. The nonaqueous liquid also served to keep the pore solutions from affecting the piezoresistive pressure transducer.

For accurate pressure measurements, it was important to have good seals wherever the pressure was not atmospheric. For the pressure transducers, the flexible Tygon tubing connection between the nipple and the probe tube was cinched at both ends with tightly twisted stainless steel wire. The probe penetration into the test cell was made through polypropylene fittings which were screwed and epoxied into the cell wall. Another potential leak was within the cell, between the cylinder wall and the clay. By using an applied stress and consolidating the soil within the cell, a tight fit was created and maintained. Since the basic clay was found to have more significant volume changes (3.1.1 Porosity), the piston was place on the cathode end of the test cell to make up for any compression there.

The soil loading procedure has been described in 3.1.1 Porosity. In the electroremediation experiments here, the kaolin clay was mixed with 10 mM NaCl solution as a background electrolyte. After the consolidation was complete, plugs from the probe fittings were removed. The internal spaces of the fittings were filled with pore liquid using a syringe to displace any trapped air. The probes were then inserted into the clay, and the fittings were wrench-tightened around the probe tube. To make sure that the experiment was starting from an equilibrium state, the cell was left with the data acquisition system running overnight. During this waiting period, the probes and electrodes were connected electrically to prevent them from developing potential differences. Pressure readings from the probes showed that the system reached mechanical equilibrium in the first few hours of the overnight wait.

Before the experiment was begun the next day, offset readings from all the transducers were taken (about 40 samples over the course of 180 s). With offsets from these readings and known gains for each transducer and amplifier, the physical quantities could be found from the transducer bit voltages. The acquisition of the actual data began when the dc voltage supply for the experiment was switched on. The sampling rate was usually between 1200 s and 3600 s. Manual measurements were made of the medium length and the
reservoir pHs (colorpHast, EM Science). All of the experiments were run with constant applied voltage across the soil and duration of about one week (6·10⁵ s).

3.3.1 Experiments with and without base addition at anode
Past work has shown that using a basic solution at the anode could promote electroosmotic flow [Shapiro and Probstein 1993]. The changes in pH seen in the simple example simulation and the pH dependence of zeta-potential seen in 3.1.5 Surface potential are some of the reasons for this behavior. Two experiments were performed to observe the differences between treating and not treating the anode reservoir; the data from these experiments are of major importance in this work. Information is generated to validate the transport model, evaluate soil chemistry models, show limitations in the approach, uncover reasons for flow variation, and explain the success of electrode treatment. The results are best presented together for comparison. In the first experiment ("no treatment"), no action was taken to control the electrolysis products at the electrodes. In the second experiment ("base addition"), NaOH was periodically added to the anode in the form of a few milliliters of concentrated solution. Both experiments were run with a constant applied potential of 100 V/m across the soil.

Figure 3.11 shows that without treatment the pH in both electrode reservoirs changes rapidly to a steady value within measurement resolution. Electrolysis and changes in H⁺ and OH⁻ concentration may proceed throughout the experiment, but the course resolution of the indicator paper and the logarithmic nature of the pH scale obscures this. Figure 3.12 shows the results of periodic base addition to the anode. The saw-tooth nature of the anode curve results from the step change in pH when the base is added. Sufficient NaOH is added to prevent the anode pH from dropping below 9, as opposed to the asymptotic value of 2 when there is no treatment. Most of the cathode curve is much like that in the first experiment, but at ≈ 4.5·10⁵ s the pH begins to increase again. This behavior will be discussed in more detail later.
Figure 3.11: pH trace (short time only) without electrode treatment showing early changes and subsequent plateaus.

Figure 3.12: pH trace with base addition at anode. Breakthrough can be seen at the cathode at \( \approx 4.5 \cdot 10^5 \) s.
Figure 3.13: Medium length under constant stress with and without base addition at anode.

Since constant stress was applied with the piston and there were pH changes, some soil volume changes occurred as is seen in Figure 3.13 (see also 3.1.1 Porosity). The change was small for the untreated experiment but more significant for the base addition case. It can be seen that the rate of consolidation increases at the same time that the cathode pH begins to increase in Figure 3.12. This makes sense in terms of the basic clay behavior seen in the porosity experiments above.

The electroosmotic velocity trace for the experiments is shown in Figure 3.14. In this and other experimental plots, only a fraction of the digital samples are plotted for clarity. Both cases begin with negative velocities (flow towards the anode), but soon reverse and rise together to $4.7 \cdot 10^{-7}$ m/s (41 mm/day) at $1.4 \cdot 10^5$ s (1.6 days). At this point the flow of the base addition experiment momentarily plateaus, and that of the untreated experiment drops by 50%, then plateaus. At $4 \cdot 10^5$ s the velocity of the base addition experiment begins to rise steadily, and at $5 \cdot 10^5$ s the velocity of the untreated experiment begins a drop towards zero. This sort of flow variation and cessation is commonly observed in experiments but has not been quantitatively explained, and that is one of the main goals of this work.

If the time-integrated velocity is normalized to the length of the medium the result is the fractional pore volume or displacement, where a dimensional pore volume is the amount of
Figure 3.14: Electroosmotic velocity trace with and without base addition (see also Figure 3.15).

Figure 3.15: Electroosmotic displacement (pore volume) trace with and without base addition (see also Figure 3.14).
liquid initially in the medium. Figure 3.15 shows this view of the electroosmotic flow for both experiments. It can be seen that the untreated experiment has just reached one pore volume when the flow begins to cease, while the base addition experiment has surpassed 2.5 pore volumes with increasing rate. This is important because uncharged contaminants move mostly with the bulk flow, and displacing one pore volume then removes most of the contaminant. Depending on the contaminant chemistry, base addition at the anode could be an effective means of enhancing removal. In comparing Figure 3.15 to its time derivative Figure 3.14, it can be seen that there is information in the velocity that is not readily detectable by eye from the displacement plot. The velocity will be used in this work as a stricter test of the flow conditions.

The spatially averaged conductivity of the medium can be defined in terms of the current density and applied field, both of which may vary in time, as

$$\langle \sigma \rangle = \frac{i(t)}{A\phi(t)/L} = \frac{i(t)}{E_{app}(t)}. \quad 3.9$$

This is a useful way to compare experiments run at different operating conditions (e.g., constant current or constant applied potential) since it describes the state of the medium independent of the applied driving force. In fact, for situations where diffusion and surface conduction can be neglected, the average conductivity is a spatially averaged measure of the ions in solution

$$\langle \sigma \rangle = \left[ \int_0^{1} \frac{1}{\sigma} \mathrm{d}x' \right]^{-1} \quad 3.10$$

where

$$\sigma = F^2 \sum z_i^2 \frac{V_i}{\tau^2} c_i. \quad 3.11$$

Because of these properties, the average conductivity will be well exercised in comparing chemical models later. Figure 3.16 shows the average conductivity traces for the two experiments. In this case of constant applied potential of 100 V/m, the average conductivity is 1/100 of the current density. Both start at about 0.05 S/m and drop together to 0.01 S/m by 5 \times 10^4 s. While the untreated experiment’s conductivity drops further and stays low, the base addition experiment’s conductivity picks up and increases rapidly after 4 \times 10^5 s. This corresponds to moving the high conductivity NaOH solution through the medium. This can also be seen in the pH plot (Figure 3.12), where the once-steady cathode pH begins to rise steadily at the same time. The initial behavior of the experiments
Figure 3.16: Average conductivity trace with and without base addition.

is different than was seen in the simple case simulation, but the long-time trend of the
untreated experiment and the simulation is similar.

Voltage and pressure measurements within the medium were obtained with three
probes. The probe data could be presented as a distribution (e.g., $\phi(x)$), but since there are
only three positions and many time samples a trace plot (e.g., $\phi(t)$) is a better choice.
Figure 3.17 shows the trace and distribution relationship schematically for a representative
profile evolution. The probe trace plots are the superposition of three $\phi(t)$ planes, one of
which is shown as the shaded plane in the figure.

Figure 3.17: Schematic of probe trace $\phi(t)$ and distribution $\phi(x)$ plots.
Figure 3.18: Probe voltage trace without electrode treatment.

Figure 3.19: Probe voltage trace with base addition at anode showing a return to near-uniform distribution.
Figure 3.18 shows the normalized probe voltage traces for the experiment without electrode treatment. In this plot, $\phi' = 1$ is the passive electrode touching the anode end of the soil and $\phi' = 0$ is the cathode end. Since the initial conductivity is uniform, the $\phi'_i(t = 0)$ values indicate the location of the probes in the medium. Nonuniform conditions are generated almost immediately, and the three probe voltages move towards the anode value. The distribution that corresponds to this condition has a steep step (see the last curve in the schematic Figure 3.17). This indicates that the conductivity from the anode through the entire probe region is relatively high compared to that near the cathode. Since the current data showed that the average conductivity decreased (Figure 3.16), this also means that the cathode region conductivity is lower than it was initially. Figure 3.19 shows the voltage trace for the base addition experiment. The initial trend is similar to the untreated experiment, but the voltages remain more evenly distributed, indicating a more even electric field and conductivity. At the same time ($4 \cdot 10^5$ s) that the base addition conductivity increases in Figure 3.16, the voltages start to drop towards their initial values in Figure 3.19. Near $6 \cdot 10^5$ s (7 days), the distribution is uniform as it was initially, although it continues to proceed through this point.

