Two-dimensional Modeling of the Removal of Contaminants from Soils by Electric Fields

by

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Abstract

This dissertation presents the mathematical model and numerical code developed to simulate the removal of contaminants from soils by electric fields in two-dimensional geometries. The model describes the coupled transport of mass and charge as well as the chemical speciation of a multicomponent system subject to an applied electric field. The transport mechanisms included are electroosmosis, pressure-driven convection, electromigration and diffusion. The model can also describe chemical reactions occurring in the bulk fluid, interactions with the soil such as heterogeneous reactions and sorption processes, and electrochemical reactions occurring at the electrodes. The chemical reactions and sorption processes are assumed to be fast compared with the transport processes, so chemical and adsorption equilibria are assumed. The transport equations are based on quantities conserved throughout chemical and sorption processes, so in the resulting system of equations only the time scale of the transport processes needs to be resolved. These equations are discretized in space using Galerkin first-order finite elements with added isotropic diffusivity and are integrated in time using a first order explicit scheme.

The results from some simple test cases which highlight the different features of the code and the comparison of model predictions with experimental data are presented. The successful explanation of the experimental observations in terms of the modeled transport and chemical processes confirms the theoretical arguments behind the model. The numerical code allows one to study many features of the contaminant removal processes and examine the impact of varying key parameters, such as electrode placement, applied potential or conditioning technique, on the effectiveness and efficiency of the electrorestoration process at a specific site. Thus, the code developed will serve as a useful tool for both improving the understanding of the relevant physical phenomena and developing field applications of the technology.

Thesis Supervisor: Ronald F. Probstein
Title: Ford Professor of Engineering
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To my mother, whose sweet memory inhabits my heart;
and to Norelis, Daniel and Natalie for whom I thank God every day.
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Chapter 1

Introduction

The removal of contaminants from soils by means of electric fields has attracted considerable attention from industry, academia and government due to its high potential to achieve safe and cost effective in situ remediation of hazardous waste sites. As occurs with most emerging technologies, this process is referred to by several names, with the most common currently used being: electrorestoration, electroremediation and electroreclamation. The technique relies mainly on the electrokinetic phenomena of electroosmosis and electromigration to drive the contaminants contained in the pore liquid toward predefined collection points.

Electroosmosis, first observed by F. F. Reuss in 1809, is due to the force generated by the applied electric field on a thin layer of charged fluid that forms near the pore wall (see figure 1-1). This layer, known as the electric double layer, results from the effect of the charged pore wall on the distribution of nearby ions: coions are repelled and counterions are attracted toward the wall, resulting in a net charge in the liquid that neutralizes the surface charge of the wall. The electric field generated force causes the fluid in the double layer to move, which in turn, sets the bulk liquid in motion by viscous interaction (see Probsttein (1994) [31]). Therefore, in the scale of the porous medium, electroosmosis can be seen as acting in the direction of the local electric field.

Applied, induced or pre-existing pressure gradients may also contribute to the observed convection velocity in any particular case. Applied pressure gradients are
Figure 1-1: Electrorestoration of a hazardous waste site (adapted from Renaud and Probstein (1987) [33])

those resulting from imposed pressure difference across electrodes, induced pressure gradients refer to those arising from the spatial variation of the electroosmotic velocity, and pre-existing pressure gradients are those naturally occurring, as for example with variations in the underground water level. The relative contribution of the pressure gradients to the flow is determined by the hydraulic permeability of the medium. In high permeability soils, even small pressure gradients are likely to offset the effect of electroosmosis and become the dominant flow driving force. On the other hand, electroosmosis is likely to dominate in low permeability soils, provided they have a finite charge. This makes the use of electroosmosis particularly advantageous precisely at the conditions at which conventional pump and treat techniques become impractical.

In terms of the flow direction, two classes of electrodes are defined: sink electrodes
are those in which the pore liquid flows from the soil into the electrode reservoir, and source electrodes are those in which the liquid flows from the electrode reservoir into the soil. In the electroosmotic purging process (see Probstein et al. (1991) [34]) a purge solution is introduced at the source electrodes to maintain saturation in the soil and to enhance the contaminant removal by either increasing the electroosmotic flow rate or favoring the mobilization of the contaminants. Because the electroosmotic flow rate is proportional to the surface charge on the soil particles, purging liquids that result in a highly charged soil surface are desirable. It has been shown (see Shapiro (1990) [38]) that by tailoring the pH of the purging liquid to the specific soil/contaminant system, a significant increase in flow rate can be achieved at essentially constant power input.

The ability to remove contaminants from low permeability soils and to control the flow direction, along with the relatively low energy costs associated with electroosmotic purging, make it a promising technology for hazardous waste site remediation.

Electromigration results from the force exerted by the electric field on the charged molecules present in the solution. The migration velocity resulting from this electric force is proportional to the ionic charge and the local electric field. This process is typically more efficient than electroosmosis as the driving force is exerted directly on the molecules and not on the bulk liquid. Since the magnitude and direction of the force depends on the ionic charge, the net effect of migration on the transport of a contaminant is very dependent on its speciation. In cases where a significant fraction of the contaminant is in charged form (i.e. dissociated acids and bases or metal complexes), electromigration is likely to be the dominant transport mechanism. Poor contaminant removal has been observed in cases where the net charge of the contaminant changes sign (as for example when passing from being mainly in a positively charged free ionic form to being in the form of a negatively charged complex) at an intermediate region between the electrodes (see Hicks and Tondorf (1994) [18]). Electromigration has been used in a number of opportunities to remove metals from soils using electric fields (see e.g. Runnells and Larson (1986) [37], Hamed et al. (1991) [13], Lageman (1993) [24], Hicks and Tondorf (1994) [18]).
A variation of the basic electrorestoration process has been proposed (see e.g. Lageman et al. (1989) [25]) in which the purge solution is replaced by a washing or conditioning solution circulated through the electrode reservoirs. This has the advantage of allowing pH control at both electrodes, thus giving a better control over the chemical speciation of the system. For example, in their one-dimensional zinc removal experiments, Hicks and Tondorf [18] observed the development of a pH jump in the interior of the test module and the subsequent accumulation of the contaminant in a narrow band of the soil. Then, by washing the cathode electrode with a neutral salt solution, these authors avoided the formation of the pH jump and allowed acidic conditions to be established throughout the soil. As a result, the zinc was maintained in the \( \text{Zn}^{2+} \) form and was removed from the cell in the cathode wash solution.

Another version of the electrorestoration process has been put forward by Acar [1]. This author proposed the use of selective membranes in the electrode reservoirs as a means to prevent the migration of the pH fronts into the soil.

In addition to electroosmosis and electromigration of ions under the influence of the electric field, diffusion of the species in solution due to gradients in the chemical potential may be an important mass transfer mechanism. Several other physicochemical phenomena may also take place during the removal of contaminants from soil by electric fields. Among the most important are: chemical reactions in the bulk liquid; precipitation/dissolution of solid species; interactions with the soil such as adsorption, ion exchange and surface complexation; and electrochemical reactions.

The complex interactions between all the physicochemical processes taking place during electrorestoration make the response of a system very dependent on the given combination of chemical species, soil matrix and geometrical configuration. Therefore, it is difficult to extrapolate the response of a system from previous experimental observations or practical experience. Also, since laboratory experiments usually take from 1 to 8 weeks, the development of an experimental database is a very time consuming process. It is because of these obstacles that significant efforts have been devoted to the development of a mathematical model of the removal of contaminants from soil by electric fields. A mathematical model would not only allow predicting
the response of a system under specific conditions but would also help improving the understanding of the fundamental phenomena, and speed the design of field applications by showing the effect of varying key process parameters on the overall level, rate and cost of the contaminant removal.

The first advances in this area were introduced by Shapiro et al. in 1989 [40]. These authors presented a one-dimensional model of the removal of contaminants from saturated soil by electric fields and applied it to simulate the removal of phenol and acetic acid from kaolin clay. This model included dissociation reactions in the bulk liquid, electrochemical reactions at the electrodes and transport due to convection, migration and diffusion. Chemical equilibrium was applied since the chemical reactions were assumed to be fast compared to the transport processes. This implementation also modeled the coupled transport of mass and charge and used the electroneutrality condition to determine the electric field distribution and as a constraint in the chemical equilibrium calculation. The basic formulation was later extended to include linear adsorption isotherms and the numerical results compared with additional experiments in Shapiro (1990) [38] and Shapiro and Probstein (1993) [39].

Recently, the one-dimensional model was updated and a new numerical code developed to speed up the calculation and to handle more complex chemical systems including arbitrary adsorption isotherms as well as complexation, dissolution and precipitation reactions (see Jacobs et al. (1994) [21]). This model was applied to simulate the removal of zinc from kaolin clay and produced very good agreement with the experimental data reported by Hicks and Tondorf [18].

Another one-dimensional simulation has been presented by Acar and Alshawabkeh [2]. They calculated the transport of hydrogen ions in a salt solution under constant current conditions. This calculation, however, also assumed constant potential difference and uniform electric field, neglected electroneutrality and the effect of other ions in solution, so it is expected to have limited applicability.

In an actual field operation, the location and shape of the electrodes, together with the applied potential difference will dramatically affect the degree, cost and rate of contaminant removal by electric fields. While the one-dimensional model of the
electrorestoration process [40, 21] provides useful information about the response of a system subject to an applied electric field, the additional degrees of freedom in multi-dimensional systems change the solution in ways not easily extrapolated from a one-dimensional simulation. For example, in one space dimension, the current density is uniform, and the spatial variation of the electric field only results from changes in the electrical conductivity of the solution and in the concentration gradients. In two and three dimensions, on the other hand, the current density varies according to the geometry of the electrode array. The electric field suffers more severe variations, and the relative contribution of convection to the species flux varies over a wider range than in the one-dimensional case. As a result, the same chemical processes may have different effects on the species distribution depending on the number of space dimensions in the problem.