The probe pressure trace for the untreated experiment is shown in Figure 3.20. Since there are uniform conditions initially, the pressure is also uniform even though there is bulk flow, as was discussed in the model chapter. The entire medium is at atmospheric pressure (plus a hydrostatic component) since the electrode reservoirs are open to atmosphere. Once the electric field becomes nonuniform, however, different regions of the soil have different contributions to the electroosmotic flow and pressure variations develop. The high field (low conductivity) region near the cathode has the greatest pumping contribution to the flow, while the low field probe region essentially has the fluid sucked through it, leading to large pressure changes. This can be seen in Equation 3.2 by noting that $u$ is uniform in one dimension, so if $|\nabla \phi|$ becomes smaller then $|\nabla p|$ becomes larger. Later in the experiment, the flow is decreasing to zero and the pressures are again returning to atmospheric. The minimum pressure (0.45 atm) is quite low for a natural medium, although it is admittedly being treated in an unnatural manner. The low gage pressure and the sharp change in pressure and velocity around $1.4 \cdot 10^5$ s lead to questions about whether the cell leaked at this point. Another experiment was done to check this, and will be discussed below in 3.3.2 Experiment with lower applied potential.

The pressure trace for the base addition experiment is shown in Figure 3.21. The pressures do not become as nonuniform nor as low as was seen above. Initially this was believed to be a physical effect due to the electrode treatment, but subsequent analysis has indicated that only probe 2 was reading properly. The other two probe channels read the
Figure 3.20: Probe pressure trace without electrode treatment.

Figure 3.21: Probe pressure trace with base addition at anode.
same voltage throughout the experiment, although the values in the plots are slightly
different because the gains were different. Probe 2 shows initial readings much like those
in the untreated experiment, which makes intuitive sense in retrospect because the voltage
distributions and flow rates were similar for the first $10^5$ s or so. At the end of the
experiment, all of the probe pressures rise dramatically. This may be a result of the
significant piston movement at the end of this experiment, noted above.

The uncertain nature of the pressure readings for the experiments undermined plans for
detailed analysis based on pressure. In retrospect, the volumetric changes in Figure 3.13 and
the orders of magnitude changes in hydraulic permeability seen in Figure 3.4 make it clear
that the system's sensitivity thwarts such efforts, even if the data acquisition had gone
smoothly. A more detailed model of the mechanical property changes that lead to this
consolidation and permeability behavior is beyond the scope of this work.

Much of the behavior seen in this section will be explored in more detail in the
applications chapter. First, some results of one additional electroremediation experiment
will be briefly presented.

### 3.3.2 Experiment with lower applied potential

The untreated experiment's radical changes in flow and pressure at $1.4 \cdot 10^5$ s were suspect,
particularly in light of the reading problems in the base addition experiment. One possibility
was that leaks had occurred from the outside of the cell (from the low pressure) or inside
along the cell walls (from the high pressure gradient). Another possibility was that the
pressure was low enough to cause dissolved gas in the pore solution to evolve, perhaps by
nucleating on the clay particles.

To determine whether the observed behavior was "real," another untreated experiment
was run with a lower applied potential (25 V/m instead of 100 V/m). In order to compare
the two experiments at different applied potentials, it is first noted that most of the transport
depends linearly on the electric field. Diffusion: transport resulting from concentration
differences is the exception, but this contribution is often small. Since the applied field for
this experiment is $1/4$ that of the experiment above, the parameters of interest here are
scaled by factors of 4. Specifically, the relationship between the scaled and measured
parameters of time, velocity, and pressure in atmospheres is

$$ t_s = \frac{E_s}{E_m} t_m, \quad u_s = \frac{E_s}{E_m} u_m, \quad \text{and} \quad p'_s = 1 - \frac{E_s}{E_m}(1 - p'_m) $$

where in this case $E_s = 4E_m$. 
Figure 3.22 shows the comparison between the untreated experiments with applied fields of 100 V/m and 25 V/m, where the lower applied field results have been scaled as in Equation 3.12. Although the agreement is not exact, the two experiments are certainly undergoing the same changes. Figure 3.23 shows the scaled pressure results for the 25 V/m experiment and should be compared with Figure 3.20. Again, the agreement is not exact, but the pressures and times of change are close to those measured before.

These results confirm that the low pressures and sudden changes in flow seen in the previous section are real phenomena of the process and are not experimental problems.

Figure 3.22: Electroosmotic velocity comparison for 100 V/m and 25 V/m (scaled), confirming the flow changes seen in the experiments.
Figure 3.23: Probe pressure trace for 25 V/m (scaled), confirming the results seen in Figure 3.20.
4. Applications of models to experiments

The previous two chapters presented the transport model and the experiments allowing model parameters and accuracy to be determined. In this chapter, the pieces are put together as model components are built from data (4.1 Empirical model for surface potential, 4.2 Equilibrium models of soil chemistry) and finally tested in full simulations (4.3 Simulations of the electoremediation experiments).

4.1 Empirical model for surface potential

In principle, the chemical and mechanical behavior of kaolin clay could be modeled beginning with surface chemistry and charge effects [James and Parks 1982, Dzombak and Morel 1990] and continuing into interparticle forces and medium-scale properties [van Olphen 1963]. In practice, however, the variation of natural materials and the complexity of the problem has kept even the fundamental issues as subjects of debate [e.g., Williams and Williams 1978, Zhou and Gunter 1992]. Given the scale of the transport problem and the relatively heterogeneous composition of real soils that drive this work, it is clear that a more empirical tack will have to be taken. Although the surface potential is in fact intimately tied to the soil chemistry, here the two are separated and treated individually.

For small potentials, it can be shown [Probstein 1994] that

\[ \zeta = q_s \left( \frac{RT}{2F^2eI} \right)^{1/2} \]  

4.1

where the zeta-potential \( \zeta \) is identified with the surface potential, \( q_s \) is the surface charge, \( I \) is the ionic strength, and the other terms are as introduced earlier. The simplest two models of a surface are constant potential and constant charge, but it can be quickly seen from this clay's zeta-potential data that \( \zeta \) is certainly not constant and, since \( \zeta \) changes sign as well, that \( q_s \) cannot be constant in Equation 4.1.

More complex models use surface complexation and potential interactions to explain the complex changes in surface potential with pH and ionic strength. The characteristics of these sorts of analyses [Dzombak and Morel 1990, Hunter 1981] are combined with the
experimental data of the previous chapter to generate a rough empirical model that involves
the two major influences of pH and ionic strength.

As aluminosilicates, clays (and particularly kaolinite) display surface charge
characteristics similar to pure metal oxides. There is typically one pH that can be identified
as the point of zero net charge pH\textsubscript{p}, which can also be the isoelectric point in terms of
electrophoretic mobility. The potential at pHs on either side of pH\textsubscript{p} are affected by the ionic
strength, with high ionic strength reducing the magnitude of ζ. At a constant pH, ζ changes
more linearly with log I than with I.

These characteristics are now applied to the measured data in Figure 4.1, which shows
the data presented in the previous chapter but without distinguishing the one and six day
data. First, the pH\textsubscript{p} is taken to be 6. Since there is little variation with solution for pH < 6,
these points are simply fit with one line. For pH > 6, there is dependence on background
ionic composition. Since the hydrosols are dilute in solid, the system is dominated by NaCl
and water, and the ionic strength of such a solution is

\[ I = OH + Cl = H + Na. \]

The lowest Na\^+ concentration is 0.1 mM, which means that \( I = Na \) for pH > 5. Thus,
the ionic strength is the Na\^+ concentration (0.1, 10, or 200 mM) for the remaining points
of interest. These few points are fit with lines with slopes that vary linearly with log I. The
entire empirical model is then

\[ \zeta = \begin{cases} \frac{(pH - 6)(-0.00168)}{} & \text{pH} \leq 6 \\ \frac{(pH - 6)(-0.01075 + 0.0035log I)}{} & 6 < \text{pH} \end{cases} \]

where ζ is in V and I has units of mol m\(^{-3}\) or mM. The ionic strength is limited to the
lowest measured value, 0.1 mM. These are the curves that are plotted in Figure 4.1.

This model attempts to include the proper dependencies in the simplest possible
manner. Although the intent is physically justified, the execution is based on too few
points. This is certainly an area that could bear further work, but in the overall effort this is
only one part.
Figure 4.1: Zeta-potential model curves with experimental data versus pH and ionic strength.
4.2 Equilibrium models of soil chemistry

The goal of this section is to develop chemical models that are simple enough to incorporate in the transport model, but that have sufficient detail to capture the important behavior seen in the chemical property experiments. Some of the concepts and all of the standard equilibrium constants in the chemical aspect of this work come from Morel and Hering [1993].

The pH and element responses seen in the titrations clearly show that the clay participates in chemical reactions. Furthermore, the results without soil chemistry in the simple example show that the alkalinity and pH ranges in the simulations are similar to the clay’s active ranges. What is not clear is how the soil affects electroremediation, and how the soil behavior should be incorporated in the transport model for predictive purposes.

The chemical formula for the clay mineral kaolinite is

\[ \text{kao} = \text{Al}_2\text{O}_3 \cdot \text{2SiO}_2 \cdot \text{2H}_2\text{O}(s) \] \hspace{1cm} 4.4

so the reactions involving Na, Cl, Ca, and Mg cannot be the result of pure kaolinite reactions. Also, starting with the equation relating gibbsite and kaolinite [Morel and Hering 1993]

\[ \text{Al(OH)}_3(s) + \text{H}_2\text{SiO}_3 = \frac{1}{2} \text{kao} + \frac{3}{2} \text{H}_2\text{O} \] \hspace{1cm} 4.5

it can be shown that the measured Al concentrations are not consistent with mineral equilibrium at the measured pHs. Heterogeneous mixtures and lack of equilibrium are typical of real soils as well. In general, a total description of all compounds in a soil will not be practical, and the system will not be well represented by mineral equilibrium equations.

The approach here is to develop artificial chemical models that approximate the measured soil chemical behavior as it affects electrochemical transport. Information about the soil composition may indicate important compounds; the pH and elemental analyses data from titrations will suggest chemical models and allow equilibrium variables to be fit; finally, running the numerical transport code with different chemical models will show how well the models reproduce the actual behavior.

It has been emphasized that mineral equilibrium does not apply on the time scale of electroremediation, yet the models proposed here are equilibrium models. The alleviating argument is that the soil responses are basically simple surface reactions, and occur on a time scale (minutes [Morel and Hering 1993]) that is short compared to electroremediation.
and mineral equilibrium. This is only an approximation, but the pH was found to be stable after one hour and the surface potential was shown to be stable up to one week, so there is experimental support for this claim.

### 4.2.1 Amphiprotic site

The simplest match to the measured pH behavior is an amphiprotic surface site $XH$ capable of accepting or donating a proton. The solid then acts as a weak acid and a weak base, buffering the medium to additions of base and acid through the reactions

$$XH + Na^+ + OH^- = X^- + Na^+ + H_2O$$  \hspace{1cm}  \text{(4.6)}
$$XH + H^+ + Cl^- = XH_2^+ + Cl^-$$

The first reaction decreases the pH by releasing $H^+$ into solution and the second does the opposite. This model ignores the effects seen in the elemental analysis. The chemical system is composed of seven species

$$\{[H^+, OH^-, Na^+, Cl^-, XH, XH_2^+, X^-]\} = \{H, OH, Na, Cl, XH, XH_2, X\}$$  \hspace{1cm}  \text{(4.7)}

whose values can be determined from three mass action equations

$$OH = K_2 \cdot H^{-1}$$  \hspace{1cm}  \text{(4.8)}
$$XH_2 = K_6 \cdot XH \cdot H$$
$$X = K_7 \cdot XH \cdot H^{-1}$$

plus four mass conservation (total) equations

$$T_e = H - OH + Na - Cl + XH_2 - X = 0$$  \hspace{1cm}  \text{(4.9)}
$$T_{Na} = Na$$
$$T_{Cl} = Cl$$
$$T_X = XH + XH_2 + X$$

Once the chemical model has been built, the totals $T_i$ are known from the composition of the mixture and the equilibrium coefficients $K_i$ are known functions. $K_2$ is simply the water equilibrium constant $K_w = 10^{-8} \text{mM}^2$. However, at this point the constant $T_X$, which is the concentration of surface sites in terms of the liquid volume, and the functions $K_6$ and $K_7$, which are equilibrium coefficients related to acid constants, have not been established.

If the $K_i$s are constant, then there is simple weak acid/base behavior; the titration curves would have shapes similar to that of Figure 4.2, where for illustration $T_X = 10^{-1.5} \text{mM}$, $K_6 = 10^{-2} \text{mM}^{-1}$, and $K_7 = 10^{-6} \text{mL^2}$ (from now on the $K$ units will be omitted, but will always be consistent). The experiments do not follow this behavior because surface charge
changes the overall $K$s with pH. Some way of incorporating varying equilibrium coefficients is needed. One approach is to define an ionization fraction

$$\alpha = \frac{XH_2 - X}{T_x}$$ \hspace{1cm} 4.10

such that $-1 \leq \alpha \leq 1$ here. Since there were two equilibrium coefficients, one more equation is needed to completely determine the system, for example,

$$XH_2 = 0 \quad \text{for} \quad \alpha \leq 0$$

$$X = 0 \quad \text{for} \quad 0 \leq \alpha$$ \hspace{1cm} 4.11

If $\alpha$ is an arbitrary function fit to the data, then $T_x$ can be given any value. The ionization fraction is related to the known concentrations from the titration by

$$\alpha = \frac{1}{T_x} \left( -H + \frac{K_w}{H} - T_{Na} + T_{Cl} \right)$$ \hspace{1cm} 4.12

In the practice of solving the chemical equilibrium problems, $H$ is often used as an iterating variable. This means that $H$ is treated as known within an iteration, so it is useful to define $\alpha$ in terms of $H$ or pH. Ionic strength is the next-most-likely candidate for $\alpha$.
dependence, but it was demonstrated in the experimental chapter that ionic strength had little effect on the titration. It is therefore proposed that $\alpha = \alpha(pH, \text{ only})$, and a polynomial curve fit of the experimentally-generated $\alpha$ is used in the chemical model.

There are some problems with the amphiprotic site approach. The most obvious is that the ion consumption and release behavior uncovered in the analysis of the pore fluid is completely ignored. Another problem is more subtle but more serious: the formulation violates assumptions in the transport model. In that development, the medium was divided into bulk liquid and solid. One way to view this is as including the charged liquid layer (if it exists) with the charged solid. The bulk liquid is always electrically neutral, so the combined solid should be as well. In Equation 4.6, however, the surface site becomes charged and so there is a net charge as well among the free ions, which is not allowed in the current development. Another way to view the situation is to include the charged surface site with the charged liquid in the bulk liquid phase, thus maintaining electroneutrality. However, this arrangement still violates the current assumptions because the surface sites do not convect with the rest of the liquid.

4.2.2 Ion exchange site

Ion exchange behavior is well known in the field of soil chemistry [e.g., Bolt et al. 1978]. Modeling the soil with ion exchange sites addresses the two problems cited above: it maintains electroneutrality of the conceptual solid and liquid phases, and it incorporates the prominent cation consumption and release seen in the elemental analysis results. Since Na\(^+\) is the major participant, a sodium ion exchange site is used,

\[
\begin{align*}
\text{XH} + \text{Na}^+ + \text{OH}^- &= \text{XNa} + \text{H}_2\text{O} \\
\text{XNa} + \text{H}^+ + \text{Cl}^- &= \text{XH} + \text{Na}^+ + \text{Cl}^-.
\end{align*}
\]

In response to base addition, Na\(^+\) consumption matches the measured behavior seen in the experiments. In response to acid addition, Na\(^+\) release is a substitute for the release of Al\(^{3+}\), Ca\(^{2+}\), and Mg\(^{2+}\). This system has six unknowns

\[
\{[\text{H}^+, \text{OH}^-, \text{Na}^+, \text{Cl}^-, \text{XH}, \text{XNa}]\} = \{\text{H}, \text{OH}, \text{Na}, \text{Cl}, \text{XH}, \text{XNa}\}
\]

and six equations

\[
\begin{align*}
T_e &= H - OH + Na - Cl = 0 \\
T_{Na} &= Na + XNa \\
T_{Cl} &= Cl \\
T_X &= XH + XNa
\end{align*}
\]
\[ \text{OH} = K_2 \cdot H^{-1} \]
\[ \text{XNa} = K_s \cdot \text{Na} \cdot \text{XH} \cdot H^{-1} \]

As was found in the amphiprotic site model, \( K_s = \text{const} \) cannot describe the experimental behavior well. With constant equilibrium coefficient, the last equation has a dependence on sodium concentration that is not supported by the titration data. In giving the equilibrium the proper functional dependence, it is convenient to replace the last Equation 4.15 with

\[ \text{XNa} = (1 - \alpha)T_x \]

4.16

where the ionization fraction \( \alpha \) can be a function of any of the concentrations. The function \( \alpha \) can now be found by fitting the titration data

\[ \alpha = \frac{1}{T_x} \left( -H + \frac{K_w}{H} \cdot T_{Na} + T_{Cl} + T_x \right). \]

4.17

Again, the varying ionic strength titration results suggest that \( \alpha = \alpha(\text{pH}, \text{ only}) \).

The ionization fraction \( \alpha \) is a good approach for working with data that has behavior better described by Equation 4.16 than constant \( K_s \) in Equation 4.15. However, there is a drawback that should be mentioned. As the transport proceeds, it is possible to develop regions with small \( T_{Na} \) but still moderate pH, and Equation 4.16 can then give \( \text{XNa} > T_{Na} \). This is physically impossible and causes negative \( \text{Na}^+ \) concentrations. One solution is to further refine the curve fit for \( \alpha \), but a simpler approach is to modify Equation 4.16 to be

\[ \text{XNa} = \min((1 - \alpha)T_x, T_{Na}). \]

4.18

This has no noticeable effect on the titration curve.

### 4.2.3 Aluminum hydroxide

A final step is now taken in the development of the soil chemical model. It was noted that the ion exchange model substituted \( \text{Na}^+ \) release in the acidic range with \( \text{Al}^{3+} \). In representing the pH response to acid, this does not matter. However, it means that subsequent transport and chemical behavior of reactive aluminum are represented by relatively nonreactive sodium. It will be seen later that there are reasons for including aluminum in the transport, so a method of doing so is now pursued.

There are several ways that the aluminum soil behavior could be included. For example, Bolt et al. [1978] suggest that some of the soil's behavior can be treated as \( \text{AlCl}_3 \). The most general approach consistent with the transport model would be to include another surface site that could bind with \( \text{Al}^{3+}, \text{Na}^+, \) and \( \text{H}^+ \), and then fit another set of equilibrium coefficient functions. Alternatively, the XH site introduced above could be allowed to bind
aluminum as $X_3Al$ and another set of equilibrium coefficient functions could be found. A simpler solution presents itself, however, after looking into the aquatic chemistry of aluminum.