The objective of this work is to develop a mathematical model and numerical code to simulate the removal of contaminants from soil by electric fields in two-dimensional geometries. The model will allow the study of important features of multidimensional systems, such as the effect of electrode placement on the level and rate of contaminant removal or the effect of spatial variations of the soil charge and the hydraulic permeability on the convection flow; but more importantly, it will allow an easier application of the numerical solution to predict the behavior of real systems.

The numerical implementation of the electrorestoration model poses great challenges, not only because of the delicate interaction between the transport of mass and charge which results in a nonuniform, time-dependent electric field; or for involving the solution of a complex system of partial differential and algebraic equations; but mainly because of the development of thin boundary layers, high localized electric fields and kinematic shocks in the solution. These factors result in severe constraints on the mesh resolution and the time step size for numerical stability and consequently yield a high computational cost. It has been an important part of this research to find ways to overcome these difficulties and produce a code that provides a practical and physically meaningful solution to the transport problem given the constraints in the computational resources available.
The code developed computes the time evolution of several state and operational variables in a multicomponent system subject to an applied electric field. Among these are the spatial distributions of: the pH and all chemical species concentrations, the electrostatic potential and pressure, the bulk liquid and individual species velocities, the electrical conductivity, and the current density.

The numerical code is capable of describing multiple-electrode configurations in an arbitrary two-dimensional domain, allowing the specification of individual boundary conditions at each electrode. These conditions include the operating mode, the applied voltage and pressure, the speciation of the purge or wash solution, and the electrochemical reactions taking place.

This dissertation presents the most important aspects of the model and its numerical implementation, including their capabilities, their limitations and the key findings made during the development process.
Chapter 2

Mathematical model

This chapter presents the mathematical model and solution procedure developed to simulate the removal of contaminants from soil by electric fields in two and three-dimensional geometries. The model describes the coupled transport of mass and charge as well as the chemical speciation of a multicomponent system subject to an applied electric field. The transport mechanisms included are electroosmosis, pressure-driven convection, electromigration and diffusion. The model can also describe the interplay between the species transport and chemical reactions occurring in the bulk fluid, interactions with the soil such as heterogeneous reactions, adsorption and ion exchange processes, and electrochemical reactions occurring at the electrodes.

The solution procedure is based on the use of conserved quantities such as elemental mass or net charge which are constant during chemical reactions and sorption processes. This approach is especially beneficial when the chemical reactions and sorption processes are fast compared with the transport processes. An illustration of the time scales typically involved in the problem is presented in Table 2.1. Observe that the time scales of the homogeneous reactions are several orders of magnitude smaller than those of the transport processes. Under these conditions, the individual species transport equations, which are very stiff due to the large range of time scales involved, can be replaced with transport equations based on the conserved quantities and complemented with chemical equilibrium relations, the basic assumption being that chemical equilibrium is achieved in the characteristic time scale of the transport
<table>
<thead>
<tr>
<th>Transport processes(^a)</th>
<th>Chemical Processes(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electromigration 10^2 s</td>
<td>Proton transfer to H(_2)O 10^{-12} s</td>
</tr>
<tr>
<td>Electroosmosis 10^4 s</td>
<td>Dissociation of strong acid 10^{-8} s</td>
</tr>
<tr>
<td>Diffusion 10^5 s</td>
<td>Dissociation of weak acid 10^{-6} s</td>
</tr>
<tr>
<td></td>
<td>Inorganic complexation 10^{-6} - 10^{-2} s</td>
</tr>
<tr>
<td></td>
<td>Adsorption/Ion exchange 10^1 - 10^4 s</td>
</tr>
<tr>
<td></td>
<td>Dissolution/precipitation 10^2 - 10^7 s</td>
</tr>
</tbody>
</table>

\(^a\) Based on a length scale of 0.01 m
\(^b\) Adapted from Morel and Hering (1993) [27]

Table 2.1: Typical characteristic time scales.

processes. The resulting system of differential and algebraic equations is much more amenable to numerical integration since the reaction terms cancel out and only the time scale of the transport processes needs to be resolved.

Another benefit of the conserved quantities approach is that the description of the chemical processes can be handled as a separate module or functional unit within the main electrorestoration model. Furthermore, the conserved quantities are typically the input data required by commercially available chemical equilibrium programs. This allows: description of different chemical systems with minimum change to the numerical code; verification of customized models of the chemical system by comparing them with standard equilibrium programs; and even use of commercial equilibrium programs as part of the electrorestoration model.

It is not always possible to assume equilibrium of all chemical reactions. For example, slow dissolution or precipitation reactions may not reach equilibrium in the time scale of the transport processes (see Table 2.1). However, the conserved quantities approach could still be successfully applied with some modifications. The first step would be to classify the reactions in two groups: those whose characteristic time is much smaller than the transport processes', assumed to be fast; and those with a characteristic time of the same order of the transport processes', assumed to be slow. (Those reactions which are much slower than the transport processes can be neglected.) In the time scale of the fast chemical reactions, little or no mass would be added to the system due to transport or slow chemical reactions, while in the time scale of the transport processes, the fast reactions would have reached equilibrium.
Thus, in the time scale of the transport processes, a pseudo-equilibrium state (see Morel and Hering (1993) Ch. 1. [27]) could be assumed to exist where the total amount of reagents and products available for chemical transformations would be controlled by the transport and the slow chemical reactions.

By including in the definition of the conserved quantities only those species taking part in the fast reactions, the corresponding transport equations will contain only the generation terms associated with the slow reactions. These equations should not be numerically stiff since, by definition, the characteristic times of the slow reactions and the transport processes are of the same order.

2.1 Transport Equations

In this section, the transport equations used to model the electrorestoration process are presented. Mass conservation is applied to derive the transport equations of the individual species. In these, the specific contribution of each transport mechanism to the species flux is derived from the corresponding phenomenological relationship and extended to an isotropic porous medium using a capillary model. Future work will address the effect of anisotropy in the medium. The basic phenomenological relationships used here are described and assembled together in the context of the electric-field-driven transport of charge and mass by Probstein in his textbook on Physicochemical Hydrodynamics [31].

The one-dimensional transport equations for species transport in a porous medium when subject to an electric field were introduced by Shapiro et al. (1989) [40]. A finite element formulation based on these equations was successfully used by Shapiro and Probstein (1993) [39] to simulate the removal of phenol and acetic acid from saturated clay by electroosmosis. The basic procedure followed by them is generalized here to handle a multidimensional domain, more complex chemical systems, and arbitrary adsorption or ion exchange isotherms.

Alshawabkeh and Acar [4] have presented a mathematical formulation of the electrorestoration process in an isotropic medium which includes expressions for the ma-
terial and charge fluxes and individual species transport equations in vector form. The basic expressions and transport equations presented by these authors are very similar to the ones presented here. However, the conserved quantities approach used to integrate these transport equations, the formulation of the boundary conditions, and the description of the coupled transport of mass and charge are unique features of this dissertation.

2.1.1 Mass transfer mechanisms

The main mechanisms affecting species transport during the electrorestoration process are: convection due to electroosmosis and pressure gradients; electromigration of charged molecules under the action of the electric field; and to a lesser effect, diffusion due to concentration gradients.

The convection velocity $u_c$ can be described in terms of the contribution from electroosmosis $u_{eo}$ and the contribution from pressure gradients $u_h$. That is,

$$u_c = u_{eo} + u_h$$

(2.1)

The electroosmotic velocity is calculated from the Helmholtz-Smoluchowski relation extended to porous media,

$$u_{eo} = \frac{\varepsilon \zeta}{\tau^2 \mu} \nabla \phi \equiv k_e \nabla \phi$$

(2.2)

Here, $u_{eo}$ is the interstitial velocity due to electroosmosis in $m/s$, $\varepsilon$ is the permittivity of the pore liquid in $F/m$, $\zeta$ is the zeta potential of the soil in $V$, $\tau$ is a nondimensional tortuosity factor, $\mu$ is the viscosity of the pore liquid in $Pa \ s$, $\phi$ is the electrostatic potential in $V$ and $k_e$ is an effective electroosmotic permeability coefficient used for convenience in the numerical formulation of the model.

The $1/\tau^2$ factor in equation 2.2 indicates a double coordinate transformation: first the transformation of the electric field from the straight porous medium coordinates into the tortuous capillary coordinates and then the transformation of the electroos-
motic velocity back into the porous medium coordinate system.

The contribution from pressure gradients is calculated by using Darcy's law for flow in a porous medium, modified to determine the interstitial velocity instead of the superficial velocity usually used,

\[ u_h = -\frac{k_h}{n\mu} \nabla p \equiv k'_h \nabla p \]  \hspace{1cm} (2.3)

Here, \( u_h \) is the interstitial velocity resulting from pressure gradients in \( m/s \), \( k_h \) is the hydraulic permeability of the medium in \( m^2 \), \( n \) is the porosity, and \( p \) is the pressure in \( Pa \). Again, an effective permeability coefficient \( k'_h \) is defined for convenience.

Electromigration originates from the electric force exerted on the ion species, as a result of the applied voltage gradient. This force acts in the direction of the local electric field and is proportional to the ion's charge and the electric field strength. The migration velocity is in turn proportional to this electric force, and for species \( i \) is given by (see Probstein (1994) [31])

\[ u_{ei} = -v_i z_i F \frac{\nabla \phi}{\tau^2} \equiv k_{ei} \nabla \phi \]  \hspace{1cm} (2.4)

Where \( u_{ei} \) is the migration velocity relative to pore liquid in \( m/s \), \( v_i \) is the mobility, defined as the velocity resulting from a unit force per mole, \( z_i \) is the charge number, \( F \) is Faraday's constant and \( k_{ei} \) is an effective mobility coefficient.

Consolidating all of these phenomenological relationships, we arrive at the definition of the total species velocity in the medium coordinate system,

\[ u_i = u_c + u_{ei} \equiv (k_e + k_{ei}) \nabla \phi + k_h \nabla p \]  \hspace{1cm} (2.5)

Thus, the species flux due to convection and migration \( j_{i}^{cm} \) is described by

\[ j_{i}^{cm} = ((k_e + k_{ei}) \nabla \phi + k_h \nabla p) C_i \]  \hspace{1cm} (2.6)

Where \( C_i \) is the molar concentration of species \( i \) in the pore liquid in \( mol/m^3 \).
Finally, the phenomenological relationship corresponding to diffusion in dilute solutions is given by Fick's law,

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

(2.7)

In case a significant velocity profile developed in the pore as a result of the applied or induced pressure gradients, \( D_i \) in equation 2.7 should refer to an effective dispersion coefficient and not to the molecular diffusivity of the species. Estimating this parameter requires resolving the internal velocity distribution inside the pore and falls out of the scope of the model. However, the role of diffusion is typically small and, as it will be seen later, altering this parameter by a significant amount resulted in little change in the global concentration distributions predicted by the model.

Consolidating the contributions from the different mass transfer mechanisms, the total flux of an individual species can be described in terms of the gradients of pressure, electrostatic potential and concentrations as

\[ j_i = (u_c + u_{ei}) C_i - \frac{D_i}{\tau^2} \nabla C_i \]  

(2.8)

\[ j_i = ((k_e + k_{ei}) \nabla \phi + k_h \nabla p) C_i - \frac{D_i}{\tau^2} \nabla C_i \]  

(2.9)

Here, \( j_i \) is the molar flux of species \( i \) per unit interstitial area, expressed in \( mol/(m^2s) \). Since all coordinate transformations have been included, both \( j_i \) and all the gradients in equation 2.9 are expressed in terms of the straight porous medium coordinates.

In the numerical implementation of these equations, a masking vector has been introduced to separate mobile and immobile species (for example, precipitated species, or surface complexes). This masking vector is zero for immobile species and one for mobile species, and multiplies the total species velocity and total flux definitions presented here.
2.1.2 Transport equations of individual species

The transport equations of individual species are derived by carrying out a mass balance in a control volume of the porous medium as depicted in Figure 2-1. The length scale of this control volume is assumed to be large compared with the pore dimensions, so the continuum assumption holds. This length scale will be the smallest length scale solvable by the transport equations. In practice, this limitation will be seldom encountered, since restrictions in the computational cost of the model will typically impose a much larger limit on the size of the computational elements. Applying mass conservation of the chemical species in the control volume and neglecting transport of adsorbed species results in

\[
\frac{\partial}{\partial t} \int_{CV} nC_i dV + \oint_{CS} \mathbf{n}_i \cdot \mathbf{n} dS = \int_{CV} n(R_i + R_i^a) dV
\]  

(2.10)

and

\[
\frac{\partial}{\partial t} \int_{CV} (1 - n) \hat{C}_i^a dV = - \int_{CV} nR_i^a dV
\]  

(2.11)

Here, \( R_i \) and \( R_i^a \) are the net volumetric rates of production of chemical species \( i \) due to chemical reactions and sorption processes, normalized with respect to the volume of liquid; \( \hat{C}_i^a \) is the molar concentration of species \( i \) in the adsorbed phase, normalized with respect to the volume of solid; and \( \mathbf{n} \) is a unit normal to the control surface.

Expressing \( \hat{C}_i^a \) in terms of the volume of liquid,

\[
C_i^a = \frac{(1 - n)\hat{C}_i^a}{n}
\]  

(2.12)

and adding equations 2.10 and 2.11, we get

\[
\frac{\partial}{\partial t} \int_{CV} n(C_i + C_i^a) dV + \oint_{CS} \mathbf{n}_i \cdot \mathbf{n} dS = \int_{CV} nR_i dV
\]  

(2.13)

which holds for a control volume of arbitrary size, provided it contains several pore diameters. Applying Gauss' divergence theorem and using an infinitesimal control
volume, equation 2.13 can be simplified to

$$\frac{\partial n(C_i + C_i^a)}{\partial t} + \nabla \cdot n\mathbf{j}_i = nR_i$$  \hspace{1cm} (2.14)

which assuming a medium of uniform porosity, results in

$$\frac{\partial (C_i + C_i^e)}{\partial t} + \nabla \cdot \mathbf{j}_i = R_i$$  \hspace{1cm} (2.15)

This is the form of the transport equations used in the development of the mathematical model and numerical formulation of the electrorestoration process presented in this work.

### 2.1.3 Conserved quantities approach

By definition, any quantity conserved throughout the chemical reactions, such as elemental mass or net charge, will have a net volumetric rate of production equal to zero. We can use this fact to devise a way of combining the transport equations
of the individual chemical species to obtain transport equations with no generation terms. For example, using conservation of elemental mass, we can determine the total amount of each element present in the system,

$$T_k = \sum_{i=1}^{N} \nu_{ik}(C_i + C_i^a), \quad \forall \; k = 1, \cdots, M$$  \hspace{1cm} (2.16)

Here, $\nu_{ik}$ is the subscript to element $k$ in the molecular formula of species $i$. $N$ is the number of species and $M$ is the number of elements in the system. Similarly, following the Tableau Method for expressing conservation principles described in Morel and Hering (1993) Ch. 1. [27], we could define $T_k$ as the total amount of each component in the system (conserved throughout chemical reactions). Then, $\nu_{ik}$ would be the number of moles of component $k$ per mole of species $i$, and $M$ would be the number of different components in the system. We could also arrive at a suitable set of conserved quantities by looking at the stoichiometry of the chemical transformation equations in the system. An important rule to remember is that the set of conserved quantities selected must be linearly independent. In any case, the set of conservation equations will have the form of equation 2.16.

Thus, for each of the conserved quantities $T_k$,

$$\sum_{i=1}^{N} \nu_{ik} R_i = 0,$$  \hspace{1cm} (2.17)

so combining the transport equations 2.15 following equation 2.17 yields,

$$\frac{\partial}{\partial t} \left( \sum_{i=1}^{N} \nu_{ik}(C_i + C_i^a) \right) + \sum_{i=1}^{N} \nu_{ik} \nabla \cdot j_i = 0, \quad \forall \; k = 1, \cdots, M$$  \hspace{1cm} (2.18)

That is,

$$\frac{\partial T_k}{\partial t} + \sum_{i=1}^{N} \nu_{ik} \nabla \cdot j_i = 0, \quad \forall \; k = 1, \cdots, M$$  \hspace{1cm} (2.19)

in which only the time scale of the transport processes needs to be resolved.

A similar way of combining the transport equations has been proposed by Walsh
et al. (1984) [43] and Cederberg et al. (1985)[7] for modeling groundwater transport of reacting multicomponent systems. These authors proposed the use of the total component concentrations as the primary variables to obtain transport equations with no generation terms. Their formulation, however, operates directly on the total component concentrations to determine the fluxes. So it involves averaging the velocities and diffusion coefficients of the individual species. The approach presented here determines the rate of change of the conserved quantities concentrations from the contribution of each individual species, so it does not involve any averaging.

Assuming that the soil is initially neutral (previous to any contact with the liquid), the total charge in the system can be obtained from the concentration of species in solution and in the solid phase. That is,

$$T_0 = F \sum_{i=1}^{N} z_i (C_i + C_i^a) \quad (2.20)$$

Here, the solid phase includes the diffuse part of the Debye layer, so

$$F \sum_{i=1}^{N} z_i C_i^a = q_s + \left(F \sum_{i=1}^{N} z_i C_i\right)_{\text{Debye}} = 0 \quad (2.21)$$

where $q_s$ is the charge density of the soil normalized with respect to the volume of liquid. This charge includes the surface complexes and the ionic species which actually bond to the soil matrix. Equation 2.21 indicates that the adsorption and ion exchange isotherms relating the concentrations in solution to the concentrations in the solid phase are not independent. In the porous medium scale, the sorbent is thought to have a fixed total capacity and merely exchange one solute for another (see Vermeulen et al. (1984) [42]).

It follows from the electroneutrality condition

$$\sum_{i=1}^{N} z_i C_i = 0 \quad (2.22)$$

that

$$T_0 = 0 \quad (2.23)$$
<table>
<thead>
<tr>
<th>Metals</th>
<th>Ligands</th>
<th>Species</th>
<th>In solution</th>
<th>Adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>H⁺</td>
<td>H⁺</td>
</tr>
<tr>
<td>Na⁺</td>
<td>A⁻</td>
<td>OH⁻</td>
<td>OH⁺</td>
<td>OH⁺</td>
</tr>
<tr>
<td></td>
<td>Cl⁻</td>
<td>HA</td>
<td>HA⁺</td>
<td>HA⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A⁻</td>
<td>A⁺</td>
<td>A⁺</td>
</tr>
<tr>
<td>Na⁺</td>
<td></td>
<td>Na⁺</td>
<td>Na⁺</td>
<td>Na⁺</td>
</tr>
<tr>
<td>Cl⁻</td>
<td></td>
<td>Cl⁻</td>
<td>Cl⁺</td>
<td>Cl⁺</td>
</tr>
</tbody>
</table>

Table 2.2: Chemical species in example 2.1 (weak acid system)

provided the solid is initially neutral.