Assuming a set of monomeric aluminum reactions in the presence of one solid [Morel and Hering 1993]

$$\text{Al(OH)}_3(s) + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O} \quad 4.19$$
$$\text{AlOH}^{2+} + \text{H}^+ = \text{Al}^{3+} + \text{H}_2\text{O}$$
$$\text{Al(OH)}_2^+ + 2\text{H}^+ = \text{Al}^{3+} + 2\text{H}_2\text{O}$$
$$\text{Al(OH)}_3^0 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$$
$$\text{Al(OH)}_4^- + 4\text{H}^+ = \text{Al}^{3+} + 4\text{H}_2\text{O}$$

and a respective set of equilibrium coefficients $pK = -8.5, -5.0, -9.3, -15.0, -23.0$, one can construct a solubility diagram. In a system with a limited amount of aluminum, the first reaction of Equations 4.19 may not hold if the total metal concentration is less than the solubility limit. These relations are used to generate the log c-pH diagram in Figure 4.3, where the total aluminum concentration is limited to 5 mM. Also shown in the plot is the concentration of Al measured in the kaolin titration.

![Figure 4.3: log c-pH diagram for Al$_T$ = 5 mM with measured Al from kaolin titration.](image-url)
There are a few comments to be made about Figure 4.3. First regarding the theoretical curves, it can be seen that all of the Al is in solution for pH < 3.8 and 12.1 < pH. Between these ranges, the precipitate is present and the solubility is relatively low. AlOH$^2$ is never a dominant species, and so can be neglected as a first approximation. Also, in the transport very small species concentrations are not a concern, so Al(OH)$_2$ and Al(OH)$_3$ can also be neglected. Next regarding the experimental points from the clay titration, it can be seen that the data can be grossly represented by the solubility curve. The agreement is poor for the pH = 3 region, but the main behavior of increasing at intermediate pHs and saturating at extreme pHs is reproduced. No chemist would be satisfied with this arrangement, but in light of the larger transport issues, this is viewed as an expeditious way of including release of reactive cations. Since the small amounts of Ca$^{2+}$ and Mg$^{2+}$ are released with Al$^{3+}$ and they can react with OH$^-$ as well, they will be considered to be part of the Al$^{3+}$ release.

Two physical explanations of this behavior will be hazarded: 1) If the aluminum comes from impurities in the clay, perhaps even Al(OH)$_3$(s), then it is reasonable that its dissolution corresponds to gibbsite and that its total amount is limited. 2) If the aluminum results from dissolution of unstable clay [Hunter 1981], then it is again reasonable that gibbsite behavior is relevant. It is not expected, though, that the total concentration would be limited in this case. The dissolution process may halt once the most unstable material is gone, or there may be a slow time progression that was not examined here. It is likely that the aluminum release continues, and this model only approximates some average behavior on the scale of one day.

An ion exchange site like the one above is included again to model the sodium consumption. The system becomes one with nine species concentrations

$$\{[H^+, Ohi^-, Na^+, Cl^-, Al^{3+}, Al(OH)_4, Al(OH)_3 - s, XH, XNa]\}$$

$$= \{H^-, OH, Na, Cl, Al, AlOH4, AlOH3s, XH, XNa\}$$

five mass conservation equations

$$T_e = H - OH + Na - Cl + 3Al - AlOH4 = 0$$

$$T_{Na} = Na + XNa$$

$$T_{Cl} = Cl$$

$$T_X = XH - XNa$$

$$T_{Al} = Al + AlOH4 + AlOH3s$$

and four equilibrium equations
\[ OH = K_2 \cdot H^{-1} \]
\[ AlOH4 = K_6 \cdot Al \cdot H^{-4} \]
\[ XNa = (1 - \alpha)T_x \]

\[
\begin{align*}
al OH3s = 0 & \quad \text{if} \quad K_{10} \cdot Al \cdot H^{-3} < 1 \\
1 = K_{10} \cdot Al \cdot H^{-3} & \quad \text{if} \quad 0 < T_{Al} - (Al + AlOH4)
\end{align*}
\]

Which version of the last equation is appropriate is not known \textit{a priori}. In practice, one version is chosen, the system is solved, and then the condition is tested to see if the other version should be used.

Since the aluminum release is assumed to come from a known amount of Al(OH)₃(s) with known equilibrium constants from literature, it only remains as before to determine the ion exchange function \( \alpha \) from the titration curve. In terms of the known \( Ts \) and measured \( H \),

\[
\alpha = \frac{1}{T_x} \left[ -H + \frac{K_w}{\mathcal{H}} - T_{Na} + T_{x} - 3Al(H,T_{Al}) + AlOH4(H,T_{Al}) \right]
\]

The aluminum species are not simple functions because the conditions of the last Equation 4.22 must be found. This approach and experimental titration were combined to produce the plot and curve fit of ionization fraction in Figure 4.4. The assumptions of \( T_{Al} = 8 \text{ mM} \) and \( T_x = 100 \text{ mM} \) were used, and it was also assumed that there is a small amount of acid with the clay, \( HCl_0 = 0.1 \text{ mM} \). This last assumption has insignificant effect on the soil behavior during the transport, it is made for aesthetic reasons of matching the zero-alkalinity initial pH. For pHs outside of the range shown in the figure, \( \alpha \) is limited to the largest measured value. The experimental pHs did not extend high enough to determine if the \( \alpha \) curve saturates, but pH = 13 was the highest seen in the electroremediation experiments.
\[ \alpha = 1 + \chi (a_1 + \chi (a_2 + \chi a_3)) \]

\[ \chi = \text{pH} - 4.336 \]

\[ \{a_1, a_2, a_3\} = \{-0.852, 0.0184, -0.00206\} \]

Based on \( \{T_X, T_{Al}\} = \{100, 8 \text{ mM}\} \)

Figure 4.4: Ionization fraction versus pH for aluminum hydroxide soil model.
4.3 Simulations of the electroremediation experiments

The purpose of this section is to evaluate the various system chemistry models in terms of the predictions of the transport model. One of the goals of this work is to show what is required to make quantitative predictions of varying electroosmotic flow. However, the flow, migration, and soil chemistry are so intimately linked that their influences become indistinguishable in the overall transport. In order to first evaluate the behavior of the chemical models, the electroosmotic flow prediction is separated from the problem in 4.3.1 Simulations with experimental flow as an input. Once the importance of a proper chemical model is established, the full predictions are then tackled in 4.3.2 Simulations predicting electroosmotic flow.

Some of the simulation parameters were common to all of the systems. The medium length and diameter were 150 mm and 54 mm, and the cathode reservoir volume was 165 mL. The anode reservoir volume depends on whether the recirculation system was used or not: for the untreated case, the volume was 71.8 mL and for the base addition case the volume was 4500 mL. The applied potential was constant at 15 V, which gives an applied field of 100 V/m. In the experiments, the medium length was not necessarily 150 mm and changed slightly over time. However, the applied potential was controlled to keep a 100 V/m applied field.

For liquid transport properties, the standard water values of permittivity \( \varepsilon = 7 \cdot 10^{-10} \text{ C V}^{-1} \text{ m}^{-1} \) and viscosity \( \mu = 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} \) were used. The medium transport properties addressed in the experimental chapter were porosity \( n = 0.55 \), tortuosity \( \tau = 1.65 \), surface conductivity \( \sigma_s = 10^{-3} \text{ S/m} \), and hydraulic permeability \( k_h = 4.3 \cdot 10^{-16} \text{ m}^2 \). The electroosmotic permeability is given by the zeta-potential which was addressed above.

The chemical system parameters will be noted in their specific sections, but in all cases the electrochemical generation reactions at the boundaries were taken to be those of water electrolysis, or

\[
R_{\text{H}+} = \frac{nA_T}{V_{\text{ra}}} \frac{i}{F} \quad \text{(anode)} \quad 4.24
\]

and

\[
R_{\text{OH}^-} = \frac{nA_T}{V_{\text{rc}}} \frac{i}{F} \quad \text{(cathode)} \quad 4.25
\]
where as usual \( n \) is the porosity, \( A_T \) is the medium (cylinder) cross sectional area, \( V \) is the reservoir volume, and \( i \) is the interstitial current density. When a soil chemistry model is used, all of the soil-related concentrations are multiplied by 2.2/1.2 = 1.833; this takes into account that the concentration of solids is higher in the consolidated soil.

The numerical code was a one-dimensional, finite-difference version of R.A. Jacobs' two-dimensional, finite-element implementation [Jacobs et al. 1994, Jacobs 1995, Jacobs and Probstein 1996]. An evenly spaced 100 point grid was used and various fractions of the Courant number were used to give stability in the time integration. Because the time steps could become very small in some cases when a local electric field was large, a minimum time step of one second was enforced. The errors associated with this are generally unimportant in terms of the total mass transport because the concentrations are small where the electric field is high. There are larger issues to be confronted later in the representation of the high field regions.

4.3.1 Simulations with experimental flow as an input

To focus on the soil chemistry effects, i.e. simulations in this section were run with the experimental convective velocity \( u(t) \) as an input. This means that the convective flow equation linking the electric and pressure potentials is not involved. All other parameters are either determined from independent experiments or calculated in the simulation, and the transport problem is still quite complex: the concentration and electric potential distributions must be found and the migration, diffusion, and chemical reactions of all species must be determined as they progress in time and space. Comparisons between simulations and experiments can be made in terms of the probe voltage distributions and the medium's average conductivity or, equivalently, the measured current. These two criteria together are stringent and complimentary: the conductivity indicates whether the overall ionic composition is accurate, while the voltage distribution reflects whether the relative distribution is represented well.