Using the electroneutrality condition, one of the transport equations in 2.19 can be replaced by an algebraic equation. In practice, eliminating the transport equation that involves the hydrogen and hydroxyl ions produces some important advantages in the numerical implementation of the model. These advantages will be discussed in chapter 3.

Once the values of the conserved quantities $T_k$ are known at a given time level from integration of equations 2.19, the individual species concentrations in the bulk solution and adsorbed in the solid can be determined by solving for chemical and adsorption equilibrium. This procedure is explained in section 2.3.

To illustrate the general approach, let us consider the following two examples:

**EXAMPLE 2.1** Conserved quantities and transport equations in a weak acid system.

This example illustrates the handling of adsorbed species in a relatively simple chemical system and the definition of the conserved quantities from inspection of the equations of chemical transformation. The metals, ligands and chemical species assumed to exist in the system are presented in Table 2.2.

Using the chemical symbol of each species to refer to its concentration, the individual species transport equations (2.14) are in this case:

$$\frac{\partial (H + H^a)}{\partial t} + \nabla \cdot \mathbf{j}_H = R_H$$

$$\frac{\partial (OH + OH^a)}{\partial t} + \nabla \cdot \mathbf{j}_{OH} = R_{OH}$$
\[
\frac{\partial (HA + HA^a)}{\partial t} + \nabla \cdot j_{HA} = R_{HA} \\
\frac{\partial (A + A^a)}{\partial t} + \nabla \cdot j_A = R_A \\
\frac{\partial (Na + Na^a)}{\partial t} + \nabla \cdot j_{Na} = R_{Na} \\
\frac{\partial (Cl + Cl^a)}{\partial t} + \nabla \cdot j_{Cl} = R_{Cl}
\]

The transport equations written in this form reflect the first step of the conserved quantities approach, since by including both the concentration of the species in solution and in the adsorbed phase, the generation terms corresponding to adsorption have been canceled.

Now, assuming that the only chemical reactions are

\[
\begin{align*}
H_2O & \rightleftharpoons H^+ + OH^- : R_1 \\
HA & \rightleftharpoons H^+ + A^- : R_2
\end{align*}
\]

where \(R_1\) and \(R_2\) refer to the net rate of advancement of each reaction, we can infer the following stoichiometric relationships:

\[
\begin{align*}
R_H &= R_1 + R_2, \quad R_{OH} = R_1, \quad R_{Na} = 0 \\
R_{HA} &= -R_2, \quad R_A = R_2, \quad R_{Cl} = 0
\end{align*}
\]

These stoichiometric relationships yield the following algebraic equations,

\[
\begin{align*}
R_H - R_{OH} - R_A &= 0 \\
R_{HA} + R_A &= 0 \\
R_{Na} &= 0 \\
R_{Cl} &= 0
\end{align*}
\]

which suggest the definition of the conserved quantities

\[
T_1 = (H + H^a) - (OH + OH^a) - (A + A^a) \\
T_2 = (HA + HA^a) + (A + A^a)
\]
\[ T_3 = Na + Na^a \]
\[ T_4 = Cl + Cl^a \]

The transport equations that result from this definition of the conserved quantities are

\[
\frac{\partial T_1}{\partial t} + \nabla \cdot (j_H - j_{OH} - j_A) = 0 \\
\frac{\partial T_2}{\partial t} + \nabla \cdot (j_{HA} + j_A) = 0 \\
\frac{\partial T_3}{\partial t} + \nabla \cdot j_{Na} = 0 \\
\frac{\partial T_4}{\partial t} + \nabla \cdot j_{Cl} = 0
\]

or, using the electroneutrality condition to eliminate the transport equation involving \( H^+ \) and \( OH^- \),

\[ T_0 = H - OH - A^a + Na - Cl = 0 \]
\[
\frac{\partial T_1}{\partial t} + \nabla \cdot (j_{HA} + j_A) = 0 \\
\frac{\partial T_2}{\partial t} + \nabla \cdot j_{Na} = 0 \\
\frac{\partial T_3}{\partial t} + \nabla \cdot j_{Cl} = 0
\]

**EXAMPLE 2.2** Conserved quantities and transport equations in a zinc system with no adsorption.

This example illustrates the use of the conserved quantities approach in a more complex system and the definition of the conserved quantities following the Tableau method (See Ch. 1. [27]). As before, let us start by listing the metals, ligands and chemical species assumed to exist in the system. This information is presented in Table 2.3. Adsorption has been neglected to limit the number of species in this example.

In this case, the conserved quantities are based on the following choice of com-
Table 2.3: Chemical species in example 2.2 (zinc system)

ponents H, Zn, CO₃, Na and Cl (H₂O is always an implicit species and component but since the activity of water is known, it is not included in the calculation). The basic approach consists of writing each species in the system in terms of the selected components. In the transport equations, solid phases are assumed to be immobile. The results are summarized in Table 2.4.

2.1.4 Concentration boundary conditions

This section presents the boundary conditions used in the integration of the transport equations. As indicated in figure 2-2, the computational domain has a boundary defined by the union of the external boundary Γ_{ext} and the boundary of each electrode reservoir Γ_ₑ. The external boundary is assumed to be formed by impermeable, non-reacting, non-conducting walls, so no-flux boundary conditions are imposed. The electrode reservoirs are assumed to have three main components: a porous wall separating the soil and the liquid inside the reservoir, an active electrode submerged in the reservoir liquid to which the external power source is connected and a passive electrode measuring the effective electrostatic potential at the soil boundary.(See figure 2-3). The interior of the electrode reservoirs is not included in the computational domain to avoid the uncertain nature of the convection flow inside the well and the complicated phenomena occurring near the active electrodes, so the concentrations of the chemical species at the porous walls separating the soil and the liquid inside
<table>
<thead>
<tr>
<th>Species</th>
<th>$T_1$</th>
<th>$T_2$</th>
<th>$T_3$</th>
<th>$T_4$</th>
<th>$T_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
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<td>$\text{Zn}^{2+}$</td>
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<td></td>
</tr>
<tr>
<td>$\text{ZnOH}^+$</td>
<td>-1</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn(OH)}_2$</td>
<td></td>
<td>-2</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn(OH)}_3^-$</td>
<td></td>
<td>-3</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$\text{Zn(OH)}_4^{3-}$</td>
<td></td>
<td>-4</td>
<td></td>
<td>1</td>
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</tr>
<tr>
<td>$\text{Zn(OH)}_2(s)$</td>
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<td></td>
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<td>$\text{CO}_3^{2-}$</td>
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<td></td>
</tr>
<tr>
<td>$\text{HCO}_3^-$</td>
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<td></td>
<td></td>
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<td></td>
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<tr>
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<td>1</td>
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<tr>
<td>$\text{ZnCO}_3(s)$</td>
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<td></td>
<td>1</td>
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<td>$\text{Cl}^-$</td>
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<tr>
<td>$\text{ZnCl}^+$</td>
<td></td>
<td>1</td>
<td></td>
<td>1</td>
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</tr>
<tr>
<td>$\text{Zn(Cl)}_2$</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>$\text{Zn(Cl)}_3^-$</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>$\text{Zn}_2(\text{OH})_3\text{Cl}(s)$</td>
<td>-3</td>
<td>2</td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

$$\partial T_1/\partial t + \nabla \cdot (j_1 - j_2 - j_5 - 2j_6 - 3j_7 - 4j_8 + j_{11} + 2j_{12}) = 0$$
$$\partial T_2/\partial t + \nabla \cdot (j_4 + j_5 + j_6 + j_7 + j_8 + j_{15} + j_{16} + j_{17}) = 0$$
$$\partial T_3/\partial t + \nabla \cdot (j_{10} + j_{11} + j_{12}) = 0$$
$$\partial T_4/\partial t + \nabla \cdot j_3 = 0$$
$$\partial T_5/\partial t + \nabla \cdot (j_{14} + j_{15} + 2j_{16} + 3j_{17}) = 0$$

Table 2.4: Conserved quantities and transport equations in example 2.2
the reservoir boundaries need to be specified. These boundary conditions are derived by applying mass conservation for each chemical species in the interior of the electrode reservoirs. In so doing, the concentration distributions inside each reservoir need to be assumed. In this work, it is assumed that the liquid inside the reservoirs is well-mixed, resulting in uniform concentration distributions.

The volume flow rate of pore liquid into the electrode reservoirs resulting from electroosmosis and pressure-driven convection is calculated by

$$Q_w = \int_{A_w} \mathbf{u}_c \cdot \hat{n} \, dA \quad (2.24)$$

where $A_w$ is the area available for mass transfer and $\hat{n}$ is a inward unit normal to the reservoir wall.

The electrodes are classified in terms of this flow rate as:

- Sink electrodes: those in which the pore liquid flows from the soil into the electrode reservoir ($Q_w > 0$), and

- Source electrodes: those in which the liquid flows from the electrode reservoir
Figure 2-3: Schematic diagram of a generic electrode reservoir

into the soil \((Q_w \leq 0)\).

Two operating conditions are considered in determining the concentration of chemical species in the electrode reservoirs:

- electrode draining: under this operating condition, the pore liquid flowing into sink electrodes overflows to effluent collectors, and the liquid flowing out of the source electrodes and into the soil is replaced by a purge solution. In both cases, a constant volume of liquid is maintained in the electrode reservoirs.