4.3.1.1 NaCl system

The NaCl system has only \( H^+ \), \( \text{OH}^- \), \( \text{Na}^+ \), and \( \text{Cl}^- \) as chemical species, and thus neglects soil chemistry effects. This is the chemical system that was run in the simple example of the model chapter.

This system can be described by
\[ T_e = H - OH + Na - Cl = 0 \]

\[ T_{Na} = Na \]

\[ T_{Cl} = Cl \]

\[ OH = K_2 \cdot H^{-1} \]

where \( K_2 = K_w \) as usual. The chemical equilibrium solution is explicit, and only two total quantities (\( T_{Na} \) and \( T_{Cl} \)) need to be followed in the transport equations.

Predictions of average medium conductivity (introduced in the experimental chapter) are plotted with the experiments results in Figure 4.5. It can be seen that the agreement is not good in either case. In the untreated electrode case, the simulation shows the conductivity increase at early times, followed by a drop to a plateau. This behavior has already been discussed in connection with the simulation of the simple example in the model chapter. The experimental conductivity, however, drops immediately. These discrepancies, however, pale in comparison to those in the case of base addition to the anode. The simulation shows the medium conductivity increasing immediately in response to the base addition, while the experiment shows an initial drop matching the untreated case. It is not until late in the experiment that the medium conductivity rises.

The voltage at the probes gives an indication of how the conductivity is distributed. The trace for the untreated electrode case is shown in Figure 4.6, where it can be seen that there

![Figure 4.5: Conductivity trace for experiments and NaCl (no soil chemistry) simulations.](image-url)
Figure 4.6: Probe voltage trace without base addition, experiment and NaCl simulation.

Figure 4.7: Voltage distribution without base addition, NaCl simulation.
is fair agreement for most of the simulation, corresponding to matching the current in Figure 4.5 except at early times. Figure 4.7 shows how the voltage distribution relates to these probe traces: all of the probes are at intermediate distances in the medium, so they are all on the plateau in the distribution.

The conductivity agreement was poor for the base addition case, and the voltage trace for this case in Figure 4.8 supports this. The model without soil chemistry predicts that the electrode treatment maintains a linear voltage distribution (hence uniform field), but the experimental data shows that this is clearly not the case. The beneficial aspects of the electrode treatment cannot be determined until this process is better understood.

It was because of the poor agreement between the simulation and experiments that soil chemistry models were pursued in the first place. The models introduced above will now be applied in the simulations.

---

**Figure 4.8**: Probe voltage trace with base addition at anode, experiment and NaCl simulation.
4.3.1.2 Amphiprotic system

The first experimental proof of the soil's chemical effect was the titration data presented earlier, and this pH effect was the initial focus. The amphiprotic site model presented above reproduces the titration pH exactly; it will now be seen how it affects the electrochemical mass transport simulation.

The average conductivity trace plot for the experiments and the amphiprotic soil chemistry simulations is shown in Figure 4.9. The noticeable improvement is in the initial behavior, where both conductivities drop instead of increasing as in the NaCl model. However, the base addition case's conductivity is not well represented. Also, although the untreated case looks good in the average conductivity plot, the probe voltage trace in Figure 4.10 shows that the distribution is not correct.

This simple model is not pursued further for two reasons: First, the model fails because it emphasizes pH but ignores other ions in solution. This doesn't matter for titrations, but for electrochemical transport this can mean neglecting the majority of the ions in solution. Consider that for an ionic strength of 10 mM, the pH does not describe the conductivity in the range 2 < pH < 12. Second, the charge density that develops violates the electroneutrality assumptions of the transport model, as was discussed in the model's introduction above.
Figure 4.9: Conductivity trace for experiments and amphiprotic site simulations.

Figure 4.10: Probe voltage trace without base addition, experiment and amphiprotic site simulation.
4.3.1.3 Ion exchange system

The ion exchange model attempts to address the drawbacks of the amphiprotic site model by 1) maintaining electroneutrality of the solid and liquid phases and 2) incorporating the cation consumption and release seen in the elemental analysis results. The results in terms of average conductivity are shown in Figure 4.11. The agreement is very good for both cases throughout the simulation time.

The voltage distribution is shown for the untreated case in Figure 4.12 and the base addition case in Figure 4.13. Both cases are well represented, with the exception of the last probe in the untreated case. It is possible that this is a smaller error than it appears, however, because the gradient of the potential is large in this region. This means that a small error in position of the gradient can make a large difference in the potential at point in space.

Incorporating the Na⁺ exchange makes physical sense based on the elemental analysis data and produces good representations of the two experiments. An explanation of the soil processes that occur with the anode treatment can now be given, but two of the earlier simulations should be recalled as references. First, Figure 4.14 shows the anode replacing

![Figure 4.11: Conductivity trace for experiments and ion exchange simulations.](image-url)
Figure 4.12: Probe voltage trace without base addition, experiment and ion exchange simulation.

Figure 4.13: Probe voltage trace with base addition, experiment and ion exchange simulation.
ion without base addition (H⁺) for the NaCl simulation. These curves have some of the steady-state characteristics of the simple example from the model chapter, although the curves here are not truly steady. The key point is that H⁺ from the anode is being destroyed by OH⁻ from the cathode, and this has caused the low conductivity zone near the cathode to develop, leading to the drop in medium conductivity (Figure 4.5, solid line). As the second reference, Figure 4.15 shows the anode replacing ion with base addition (Na⁺) for the NaCl simulation. Since Na⁺ does not react with OH⁻, it passes on to the cathode. Much more uniform concentration and conductivity result, and the conductivity increases with time (Figure 4.5, dashed line). Finally, Figure 4.16 shows the Na⁺ distributions for the base addition case from the ion exchange model, which is considered to be the realistic representation. What happens, in effect, is that the normally nonreactive Na⁺ ions react with the soil, releasing H⁺ ions which can then react with OH⁻ from the cathode

\[
XH + Na^+ = XNa + H^+
\]

\[
H^+ + OH^- = H_2O
\]

4.27
to give a low conductivity region. Eventually the XH sites are exhausted and Na⁺ again makes its way unmolested to the cathode, and this is observed in the "breakthrough" in the cathode pH seen in the experimental chapter. Also, when the low conductivity region is flushed out, the current increases dramatically. The sharp wave for the last time in Figure 4.16 is probably not resolved well in this model, but the overall profile is realistic.

The effect of the anode treatment, then, is to eventually raise the pH of the medium and make the electric field uniform. This effect is delayed by the soil chemistry, which rather ironically reacts with the "nonreactive" replacing ion.
Figure 4.14: H⁺ distribution (anode replacing ion without base addition), NaCl simulation.

Figure 4.15: Na⁺ distribution (anode replacing ion with base addition), NaCl simulation.
4.3.1.4 Ion exchange and aluminum hydroxide system

Although some success was achieved with the ion exchange model above, the agreement for the untreated case was not complete. The soil model that adds aluminum hydroxide behavior to the sodium ion exchange was run to see if there would be an improvement. The conductivity results in Figure 4.17 show a good match for both cases. The probe voltage traces without treatment (Figure 4.18) are better than the results for the ion exchange model alone (Figure 4.12). In the base addition case (Figure 4.19 versus Figure 4.13), the differences are not large.

It seems likely that, since the acid behavior is more important in the untreated case, the more realistic Al\(^{3+}\) release in this model (instead of Na\(^{+}\) release) gives better results. In the case with base addition, the sodium ion exchange dominates both models. The small differences between the two models during the radical changes late in the experiment are not considered important here.

![Conductivity trace for experiments and ion exchange with aluminum hydroxide simulations.](image-url)
Figure 4.18: Probe voltage trace without base addition, experiment and ion exchange with aluminum hydroxide simulation.

Figure 4.19: Probe voltage trace with base addition, experiment and ion exchange with aluminum hydroxide simulation.
4.3.2 Simulations predicting electroosmotic flow

In this section, the single “free” input to the simulation above—the convective flow velocity—is no longer specified. Instead, the empirical surface potential model developed earlier in this chapter is used in determining the local contributions to the electroosmotic flow. The inputs are all determined from independent experiments, and the evolution in time is determined solely by the numerical model. In this case, the test of the model is in its ability to quantitatively predict varying electroosmotic flow, a challenge which has not been overcome to date.

4.3.2.1 NaCl system

It was shown above that the system without soil chemistry did not represent the experiments well, but the simulation velocity results for the model are given in Figure 4.20 for reference. The initial velocity is wrong because the initial pH is incorrect, which gives a negative zeta-potential and positive flow in the model. The model does show a flow increase as do the experiments, but the predicted velocities are too high.

The no treatment simulation becomes unstable because of the sharp potential and pH gradients that develop. In that condition, small changes are fed back into a large driving field. The base addition curve looks more plausible, but it is based on an even field at a high conductivity, which was shown to be incorrect.

4.3.2.2 Ion exchange and aluminum hydroxide system

The velocity predictions for the best of the soil chemical models is shown in Figure 4.21. The initial predicted flow rates are negative (towards the anode) and are in good agreement with the experimental values. The predicted velocities for the two cases increase together, as do the experiments’. However, the early experimental velocities are considerably larger than the simulations’. All of the values match for $0.55 \cdot 10^5 < t < 1.4 \cdot 10^5$ s (0.6 to 1.6 days), at which point all four curves diverge. While the experimental base addition velocity plateaus and the untreated velocity drops, the simulated base addition velocity continues to increase while the untreated velocity plateaus. Once the flow prediction goes awry, the species distributions cannot be correct and it is unlikely that the simulation can return to match the experiment. The deviation of the curves that occurs will be discussed in more detail shortly.
Figure 4.20: Electroosmotic velocity traces for experiments and NaCl simulations.

Figure 4.21: Electroosmotic velocity traces for experiments and ion exchange with aluminum hydroxide simulations.
Figure 4.22: Probe pressure trace without base addition, experiment and ion exchange with aluminum hydroxide simulation.

Figure 4.23: Pressure distributions for early times, ion exchange with aluminum hydroxide simulation.
The pressure indicates the relative distribution of contributions to the bulk liquid flow, just as the voltage indicated the relative distribution of contributions to the ion flow (current). Figure 4.22 shows the probe pressures from the untreated experiment and simulation. The early pressure predictions are somewhat high because the predicted velocity is also high, but then the curves cross. Later, as the experimental pressures begin to even out again, the simulation continues to generate progressively lower pressures, finally reaching impossible negative values. By this time, the simulation is clearly not providing reasonable results. To show what is going on in the overall pressure development, the pressure distributions for early times are shown in Figure 4.23. This indicates that only the soil near the cathode is actively contributing to the electroosmotic flow; the rest of the soil is having the liquid passively dragged through it, and so has a near-linear pressure drop as in standard porous medium flow. This behavior will be discussed in more detail in the conclusions chapter.

At this point the changes that occur at $1.4 \times 10^5$ s can (and should) be discussed. There are two types of deviations that occur in the velocity plot: the simulation curves deviate from the experimental curves, and the two electrode treatment cases deviate from each other in both the experiments and simulations. It will not be surprising that these occurrences are related.

Ionic strength is the key indication of these deviations. Figure 4.24 shows the distribution from the untreated electrode case, and Figure 4.25 shows the results with base addition. Both cases develop significant regions with low ionic strength, and at $1.5 \times 10^5$ s the untreated case’s region is still growing in extent, while the base addition case’s is shrinking. The ionic strength is not important in itself, but in how it affects the Debye length. The dimensionless Debye length was given in the model chapter as

$$\lambda' = \frac{1}{a} \left[ \frac{\varepsilon RT}{21F^2} \right]^{1/2}.$$  \hspace{1cm} (4.28)

Using the capillary model’s hydraulic permeability to roughly estimate an effective pore radius and then inserting the values found earlier,

$$\lambda' = \frac{1}{\sqrt{I}} \left[ n \frac{\varepsilon RT}{16 \tau^2 k_h F^2} \right]^{1/2} = \frac{0.074 (\text{mol m}^{-3})^{1/2}}{\sqrt{I}}.$$  \hspace{1cm} (4.29)

For an ionic strengths of 0.1 and 0.01 mM, the dimensionless Debye lengths are 0.23 and 0.74. This means that the Debye length is no longer small compared to the pore dimension $(\lambda' \ll 0.1)$, and the assumptions that lead to the proportional relationship

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Figure 4.24: Ionic strength distribution without base addition, ion exchange with aluminum hydroxide simulation.

Figure 4.25: Ionic strength distribution with base addition, ion exchange with aluminum hydroxide simulation.
between surface potential and electroosmotic permeability break down. Applying the cylindrical, uniform parameter results [Rice and Whitehead 1965], the attenuation factors would be 0.60 and 0.18 for Debye lengths of 0.23 and 0.74. Although this analysis is not really applicable here, it does show that there could be a significant error in using the small-Debye-length assumption to find the electroosmotic flow contribution in these regions.

There are two related effects from the low ionic strength region: 1) the experimental cases’ flow rates diverge because the electrode treatment begins to have an effect on the low \( I \) region, and 2) the simulations diverge from the experiments because the model does not take into account the electroosmotic attenuation with low \( I \).

Finally, to see the effect of the rather weak surface potential model, another model based on a curve fit of Lorenz’s data shown in the experimental chapter [Lorenz 1969, Eykholt and Daniel 1994] was used. In this case, the zeta-potential is a function of pH only instead of pH and ionic strength. Qualitatively, Lorenz’s data has a lower pH, and larger negative \( \zeta \) in the near-neutral pH range. This results in the higher initial velocities seen in Figure 4.26. In fact, this model of \( \zeta \) may give better results although it was for a different form of kaolinite (\( Na^+ \) instead of \( H^+ \)). Basing the model in this chapter on linear fits of few points may have been too cavalier. In any case, it can be seen that the different models affect the flow rates significantly, but the behavior is the same.
Figure 4.26: Electroosmotic velocity traces, experiment and simulations with different zeta-potential models.
5. Closing

The sections concluding this enterprise are Extensions, Conclusions, and Future work.

5.1 Extensions

The material up to this point has been devoted to a few cases in excruciating detail. The goal of this section is to extend the results into wider application. For example, quantitatively predicting electroosmotic flow was a stated goal that was achieved (until the Debye lengths became large) by including a sufficient level of detail, most notably in a functional soil chemistry model. The value of this achievement is not in the flow prediction itself, but in developing a model with enough realism to give more fundamental understanding of the processes. The plan is to start with specifics reminiscent of the previous discussions, then move into progressively more general areas.

5.1.1 Electroosmotic flow initiation

In many electroremediation experiments in kaolin clays, it is observed that there is an initial period of flow towards the anode (here \( u < 0 \)) as was seen in this work [Shapiro and Probstein 1993, Eykholt and Daniel 1994]. In an experimental setup that cannot measure reversed flow, this could be mistakenly interpreted as a period of zero flow [Acar et al. 1994]. Negative initial flow is not surprising given that 1) the electroosmotic permeability can be negative (\( \zeta > 0 \)) for pH < 6, and 2) clays that give a significantly acidic initial pH are often used. The more interesting question is why the flow would ever become positive. The answer can be found in the distribution of the electroosmotic contribution to the bulk flow. The flow equation can be rewritten to give the local electroosmotic flow contribution in velocity units as

\[
\frac{k_e}{n \mu} E = u + \frac{k_s}{n \mu} \nabla p. \tag{5.1}
\]

Knowing that \( k_e < 0 \) for low pH and \( k_s > 0 \) for high pH gives the direction of the contribution, but the magnitude will depend on the local electric field strength \( E \). Equation 5.1 can be computed from the simulation data, and the short time results for the untreated simulation are shown in Figure 5.1. Initially the contribution is uniform and
Figure 5.1: Electroosmotic flow contribution for early times, including flow direction reversal.

slightly negative, so the flow is negative. At the next time (1.8·10⁴ s or 5 hours) most of the medium’s contribution is unchanged, but there is a small area near the cathode developing a relatively large positive contribution. At this point the flow is still negative but is slowing. By the next time (10 hours), the positive region has grown to the extent that the flow is now positive.

The key, then, is that E becomes large precisely where \( k_e \) takes on significantly positive values. The electric field strength is relatively large because the conductivity is relatively small there. To understand this from the transport chemical changes, consider a dimensionless conductivity change difference as

\[
\Delta \sigma' = \frac{\sum_{\text{react.\& prod.}} v_i z_i^2 v_i}{-\sum_{\text{react.}} v_j z_j^2 v_j}.
\]

This is designed to give a change from an initial conductivity in terms of moles reacted, where \( \Delta \sigma' > 0 \) indicates a conductivity increase. Near the anode, the transport has the rough effect of generating HCl by moving H⁺ and Na⁺ (see the simple example in the model chapter). Representing this change without soil chemistry gives
\[ \text{Na}^+ + \text{Cl}^- + \left(\text{H}^+ - \text{Na}^+\right) = \text{H}^+ + \text{Cl}^- \]

where the parentheses are used to indicate that the transport is not really a reactant and will not be included in the conductivity. This gives a conductivity change of

\[ \Delta \sigma' = \frac{v_H - v_{Na}}{v_{Na} + v_{Cl}} = 2.37. \]

In the simple example, this is manifested as a higher conductivity and hence lower field near the anode since \( \text{H}^+ \) has a significantly higher mobility than \( \text{Na}^+ \). Near the cathode, the version of Equation 5.3 is

\[ \text{Na}^+ + \text{Cl}^- + \left(\text{OH}^- - \text{Cl}^-\right) = \text{Na}^+ + \text{OH}^- \rightarrow \Delta \sigma' = 0.96. \]

This indicates that without soil chemistry effects, the conductivity will increase near the cathode and anode, as was shown in the simple example earlier. However, the field will be larger near the cathode since the relative conductivity increase is smaller. This is a result of the large difference in mobilities between \( \text{H}^+ \), the fastest commonly encountered ion, and \( \text{Na}^+ \), one of the slowest.