- electrode washing: under this operating condition, an external solution is circulated through the electrode reservoir also maintaining constant volume of liquid. The wash solution flow rate is high enough as to maintain a near-constant pH in the electrode well.

The boundary conditions for each operating mode are presented in the following sections.
Electrode draining

In this case, the boundary conditions are derived by assuming a uniform concentration inside each well and applying mass conservation, leading to the following ordinary differential equation

\[ V_w \frac{\partial (C_i^\text{well})_w}{\partial t} = \oint_{A_w} \mathbf{j}_i \cdot \mathbf{n} \, dA - Q_w (C_i^{\text{io}})_w + V_w (R_i + R_i^e) \]  \hspace{1cm} (2.25)

In this equation, \( V_w \) is the volume of the reservoir, \((C_i^\text{well})_w\) is the concentration of species \(i\) inside reservoir \(w\), \(R_i^e\) is the net volumetric rate of production due to electrochemical reactions, and \((C_i^{\text{io}})_w\) is the concentration of species \(i\) in the solution going in or out of the system. For source electrodes it refers to the concentrations in the purge solution, while for sink electrodes it refers to the concentrations in the effluent. That is,

\[
(C_i^{\text{io}})_w = \begin{cases} 
(C_i^{\text{purge}})_w & \text{if } Q_w \leq 0 \\
(C_i^\text{well})_w & \text{if } Q_w > 0
\end{cases} \hspace{1cm} (2.25)
\]

Assuming that the electrochemical reactions are occurring in steady state, the rate of production due to electrochemical reactions is calculated from Faraday's law,

\[ R_i^e = \frac{\nu_{ie}}{V_w} \oint_{A_w} \left( \frac{\mathbf{n} \cdot \mathbf{j}_i}{F} \right) \, dA \]  \hspace{1cm} (2.27)

where \(\nu_{ie}\) is the number of moles of species \(i\) produced in the electrochemical reactions per mole of electrons circulated in the external circuit. For example, in the water electrolysis reactions,

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2(g) \quad \text{(cathode)} \\
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2(g) + 4e^- \quad \text{(anode)}
\]  \hspace{1cm} (2.28)

the stoichiometric coefficient \(\nu_{ie}\) is 1 for both the hydrogen and hydroxyl ions.

This relation can also be used for simultaneous electrochemical reactions, as each reaction can be assumed to occur independently and the total current in the external circuit is the sum of the currents due to the different reactions. (See e.g. Newman
Now, combining equations 2.25 according to the definition of the conserved quantities (Equation 2.16), we get the set of equations describing the boundary conditions actually used in the integration of the transport equations:

$$V_w \frac{\partial (T_{k}^{\text{well}})_w}{\partial t} = \sum_{i=1}^{N} \nu_{ik} \left( \oint_{A_w} j_i \cdot \hat{n} \, dA \right) - Q_w (T_{k}^{\text{i}o})_w + V_w \sum_{i=1}^{N} \nu_{ik} R_i^{e} \quad (2.29)$$

where

$$(T_{k}^{\text{well}})_w = \sum_{i=1}^{N} \nu_{ik} (C_{i}^{\text{well}})_w \quad (2.30)$$

is the concentration of the conserved quantity $k$ in the electrode well, and

$$(T_{k}^{\text{i}o})_w = \sum_{i=1}^{N} \nu_{ik} (C_{i}^{\text{i}o})_w \quad (2.31)$$

is the concentration of the conserved quantity $k$ in the solution going in and out of the system. Note that the sum in equation 2.31 includes only the species in solution while the sum in equation 2.30 includes all the species.

**Electrode washing**

In this case, the mass balance results in

$$V_w \frac{\partial (C_{i}^{\text{well}})_w}{\partial t} = \oint_{A_w} j_i \cdot \hat{n} \, dA + Q_{\text{wash}} (C_{i}^{\text{wash}})_w - (Q_{\text{wash}} + Q_w) C_{i}^{\text{well}} + V_w (R_i + R_i^{e}) \quad (2.32)$$

where $Q_{\text{wash}}$ is the wash flow rate and $C_{i}^{\text{wash}}$ is the concentration of species $i$ in the wash solution.

The wash flow rate required to maintain near-constant pH depends on the chemical and electrochemical properties of the system and the composition of the wash solution. For example, assuming that electrolysis of water is occurring at the cathode, it could be considered to circulate an acidic solution, a buffered solution or a salt solution to control the pH rise at the well. Each would have a different impact on the equilibrium pH and thus would require a different wash flow rate.
Typically, the wash flow rate is large compared to the convection flow rate resulting from electroosmosis and pressure gradients in the soil, so equation 2.32 can be rewritten as

\[ V_w \frac{\partial (C_i^{\text{well}})_w}{\partial t} = \oint_{A_w} \mathbf{j}_i \cdot \mathbf{n} \, dA + Q_{\text{wash}} \left( (C_i^{\text{wash}})_w - C_i^{\text{well}} \right) + V_w (R_i + R_i^e) \]  

(2.33)

For a nearly constant pH, this equation applied to either H\(^+\) or OH\(^-\) yields

\[ \oint_{A_w} \mathbf{j}_i \cdot \mathbf{n} \, dA + Q_{\text{wash}} \left( (C_i^{\text{wash}})_w - C_i^{\text{well}} \right) + V_w (R_i + R_i^e) \approx 0 \]  

(2.34)

This equation suggests some of the options available for pH control at the electrode: acid/base reactions which balance the accumulation of H\(^+\) or OH\(^-\) (i.e. neutralization, buffering); pure washing, in which the excess ions are carried away in the wash solution; or a combination of both.

The equation for the boundary conditions in terms of the conserved quantities is

\[ V_w \frac{\partial (T_k^{\text{well}})_w}{\partial t} = \sum_{i=1}^{N} \nu_{ik} \left( \oint_{A_w} \mathbf{j}_i \cdot \mathbf{n} \, dA \right) + Q_{\text{wash}} \left( (T_k^{\text{wash}})_w - (T_k^{\text{well}})_w \right) + V_w \sum_{i=1}^{N} \nu_{ik} R_i^e \]  

(2.35)

where

\[ (T_h^{\text{wash}})_w = \sum_{i=1}^{N} \nu_{ik} (C_i^{\text{wash}})_w \]  

(2.36)

If the wash flow rate is large enough, the circulation time scale will be small compared to the time scale of the transport and electrochemical processes resulting in

\[ (T_k^{\text{well}})_w \approx (T_k^{\text{wash}})_w \]  

(2.37)

The values determined for \((T_k^{\text{well}})_w\) under either operating mode are imposed as boundary conditions at each time level using

\[ T_k |_{t_w} = (T_k^{\text{well}})_w \]  

(2.38)
2.2 Electric field and pressure distributions

In this section, the coupled transport of charge and mass is examined in deriving the equilibrium equation defining the electrostatic potential distribution. Also, mass conservation of the bulk fluid is used to determine the pressure distribution in a saturated, isotropic, incompressible porous medium.

2.2.1 Electric field distribution

The condition of electroneutrality is the constraint coupling the transport of charge and mass in a chemical system subject to an applied electric field. This relationship is made apparent by looking at the transport of charge in the system. Using the charge numbers in place of the usual stoichiometric coefficients in equation 2.18 and assuming that the soil matrix is conducting, the charge transport equation is

$$\frac{\partial}{\partial t} \left( F \sum_{i=1}^{N} z_i (C_i + C_i^a) \right) + F \sum_{i=1}^{N} z_i \nabla \cdot j_i + \nabla \cdot i_s = F \sum_{i=1}^{N} z_i R_i = 0 \quad (2.39)$$

In this equation, $i_s$ is the current density in the soil, normalized with respect to the interstitial area. This current is given by Ohm's law,

$$i_s = -\sigma_s \nabla \phi \quad (2.40)$$

where $\sigma_s$ is the electrical conductivity of the soil.

Defining the total current density as

$$i = F \sum_{i=1}^{N} z_i j_i - \sigma_s \nabla \phi, \quad (2.41)$$

equation 2.39 can be rewritten as

$$\frac{\partial}{\partial t} \left( F \sum_{i=1}^{N} z_i (C_i + C_i^a) \right) + \nabla \cdot i = 0 \quad (2.42)$$
This shows that if there is current continuity, that is if

\[ \nabla \cdot \mathbf{i} = 0, \quad (2.43) \]

a system which is initially neutral will maintain electroneutrality.