The first soil chemistry model introduced in this work was the amphiprotic site model. Although it was subsequently rejected, its versions of Equations 5.3 and 5.5 are now given:

\[ \begin{align*}
\text{Na}^+ + \text{Cl}^- + \text{XH} + \left(\text{H}^+ - \text{Na}^+\right) &= \text{Cl}^- + \text{XH}_2 \quad \rightarrow \quad \Delta \sigma' = -0.40 \\
\text{Na}^+ + \text{Cl}^- + \text{XH} + \left(\text{OH}^- - \text{Cl}^-\right) &= \text{Na}^+ + \text{X}^- + \text{H}_2\text{O} \quad \rightarrow \quad \Delta \sigma' = -0.60.
\end{align*} \]

For the more successful ion exchange soil chemistry model, the versions of Equations 5.3 and 5.5 are

\[ \begin{align*}
\text{Na}^+ + \text{Cl}^- + \text{XNa} + \left(\text{H}^+ - \text{Na}^+\right) &= \text{Na}^+ + \text{Cl}^- + \text{XH} + \text{H}_2\text{O} \quad \rightarrow \quad \Delta \sigma' = 0 \\
\text{Na}^+ + \text{Cl}^- + \text{XH} + \left(\text{OH}^- - \text{Cl}^-\right) &= \text{XNa} + \text{H}_2\text{O} \quad \rightarrow \quad \Delta \sigma' = -1.
\end{align*} \]

In the ion exchange with aluminum hydroxide soil chemistry model, the corresponding equations for the anode and cathode regions become

\[ \begin{align*}
\text{Na}^+ + \text{Cl}^- + \frac{1}{2}\text{Al(OH)}_3(\text{s}) + \left(\text{H}^+ - \text{Na}^+\right) &= \frac{1}{2}\text{Al}^{3+} + \text{Cl}^- + \text{H}_2\text{O} \quad \rightarrow \quad \Delta \sigma' = 0.09 \\
\text{Na}^+ + \text{Cl}^- + \text{XH} + \left(\text{OH}^- - \text{Cl}^-\right) &= \text{XNa} + \text{H}_2\text{O} \quad \rightarrow \quad \Delta \sigma' = -1.
\end{align*} \]

The individual values for these conductivity changes are not meaningful, but the relative differences are. In all four chemistry models the cathode region conductivity is relatively lower than that of the anode. In the last two soil chemistry cases the relative drop is very significant. These all indicate that the "active" region of the medium will be near the cathode.
since the electric field strength becomes concentrated there, and since $k_e$ is positive ($\zeta < 0$) for basic kaolinite conditions, the flow tends to be driven towards the cathode as the process develops. The point of flow reversal from negative to positive comes when the small region of high positive contribution outweighs the larger region of slightly negative contribution. Note that the soil chemistry analysis is applicable only until the sites are exhausted; at that point the changes follow those of the NaCl solution. Because of a buildup of ions in the electrode reservoir, the conductivity is high next to the cathode, and the low conductivity cathode region is somewhat away from that interface.

Other soils have less variable surface potential (e.g., montmorillonite) and may not display flow reversal or wide flow variations in time. In particular, for a medium with constant $k_e$ and $k_n$, the one-dimensional flow equation can be integrated to give

$$u = \frac{k_e}{\eta \mu} \Delta \phi - \frac{1}{\eta \mu} \int_{p_0}^{p_1} k_n dp.$$  \hspace{1cm} (5.9)

This means that the electroosmotic contribution depends only on the overall applied potential and not on the distribution of the field. A similar conclusion was discussed earlier for the pressure contribution. Although conductivity changes may cause large variations in the electric potential distribution, the electroosmotic contribution depends only on the applied boundary conditions, and so may be constant from the beginning. However, the analysis above does not take into account the attenuation at large Debye lengths, which is discussed next.

### 5.1.2 Electroosmotic flow cessation

The electroremediation literature is rife with observations of electroosmotic flow cessation [Shapiro et al. 1989, Hamed et al. 1991, Jacobs et al. 1994, Acar et al. 1995]. Despite (or perhaps because of) the undesirability of this occurrence, the phenomenon tends to be mentioned in passing. The most prevalent qualitative explanation of flow cessation involves the soil isoelectric point (pH$_0$, where $\zeta = 0$). However, it is unlikely that the pH in the high field region is exactly pH$_0$. A low ionic strength effect on the surface potential is not a likely cause either; experiments on clays and oxide surfaces show the magnitude of the surface potential increasing as ionic strength decreases.

Although the model in this work did not predict flow cessation, the reason for its occurrence can be found from the observations here. Stated briefly, the cause of flow cessation is the low ionic strength region. The fundamental physicochemical effect is the development of large Debye lengths which greatly attenuate the electroosmotic permeability $k_e$, even if the surface potential is constant. An associated transport effect is low
and hence high field in the region. This means that most of the electrical effort is being applied right where it is least effective. There is also an experimental effect that may play a role in some observations: the high field region creates low pressures and large pressure gradients, which may not be supportable in some apparatuses. Low pressures can cause external leaks, and large pressure gradients can cause “short-circuiting” along the walls of the test cell.

5.1.3 Practical sensitivity of electroosmosis

There are implications of the developments here that will be important for electroosmosis as an electoremediation tool. Some of these are discussed below, but others related to flow cessation and attenuation are given here.

If the issues of 5.1.4 Relative chemical concentration of soil and 5.1.5 Electrode treatment are not heeded, then a low ionic strength region may develop in the soil. In the extreme, this can cause flow cessation as discussed above. Even if the ionic strength is not low enough to greatly reduce the flow, the nonuniform field will give rise to low pressures. Low pressures in the field may cause the velocity distribution to change in ways not desired, which could lead to expending energy to move liquid that is not contaminated. Low pressure could also cause evolution of dissolved gases, breaking the ionic conductance in the region. In another gas generation effect, the high field region will be associated with high local heating, and lowering the pore pressure will lower the boiling point of the liquid.

In addition to low pressures, pressure gradients will pose a problem in the field. One original advantage of electroosmosis was applying a uniform body force to the fluid in the medium, thus generating a uniform flow even in heterogeneous hydraulic permeability. Once pressure gradients arise, however, the velocity field will once again be influenced by the medium heterogeneity. In particular, flow channeling through high permeability zones can reduce the effectiveness of the process.

Finally, note that there is now sensitivity to low hydraulic permeability as well. If the medium is composed of three zones (1 anode interface and anode region, 2 cathode region, and 3 cathode interface region) with constant $k_s$ and $k_e$ within a zone, then $\Delta \phi_1 = \Delta \phi_3 = 0$ and Equation 5.9 can be integrated in each zone to give

$$u = \frac{k_s k_1}{n \mu L} \Delta p_1 = \frac{k_s k_2}{n \mu L} \Delta \phi_2 + \frac{k_s k_2}{n \mu L} \Delta p_2 = \frac{k_s k_3}{n \mu L} \Delta p_3.$$  \hspace{1cm} 5.10

The largest that $\Delta p_1$ can be is one atmosphere, so the maximum velocity is dependent on the hydraulic permeability. A similar argument can be made for $k_{s3}$. This means that if the
soil near the anode or cathode is compressed by electrode emplacement or by mechanical stresses from the high electrical field, the maximum possible electroosmotic velocities are correspondingly reduced.

5.1.4 Relative chemical concentration of soil

Whether run at constant potential or constant current conditions, most electroremediation experiments display a nearly instantaneous immediate drop in conductivity, then reach a plateau. However, in some cases there is a significant initial rise in conductivity before the drop and plateau [Tondorf 1992, Jacobs et al. 1994, Acar et al. 1994]. The time scale of this behavior is such that the convective movement is negligible. The conductivity changes are a result of the migration transport, and the differences in the direction of the changes can now be identified as results of soil chemistry interactions.

The conductivity increase was seen in the NaCl simulations, and the conductivity decrease in the simulations including soil chemistry. In fact, the semi-quantitative, semi-intuitive tools for understanding these changes were introduced in the $\Delta \sigma'$ reactions given in 5.1.1 Electroosmotic flow initiation. There it was shown that there was a relative conductivity increase for the NaCl case and decreases for all three soil chemistry models. The implicit assumption in those analyses was that the soil concentration was on the order of the background electrolyte (NaCl) concentration. When the background electrolyte concentration is high compared to the soil's effective concentration, the system will behave as if the soil is not present. This is, in effect, what occurred in the literature experiments with conductivity increases noted above. Among experiments performed in similar clays, the ones with the highest initial background electrolyte concentrations where the ones that showed the conductivity increase.

A similar extrapolation can be illustrated with the transport simulation. In this case, the ion exchange soil model was run with the same initial background electrolyte (10 mM NaCl) but with three different soil concentrations: $T_x = \{55, 550, 5500 \text{ mM}\}$, the intermediate value being that found for the kaolin clay here. The early conductivity results are shown in Figure 5.2. It can be clearly seen that for low soil concentration, the curve is similar to the NaCl-only behavior. It is also noted that for soil concentrations high enough that the sites are not exhausted, the soil concentration does not matter. Generalizations that are too strong should not be made because these results will depend on how the soil chemistry model is defined, but the fundamental idea is valid.

Those who want to know whether they need to worry about soil chemistry should consider the concentrations of background electrolyte in the soil compared to some soil site concentration. In this ion exchange model, the ionization fraction had an initial value
Conductivity traces for three soil concentrations.

\( \alpha_0 = 0.5 \) and a range \( 0.2 < \alpha < 0.8 \). This makes an ion exchange capacity of \( \Delta \alpha T_x \in \{16.5, 165, 1650 \text{ mM}\} \) to acid or base. With an initial background electrolyte concentration of 10 mM, it makes sense that the two higher ion exchange capacities take over the system behavior. The pore electrolyte itself can never be “neglected” because it carries the current in the medium.

Similar analyses could be carried out to determine whether the background electrolyte dominates the contaminant chemistry as well. Jacobs [1995] used a related approach to determine when a system’s chemical equilibrium calculation could be simplified.

Some soils \( \text{e.g.}, \) sandy ones \) will have fewer reactive sites per volume and may have little soil chemical capacitance. Others \( \text{e.g.}, \) those rich in humates, clays with smaller particle size \) may have significantly higher reactive site concentrations than those observed here. The specific chemical models here have little general validity, but the approach and concepts introduced in this work could be useful in many electroremediation applications.