The constraint imposed by this condition on the electrostatic potential is realized by including the definition of the species fluxes (equations 2.8 and 2.9) in equation 2.43 to get

\[ \nabla \cdot F \left( \sum_{i=1}^{N} z_i C_i + \sum_{i=1}^{N} z_i u_{ei} C_i - \sum_{i=1}^{N} z_i \frac{D_i}{\tau^2} \nabla C_i \right) - \nabla \cdot (\sigma \nabla \phi) = 0 \quad (2.44) \]

Since the liquid is electrically neutral, we neglect the contribution of convection to the current density and rewrite equation 2.44 as

\[ \nabla \cdot \left( F \sum_{i=1}^{N} z_i u_{ei} C_i \right) - \nabla \cdot (\sigma \nabla \phi) = \nabla \cdot \left( F \sum_{i=1}^{N} z_i \frac{D_i}{\tau^2} \nabla C_i \right) \quad (2.45) \]

Including the definition of the migration velocity \( u_{ei} \) (equation 2.4) results in

\[ - \nabla \cdot \left( \frac{F^2}{\tau^2} \sum_{i=1}^{N} z_i^2 u_i C_i \nabla \phi \right) - \nabla \cdot (\sigma \nabla \phi) = \nabla \cdot \left( F \sum_{i=1}^{N} z_i \frac{D_i}{\tau^2} \nabla C_i \right) \quad (2.46) \]

or

\[ - \nabla \cdot (\sigma \nabla \phi) = \nabla \cdot \left( F \sum_{i=1}^{N} z_i \frac{D_i}{\tau^2} \nabla C_i \right) \quad (2.47) \]

which is the basic equation used to determine the electric field distribution. In this equation, \( \sigma \) is the electrical conductivity of the medium defined by

\[ \sigma = \frac{F^2}{\tau^2} \sum_{i=1}^{N} z_i^2 u_i C_i + \sigma_s \quad (2.48) \]

**Boundary conditions**

Two sets of operating conditions have been typically considered in electrorestoration applications: fixed potential conditions, in which a constant potential is maintained
at the boundary of the electrode reservoirs (each passive electrode would measure a constant voltage); and fixed current conditions, in which the applied potential is varied to maintain a constant current at each electrode. These operating conditions are easily translated into boundary conditions for the electrostatic potential in one-dimensional calculations.

The fixed potential operating conditions are readily applied to multidimensional systems using

\[ [\phi]_{\Gamma_w} = \phi_w \]  

(2.49)

where \( \phi_w \) is voltage at the wall of each electrode reservoir.

However, translating fixed current conditions into electric field boundary conditions in multidimensional systems poses special problems due to the additional degrees of freedom introduced. To realize this, let us first determine the total current at each electrode by integrating the current density over the boundary of the reservoir. Including the definition of the current density in terms of the species fluxes, we get

\[ I_w = \left( \sum_{i=1}^{N} z_i \oint_{A_w} \mathbf{j}_i \cdot \mathbf{n} \, dA \right) - \oint_{A_w} \sigma_s \nabla \phi \cdot \mathbf{n} \, dA \]  

(2.50)

Now, incorporating the definition of the species fluxes and neglecting the contribution of convection to the current, equation 2.50 can be rewritten as

\[ I_w = \left( \sum_{i=1}^{N} z_i \oint_{A_w} \left( k_{ei} C_i \nabla \phi - \frac{D_i}{\tau^2} \nabla C_i \right) \cdot \mathbf{n} \, dA \right) - \oint_{A_w} \sigma_s \nabla \phi \cdot \mathbf{n} \, dA \]  

(2.51)

Note that this equation defines a constraint on the integral of the electric field over the area of the electrode reservoir and not on the local value of the electric field at the boundary which is the required boundary condition. In the absence of clearly defined electric field boundary conditions, a separate procedure has to be used at each time level to determine the applied potentials that would produce the desired currents and then determine the electric field distribution as in the fixed potential case. For example, in a system with \( n \) anodes and \( m \) cathodes, and assuming that all cathodes are grounded, at each time level we would need to solve a system of equations of the
form

\[ G_j(\phi_1, \ldots, \phi_n) = F_j(\phi_1, \ldots, \phi_n) - I_j = 0 \quad \text{for } j = 1, n \]  (2.52)

where the F functions represent the relationship between the applied potentials and the electrode currents and would be evaluated numerically. In the general case, this system of equations could be nonlinear, requiring an iterative solution procedure. Also, the Jacobian of these functions would change in time as the species concentrations and electrical conductivity of the system vary.

Alternatively, the current density could be assumed to be uniform on the electrode reservoirs. In that case, equation 2.51 would actually provide the required boundary conditions. However, the current density is typically not uniform on the periphery of the electrode reservoirs and further study is required to determine the effect of this assumption on the electrostatic potential distribution.

In both operating modes, no-flux boundary conditions are imposed on the external boundary \( \Gamma_{ext} \).

### 2.2.2 Pressure distribution

In a saturated incompressible porous medium, the pressure distribution is determined with a method analogous to the electrostatic potential distribution. This method is used in this work as a first approximation. Future work will address the effects of compressibility and non-saturation on the bulk liquid velocity and pressure distributions.

Starting with mass conservation of the incompressible bulk fluid, we have

\[ \nabla \cdot u_c = 0 \]  (2.53)

which, including the definition of the convection velocity \( u_c \) (equation 2.1), results in

\[ - \nabla \cdot (k_h \nabla p) = \nabla \cdot (k_c \nabla \phi) \]  (2.54)
Equation 2.54 can be used to determine the pressure distribution once the electrostatic potential distribution is known. In this case, fixed pressure boundary conditions are applied at the electrodes and no-flux boundary conditions are imposed on the external boundary.

2.3 Chemical and sorption equilibrium

Many different approaches have been proposed for the solution of the chemical equilibrium problem. In fact, there are many commercially available programs designed to solve for chemical equilibrium in complex chemical systems. However, the numerical implementation of the electrorestoration model presented here requires solving the chemical equilibrium problem at each computational element and at each time step, resulting in the need for some features not generally available in commercial programs. Specifically, the numerical implementation of the model required the chemical equilibrium solver to have a special interface (to be handled as a subroutine of the main transport code) and to be fast even at the expense of some generality. Thus, writing a customized model of each chemical system was the best practical solution.

This section presents the approach and special simplifications used to solve the chemical and adsorption equilibrium problem as part of the overall transport model.

2.3.1 Basic calculation

In the context of the electrorestoration model, the chemical equilibrium problem consists in finding the chemical speciation of the system (concentration of each individual species in the bulk solution and adsorbed into the soil) in terms of the conserved quantities determined from the transport equations.

For a chemical system with $N$ chemical species and $M$ conserved quantities, we have a system of $2N$ equations with $2N$ unknowns set up as follows:

- $2N$ Unknowns: Concentrations of the individual species in solution and adsorbed in the soil $\{C_1, \ldots, C_N\}, \{C_1^a, \ldots, C_N^a\}$
• 2N Equations:

  - M conservation equations (2.16)

\[
T_k = \sum_{i=1}^{N} \nu_{ik}(C_i + C_i^a)
\]

  - N adsorption and ion exchange isotherms

\[
C_i^a = f_i(C_1, \ldots, C_N)
\] (2.55)

  - and r = N - M mass action equations of the form

\[
K_j = \prod_{i=1}^{N} (C_i)^{\nu_{xj}}
\] (2.56)

where \(K_j\) is the equilibrium constant and \(\nu_{xj}\) the stoichiometric coefficient of each species \(i\) in the \(j^{th}\) equation of chemical transformation.

Typically, one of the \(M\) conservation equations is

\[
\sum_{i=1}^{N} z_i(C_i + C_i^a) = 0
\] (2.57)

As mentioned in section 2.1.3, the set of sorption isotherms is not independent, but constrained by

\[
\sum_{i=1}^{N} z_i C_i^a = 0
\]

where the species in the electric double layer are considered to be in the solid phase, so equation 2.57 is equivalent to the usual form of the electroneutrality condition,

\[
\sum_{i=1}^{N} z_i C_i = 0
\]

Two basic strategies are proposed for solving this system of equations. These strategies and the conditions under which they are applied are presented in the following sections.
Direct substitution of analytical expressions

The goal of this approach is to reduce the dimension of the system by advancing as much as possible in its analytical solution. It is applied in relatively simple chemical systems when adsorption is not included or there are analytical expressions available for the adsorption isotherms.

The first step is to select an independent variable $X$ for the electroneutrality condition or the conservation equation involving the hydrogen and hydroxyl ions and $M - 1$ additional independent variables $Y_k$ for the other conservation equations. Since the pH is typically a dominant factor in the chemical speciation of the system, the concentration of either hydrogen or hydroxyl ions is usually a convenient choice for the top level independent variable $X$. The selection of independent variables in the other conservation equations is arbitrary. Recall that

$$pH = -\log([H^+]) \cong 14 + \log([OH^-]) \quad (2.58)$$

Combining the mass action equations and adsorption isotherms with the conservation equations, we can obtain $M$ equations of the form

$$G_k(X, Y_1, \ldots, Y_{M-1}) = 0 \quad (2.59)$$

in terms of known parameters or functions (i.e., the conserved quantities $\{T_1, \ldots, T_M\}$, the equilibrium constants $\{K_1, \ldots, K_r\}$, and the adsorption isotherms $\{f_1, \ldots, f_N\}$).

This system of $M$ equations in $M$ unknowns is usually much smaller than the original $2N \times 2N$ system. Thus, significant savings in computational time are realized in its numerical solution.

Moreover, an analytical solution can be usually obtained for the $M - 1$ equations in the $Y_k$ variables if the value of the top level independent variable $X$ is assumed known. In that case, the system is reduced to a single equation in one variable ($X$) which is solved numerically. This approach typically leads to the best performance. Alternatively, the system of $M - 1$ equations in the $Y_k$ variables can be solved numer-
ically by a Newton-Raphson or similar method. Under certain conditions discussed later in section 2.3.2, the iteration in the $X$ variable can be avoided, greatly speeding up the calculation.

**Two-level hierarchical iteration**

When the chemical system includes polymeric compounds (for example $\text{Pb}_3(\text{OH})^{2+}_4$, $\text{Pb}_4(\text{OH})^{4+}_4$, $\text{Pb}_6(\text{OH})^{4+}_8$, etc.) or the adsorption isotherms are complex, replacing the mass action equations and adsorption isotherms manually in the conservation equations can become impractical. An alternative procedure is to solve the $G_k$ equations (2.59) numerically. Again, the equation involving the hydrogen or hydroxyl ion is typically the most complex, so choosing one of these as the top level independent variable $X$ and assuming that its value is known significantly simplifies the solution of the reduced $(M - 1)$-equation system. In addition, this approach allows us to take advantage of the simplifications to be discussed in section 2.3.2.

The hierarchical iteration procedure is set up as follows:

- A top level iteration which finds the value of the independent variable $X$ that satisfies the corresponding conservation equation. (Typically the electroneutrality condition.)

- A second level iteration which finds the solution to the system of $(M - 1)$ equations in the $Y_k$ variables for each value of $X$.

In other words, the second level iteration finds the chemical speciation of the system for a given pH and the top level iteration finds the pH at equilibrium. When the top level iteration converges, the whole chemical speciation of the system has been determined.

**Example 2.3** Chemical equilibrium in the zinc system of example 2.2. Case with no solid species present.

This example illustrates the application of the strategies described to solve for chemical equilibrium in the chemical system of example 2.2. In this case, however, it
<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
<th>Conserved Quantity</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+$</td>
<td>$C_1$</td>
<td>TOT(Charge)</td>
<td>$T_0$</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>$C_2$</td>
<td>TOT(Zn)</td>
<td>$T_1$</td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>$C_3$</td>
<td>TOT(CO$_3$)</td>
<td>$T_2$</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}$</td>
<td>$C_4$</td>
<td>TOT(Na)</td>
<td>$T_3$</td>
</tr>
<tr>
<td>$\text{ZnOH}^+$</td>
<td>$C_5$</td>
<td>TOT(Cl)</td>
<td>$T_4$</td>
</tr>
<tr>
<td>$\text{Zn(OH)}_2$</td>
<td>$C_6$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn(OH)}_3^-$</td>
<td>$C_7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn(OH)}_4^{2-}$</td>
<td>$C_8$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn(OH)}_2(s)$</td>
<td>$C_9$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_3^{2-}$</td>
<td>$C_{10}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{HCO}_3^-$</td>
<td>$C_{11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3$</td>
<td>$C_{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{ZnCO}_3(s)$</td>
<td>$C_{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cl}^-$</td>
<td>$C_{14}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{ZnCl}^+$</td>
<td>$C_{15}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn(Cl)}_2$</td>
<td>$C_{16}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn(Cl)}_3^-$</td>
<td>$C_{17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn}_2(\text{OH})_3\text{Cl}(s)$</td>
<td>$C_{18}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5: Nomenclature for example 2.3

is assumed that no solid species are present. The set of mass action equations in the chemical equilibrium calculation depends on what solids are assumed to be present, so when several possible solid species may be formed, separate criteria are needed to determine the saturation state of the system (see Morel and Hering (1993) Ch. 5. [27] for details). Nevertheless, for each saturation state, a procedure similar to the one presented here can be applied.

In this example, we will use the electroneutrality condition in place of the TOT(H) equation in table 2.4. Then, based on the nomenclature presented in table 2.5, we have:

- 15 Unknowns: \{$C_1, \ldots, C_{18}$\} excluding the solid species $C_9$, $C_{13}$ and $C_{18}$.

- 15 Equations:
- 5 conservation equations:

\[
\begin{align*}
T_0 &= C_1 - C_2 + C_3 + 2C_4 + C_5 - C_7 - 2C_8 - 2C_{10} - C_{11} - C_{14} + C_{15} - C_{17} \\
T_1 &= C_4 + C_5 + C_6 + C_7 + C_8 + C_{15} + C_{16} + C_{17} \\
T_2 &= C_{10} + C_{11} + C_{12} \\
T_3 &= C_3 \\
T_4 &= C_{14} + C_{15} + 2C_{16} + 3C_{17}
\end{align*}
\]

with \( T_0 = 0 \) and \( \{T_1, \ldots, T_4\} \) determined from the transport equations,

- and 10 mass action equations

\[
\begin{align*}
K_1 &= C_1C_2 & K_2 &= C_4C_2/C_5 \\
K_3 &= C_4C_3^2/C_6 & K_4 &= C_4C_3^2/C_7 \\
K_5 &= C_4C_2^2/C_8 & K_6 &= C_{10}C_1/C_{11} \\
K_7 &= C_{10}C_2^2/C_{12} & K_8 &= C_4C_{14}/C_{15} \\
K_9 &= C_4C_{14}^2/C_{16} & K_{10} &= C_4C_{14}^2/C_{17}
\end{align*}
\]

Selecting \( C_1 \) as the top level variable and \( C_4, C_{10} \) and \( C_{14} \) as the second level variables (the equation for \( C_3 \) has a trivial solution) and including the mass action equations in the conservation equations, we get a set of four equations in four unknowns. Assuming that the value of \( C_1 \) is known, the equation involving \( C_{10} \) is easily solved

\[
C_{10} = \frac{T_2}{1 + C_1 \left( \frac{1}{K_6} + \frac{C_1}{K_7} \right)}
\]

and we are left with a small system of two equations in two unknowns

\[
\begin{align*}
G_2 &= T_1 - C_4 \left( A + C_{14} \left( \frac{1}{K_8} + C_{14}/K_9 + C_{14}^2/K_{10} \right) \right) = 0 \\
G_4 &= T_5 - C_{14} \left( 1 + C_4 \left( \frac{1}{K_8} + 2C_{14}/K_9 + 3C_{14}^2/K_{10} \right) \right) = 0
\end{align*}
\]
where

\[ A = \left(1 + K_1/(K_2C_1) + K_1^2/(K_3C_1^2) + K_1^3/(K_4C_1^3) + K_1^4/(K_5C_1^4)\right) \]

which can be readily solved to get the values of \( C_4 \) and \( C_{14} \). The results are substituted back into the mass action equations and into the electroneutrality condition and iteration is stopped when the value assumed for \( C_1 \) yields a sufficiently small net charge.

### 2.3.2 Simplifications

The simplifications to the chemical equilibrium calculation are applied by identifying the conditions under which the nonlinear terms in the equation of electroneutrality can be neglected. In that case, the iteration in the top level variable \( X \) described in the previous section can be avoided, resulting in significant savings in computer time.

In a typical equilibrium calculation, the top level variable is the concentration of either hydrogen or hydroxyl ions, and the top level equation is the electroneutrality condition (equation 2.22). The conditions for simplification are readily identified by isolating three groups of species: the hydrogen and hydroxyl ions, the charged species not taking part in chemical reactions (identified as strong acids and bases for the purpose of this discussion), and all other species involved in chemical reactions (identified as weak acids and bases in this discussion). Rewriting the electroneutrality condition in terms of these groups, and assuming that the species are numbered separately within each group, we get

\[
H^+ - OH^- + \sum_{i=1}^{W} z_i C_i = -\sum_{i=1}^{S} z_i C_i \tag{2.60}
\]

where \( W \) is the number of species in the weak acid/base group, and \( S \) is the number of species in the strong acid/base group, so \( W + S + 2 = N \).

Note that if the net charge of the strong acids and bases is large compared with
the net charge of the weak acid and bases, equation 2.60 can be simplified to

\[ H^+ - OH^- = - \sum_{i=1}^{S} z_i C_i = -\text{Alk} \quad (2.61) \]

which is a quadratic equation in either \(H^+\) or \(OH^-\). Since the strong acid and bases do not take part in any chemical reaction, the alkalinity \(\text{Alk}\) is directly obtained from the integration of the transport equations. If the absolute value of the alkalinity is large compared to \(\sqrt{K_w}\), the solution to equation 2.61 can be approximated by

\[ H^+ = \begin{cases} 
-\text{Alk} & \text{if } \text{Alk} < 0 \\
K_w/\text{Alk} & \text{if } \text{Alk} > 0 
\end{cases} \quad (2.62) \]

Now, the net charge of the weak acid and bases in equation 2.60 is not known \textit{a priori}, so a separate criterion is needed to decide when to apply this simplification. A simple criterion is devised by estimating a bound to the net charge of the weak acid and bases. Note that the maximum charge of the weak acids and bases occurs when all the material is in the form of the species with the highest positive charge number. For example, in the zinc system of example 2.3 the maximum charge number of the zinc-containing species is 2 for \(Zn^{+2}\), so the maximum charge of the zinc-containing species would occur if all the zinc is in the \(Zn^{+2}\) form. Similarly, the minimum charge of the weak acids and bases occurs when all the material is in the form of the species with the lowest negative charge number (\(Zn(OH)_4^{2-}\) in the case of zinc system).

It can be expected that the buffer capacity of the weak acids and bases will be exhausted if the alkalinity is larger than the difference between the maximum and the minimum charge as estimated above. In other words, the maximum buffer capacity of the weak acid and bases, \(BC\), can then be estimated from

\[ BC = \max \left( \sum_{i=1}^{W} z_i C_i \right) - \min \left( \sum_{i=1}^{W} z_i C_i \right) = \sum_{k=1}^{M} \Delta z_k T_k \quad (2.63) \]

where the sum on the right hand side includes only those conserved quantities involving weak acid and bases and \(\Delta z_k\) is the range of charge numbers spanned by the
species in the conserved quantity $k$.

Using the bound BC defined in equation 2.63, the criterion for applying the simplified solution of the electroneutrality condition (equation 2.62) is

$$\frac{|\text{Alk}|}{\text{BC}} \geq \alpha$$

(2.64)

Using $\alpha = 3$ has produced results with an error of less than 0.1 pH units with respect to the solution of the full electroneutrality equation. In practice, the value assigned to this parameter should result from a trade off between the accuracy and speed of the equilibrium calculation.