### 5.1.5 Electrode treatment

Much of this work has discussed electroosmotic flow, but migration was always an integral part of the process, and often the dominant one. The low conductivity region that proved detrimental to electroosmotic flow will pose difficulties for charged contaminant removal by
migration as well. When a large electric field is formed in one thin region, the field is small in the rest of the medium. This means that the migration velocities of charged contaminants in these areas will be small, so the process will take a very long time. It was also discussed in connection with the simple example that approaching a limiting current condition reduces the migration efficiency of the process. Furthermore, when the low conductivity region is formed by $\text{H}^+$ and $\text{OH}^-$ reaction, there will be a pH jump that focuses metal contaminants within the medium, while the objective is to move them to the electrode reservoirs.

Successful and robust electroremediation practice will involve control of the electric field, pH, and redox potential throughout the medium. Electrode treatment is the primary means through which control can be asserted, and great deal of the understanding developed in this work applies to the mechanisms of electrode treatment. Although this topic is too complex to address fully here, a few points will be made.

It was shown early on that the low conductivity region could be formed by $\text{H}^+$ and $\text{OH}^-$ reaction when the electrochemical processes at the electrodes were not controlled. This was an unstable process because of the positive feedback through the increasing electric field at that point. When soil chemistry played a role, the low conductivity region could be formed by reactions of pore solution ions with the soil. In simple terms, the low conductivity regions resulted when the replacing ions from one electrode could not make it to the opposite electrode. Electrode treatment to avoid nonuniform field could consist of introducing ions that do not have annihilating reactions with the soil medium or with the replacing ions from the opposite electrode. This will depend on the system chemistry and on the electrode reactions chosen.

Even if introducing reactive species cannot be reasonably avoided, the electric field development may be more easily controlled than that here. It was noted in the short-time analysis in the modeling chapter that there are two distinct types of replacing ion introduction: diffuse- and shock-wave behavior [Denisov et al. 1996]. The diffuse behavior was seen here, where nonuniform concentrations and electric fields were generated throughout most of the medium. Despite the intimidating name, the shock behavior could be more desirable because it creates two regions with uniform electric fields. Which type of behavior occurs depends on the relative mobilities of the initial and replacing ions, so the choice of the replacing ion should reflect this.

The pH is determined, of course, by the concentration of $\text{H}^+$. It would be unwise to consider the transport primarily in terms of $\text{H}^+$, however, because 1) its movement is linked to all of the other ions through the electroneutrality condition and 2) it is generated and annihilated in many reactions, including one with the most abundant chemical, $\text{H}_2\text{O}$. A better viewpoint comes from considering that because of electroneutrality, the pH is
determined by the concentration of all of the other species in solution. It was shown in connection with the experimental titrations that in systems dominated by strong acids and bases, the pH is determined by the alkalinity, which is the net charge from the nonreactive component of strong acids and bases. Controlling the pH in the medium, then, once again becomes a matter of introducing relatively nonreactive ions from the electrodes. By fully substituting Na⁺ for H⁺ at the anode but allowing OH⁻ to come from the cathode, a highly basic condition was created. This was somewhat modified by the soil chemistry, however, which effectively changed Na⁺ back into H⁺. The pH could be moderated by substituting various fractions of Cl⁻ for OH⁻ and Na⁺ for H⁺. This could be accomplished in practice with an automatic pH controller.

At one extreme of electrode treatment, the goal would be to introduce ions that exactly match what is initially in the medium (with the exception of the contaminant, of course). This would maintain the initial conditions throughout the process.

5.2 Conclusions

One major conclusion of this work is that soil chemistry affects the electroremediation process and also affects attempts to describe the process. The nature and importance of the effects will vary depending on the types and concentrations of the soil, contaminant, and background chemistry. In this work, the medium conductivity (hence species migration) and the electroosmotic flow rate could not be predicted accurately without including these effects.

The specific soil model constructed here will not be applicable for most natural soils, but the framework and procedure used will be useful and should be included as part of site characterization and process design. The general steps (with reference to this work in parentheses) are

1. Carry out chemical analyses of samples to find the initial composition of the pore solution and solid material. (The pore solution contained primarily NaCl.)
2. Use electrochemical species transport models to determine how the chemical compositions would change in the absence of more complicated soil chemistry, including the effects of different electrode treatments. (The formation of HCl and NaOH was seen in the simple example of the Model chapter, and the electrode treatment chemical was NaOH.)
3. Perform batch chemical experiments to explore the soil response to the expected changes from step 2. (NaOH/HCl titrations were performed and the pore solutions were analyzed for changes in H, Na, Al, Ca, Fe, K, Mg, and Cl.)
4. Develop chemical models that include the soil response seen in step 3. (Chemical equilibrium models of amphiprotic (acid/base), ion exchange, and aluminum reactions were considered.)

5. Use the electroremediation transport model again to predict the process evolution including soil chemistry effects, and verify the predictions with laboratory experiments. (A sodium ion exchange/aluminum hydroxide chemistry model reproduced the experimental results best.)

6. Design and refine electrode treatments and other control strategies to provide the best contaminant removal process. (This step was not fully taken here. However, the simulations showed why the base addition at the anode was not immediately effective: chemical changes were being caused by the soil at the cathode end.)

7. Apply what has been learned to design, monitor, and control the field process.

The term “soil” above should be taken to include anything that has not been specifically identified as contaminant or dissolved species.

Another conclusion is that varying electroosmotic flow can be quantitatively predicted from independent experiments and modeling. It was shown that a rather high level of detail is required to do this, including properly modeling the soil chemical response, the surface potential behavior, and the distribution of the electric field. The transport model used here performs well until large Debye lengths develop, violating the model’s assumptions.

The ability to predict varying electroosmotic flow led to the conclusion that the cause of flow cessation was the low ionic strength region that develops in many cases. This conclusion contradicts the most prevalent qualitative explanations which involve pH effects on the surface potential, $\zeta$.

The flow predictions here also showed how flow reversal comes about. The qualitative conclusion is that as the process develops, higher field strengths combine with higher pH (and decreasing negative surface potential) near the cathode to change the flow direction.

The development of a low ionic strength region was shown to be a common occurrence. Associated with this region are low overall conductivity, high local electric fields, a jump in pH, and large Debye lengths, all of which generally have a detrimental effect on the electroremediation process. Treating the electrode reservoirs to control the conductivity developments can be effective, but requires an understanding of the distributed electrochemical processes and the medium chemistry.

It was seen that a combination of potential information (voltage and pressure distributions) with corresponding flow information (conductivity and bulk velocity) could be powerful diagnostic tools. In particular, the voltage and conductivity pair was effective
in analyzing individual electroremediation processes and in comparing experiments with numerical simulations.

5.3 Future work

Future efforts might involve specific improvements to the work here and more general efforts improving understanding and practice of electroremediation. Some suggestions are given here in order of increasing scope, which largely corresponds to increasing importance.

Within the current framework, the weakest link is the empirical surface potential (zeta-potential) model. Given the dependence on pH and ionic strength that was found, too few experimental points were obtained to generate detailed parametric fits. In particular, literature data showed steeper changes with pH than were modeled using a linear curve fit. However, more detailed modeling will probably not reveal new phenomena, and the problems with the surface potential model are probably overshadowed by other shortcomings.

The chemistry models developed here are unparalleled in the field of electroremediation but are no doubt woefully oversimplified from a chemist’s point of view. Chemical equilibrium was used with the argument that time scale of the titrations approximated the time scale of chemical change in transport. This may not be the case. For example, it was seen that the flow rates and currents could be significantly different in the systems, so the chemical residence times would also be different. Another problem is assuming that the titration excursions in two parameters (alkalinity and ionic strength) sufficiently test the behavior of the system. Although these are the two most important parameters, the electrochemical transport process can develop many other solutions, which may be important if the ions have specific reactions with the solid. For example, in the titrations the aluminum concentrations were limited to what was released by the clay locally; in the transport problem, aluminum from other areas of the soil can be moved to one area at a concentration that is much higher. One experimental omission was not analyzing the clay pore solutions for silicon, which may be as important an element in the system as aluminum.

It would be very intellectually attractive to tie the observed chemical changes to surface potential changes through a surface complexation model. However, on the scale of the electroremediation problem in real soils, this effort would not be a wise use of energy.

The success in predicting the varying electroosmotic flow ended when the Debye lengths became significant. A model for correcting the electroosmotic permeability for
larger Debye length would be useful, but is not available at this point. There is a classic correction available for cylindrical capillaries with constant surface potential and electric field, and perhaps this could be used [e.g., Eykholt 1992]. However, in this case these parameters are not constant. More importantly, the geometry of the medium becomes significant if the Debye lengths become large, and the cylindrical geometry will not represent the particulate medium well.

The low ionic strength region emerged with major importance in this work, but it is not represented well in the physical model. The problem is that the model medium essentially has two phases: the bulk liquid and the solid which includes the charged surface and the charged liquid layer. This neglects transport in the double layer, which is not always a good assumption. The surface conductivity was introduced as a first cut at addressing this. A more rigorous way of dealing with the problem would be to consider a three-phase model composed of charged solid, equally charged double layer, and neutral bulk liquid. One obvious difficulty is keeping track of another phase in the mass transport; other difficulties have to do with the changing nature of the transport equations. For example, this would cause the current to be affected locally by the convective flow, which would couple some of the terms that are now separate.

By introducing more rigor in describing the changes during electroremediation, this work has emphasized the importance of understanding nonuniformities that naturally develop. A great deal of future work should be focused on electrode treatment strategies in avoiding these nonuniformities and controlling the electroremediation process.
6. References