### 2.4 Solution procedure

With all the elements of the model in hand, the calculation steps required to advance the solution from a known state at time level $t$ to the next time level are summarized as follows:

Starting from the known spatial distribution of the individual species at time level $t$, $\{C_1, \ldots, C_N\}^t$, $\{C_1^a, \ldots, C_N^a\}^t$

1. Calculate the value of the variable properties that depend on the ionic environment or local conditions (e.g. zeta potential).

2. Solve for current continuity, $\nabla \cdot \mathbf{i} = 0$ (equation 2.47), subject to appropriate boundary conditions to get the spatial distribution of the electrostatic potential $\phi(x, y, z, t)$.

3. Solve for mass conservation of the pore liquid, $\nabla \cdot \mathbf{u}_c = 0$ (equation 2.54), subject to appropriate boundary conditions to get the pressure distribution $p(x, y, z, t)$.

4. Calculate the species fluxes $\mathbf{j}_i$ from the known concentration distributions and the electrostatic potential and pressure distributions determined in steps 2 and 3.
5. Integrate the ordinary differential equations describing the boundary conditions to get the values of the conserved quantities in the electrode reservoirs $(T^\text{well})_w$ at the new time level $t + \Delta t$.

6. Integrate the transport equations, subject to the specified boundary conditions, to get the value of the conserved quantities $T_k(x, y, z)$ at the new time level $t + \Delta t$.

7. Solve for chemical and adsorption equilibrium to get the spatial distribution of the individual species at the new time level $t + \Delta t$. \[ \{C_1, \ldots, C_N\}^{t+\Delta t}, \{C^a_1, \ldots, C^a_N\}^{t+\Delta t}. \]
Chapter 3

Numerical Implementation

The numerical implementation of the electrorestoration model poses great challenges, not only because of the coupled transport of mass and charge which results in a nonuniform, time-dependent electric field; or for involving the solution of a complex system of partial differential and algebraic equations; but also because of the development of thin boundary layers, high localized electric fields and kinematic shocks in the solution. These factors result in severe constraints on the mesh resolution and the time step size for numerical stability and consequently yield a high computational cost. It has been an important part of this research to find ways to overcome these difficulties and produce a code that provides a practical and physically meaningful solution to the transport problem given the constraints in the computational resources available. In this endeavor, several integration schemes, such as the fluctuation splitting schemes used in gas dynamics (see Roe (1981) [35, 36], Deconinck (1993) [8], or Deconinck et al. (1994) [9]), the Petrov-Galerkin finite element methods for convection-dominated flows (see e.g. Hughes (1989) [19] or Johnson (1992) [22]), and the Galerkin method with added isotropic or streamwise diffusivity (see e.g. Ames (1992) [5] or Lapidus and Pinder (1982) [26]), have been considered. Also, the use of explicit versus implicit time integration has been evaluated, in the context of a general electrorestoration application, in terms of its impact on the modeling time. Finally, speed up strategies were investigated with the aim of reducing the overall execution time of the code. This chapter presents the most important aspects of this work.
3.1 Spatial discretization

As was mentioned in chapter 2, the boundary of the computational domain is defined by the union of the external boundary $\Gamma_{ext}$ and the boundaries of the electrode reservoirs $\Gamma_1, \cdots, \Gamma_W$ (see figure 2-2). That is,

$$\partial \Omega = \Gamma_{ext} \cup \left( \bigcup_{w=1}^{W} \Gamma_w \right)$$  \hspace{1cm} (3.1)

The external boundary is assumed to be formed by impermeable, non-reacting, non-conducting walls, so no-flux boundary conditions are imposed. The essential boundary conditions at the electrode reservoirs are either directly specified in the input file or calculated as explained in sections 2.1 and 2.2.

The computational domain is discretized with $\mathcal{K}$ linear triangular elements $\Omega^\kappa$ so

$$\Omega = \bigcup_{\kappa=1}^{\mathcal{K}} \Omega^\kappa$$  \hspace{1cm} (3.2)

The vertices of the triangles form a set of global nodes \{X_1, \cdots, X_N\} uniquely identified by a global node numbering system, so

$$X_i \neq X_j \text{ if } i \neq j$$  \hspace{1cm} (3.3)

Locally, the nodes are numbered counterclockwise as indicated in figure 3-1. Each local node $\hat{X}_\alpha^\kappa$ is uniquely mapped to the corresponding global node by a local to global index $g_\alpha^\kappa$, so that for all local nodes

$$X_i = \hat{X}_\alpha^\kappa \text{ if } i = g_\alpha^\kappa$$  \hspace{1cm} (3.4)

In the computational domain, all functions are expressed in terms of $\mathcal{N}$ linear basis functions $\psi_i$ satisfying

$$\psi_i(X_j) = \delta_{i,j}$$  \hspace{1cm} (3.5)

where $\delta_{i,j}$ is the Kronecker delta.
Linear basis functions were chosen with the aim of using the fluctuation splitting schemes, so successfully applied in $\omega[D\omega]$ gas dynamics to model high Reynolds number flows, since these methods assume linear variation of all variables within each triangle. The fluctuation splitting schemes seemed to have great potential for application in the electrorestoration model because of the similitude between modeling the transport of momentum in supersonic flow, where they have been traditionally applied, and modeling the transport of mass in electrorestoration applications. As will be explained in section 3.3, however, the coupling between the transport of mass and charge, and the complex algebraic equations of chemical equilibrium limited the applicability of these methods to only very specific and simple cases.

The linear basis functions in equation 3.5 can be represented within each element by elemental basis functions $h_\alpha$ through the use of a coordinate transformation from the global coordinates $\mathcal{X}$ to the reference element's coordinates $\xi$ as illustrated in figure 3-2. That is,

$$\psi_i(\mathcal{X})/\Omega = h_\alpha(F^\xi(\mathcal{X})), \quad i = g_\alpha$$

(3.6)
where the elemental basis functions are

\[ h_1 = \xi_1 \quad h_2 = \xi_2 \quad h_3 = 1 - \xi_1 - \xi_2 \] (3.7)

The mapping function \( F^\kappa \) is given by \([5, 30]\)

\[
\begin{pmatrix}
\xi_1 \\
\xi_2 \\
\end{pmatrix}
= 
\begin{pmatrix}
\hat{\mathcal{C}}^\kappa_1 \\
\hat{\mathcal{C}}^\kappa_2 \\
\end{pmatrix}
+ 
\begin{pmatrix}
\hat{D}^\kappa_{11} & \hat{D}^\kappa_{12} \\
\hat{D}^\kappa_{21} & \hat{D}^\kappa_{22} \\
\end{pmatrix}
\begin{pmatrix}
\mathcal{X}_1 \\
\mathcal{X}_2 \\
\end{pmatrix}
\] (3.8)

where, denoting \( \hat{x}_a^\kappa \) and \( \hat{y}_a^\kappa \) the coordinates of the local node \( \hat{X}_a^\kappa \) in the global coordinate system, \( \hat{\mathcal{C}}^\kappa_i \) and \( \hat{D}^\kappa_{ij} \) are

\[
\hat{\mathcal{C}}^\kappa_i = \frac{1}{2\text{area}^k} \left( \hat{x}_{[i+1]}^\kappa \hat{y}_{[i+2]}^\kappa - \hat{x}_{[i+2]}^\kappa \hat{y}_{[i+1]}^\kappa \right)
\] (3.9)

and

\[
\hat{D}^\kappa_{ij} = \frac{1}{2\text{area}^k} \begin{cases} 
(\hat{y}_{[i+1]}^\kappa - \hat{y}_{[i+2]}^\kappa) & \text{if } j = 1 \\
(\hat{x}_{[i+2]}^\kappa - \hat{x}_{[i+1]}^\kappa) & \text{if } j = 2 
\end{cases}
\] (3.10)
In these equations, area\(^*\) refers to the area of each triangle, calculated from

\[
\text{area}^* = \frac{1}{2} \det \begin{bmatrix}
1 & \hat{x}_1^* & \hat{y}_1^* \\
1 & \hat{x}_2^* & \hat{y}_2^* \\
1 & \hat{x}_3^* & \hat{y}_3^*
\end{bmatrix}
\tag{3.11}
\]

and the \([i]\) operator is defined by

\[
[i] = \begin{cases} 
 i \mod 3 & \text{if } i \mod 3 \neq 0 \\
3 & \text{otherwise}
\end{cases}
\tag{3.12}
\]

Based on the mapping and elemental basis functions presented, the integral of a scalar field over one computational element can be determined from

\[
\int_{\Omega^*} f(\mathbf{x}) \, dx \, dy = 2\text{area}^* \int_0^1 \left\{ \int_0^{1-\xi_2} f \left( (F^*)^{-1}(\xi) \right) d\xi_1 \right\} d\xi_2
\tag{3.13}
\]

Also, since the basis functions are linear, any interpolated function will have a constant gradient within each element, given by

\[
\nabla f/\Omega^* = \sum_{\alpha=1}^3 f(\hat{X}_\alpha^*) \left( \hat{\mathbf{D}}_{\alpha,1} \hat{\mathbf{i}} + \hat{\mathbf{D}}_{\alpha,2} \hat{\mathbf{j}} \right)
\tag{3.14}
\]

This property creates opportunities for simplifying the construction of the elemental matrices and accelerating the execution of the numerical code. These opportunities are explored in more detail later in this chapter.

A very robust and flexible mesh generator [14] was generously provided by Hecht and Saltel. Their program can automatically generate the mesh of an arbitrary two-dimensional shape via a set of points describing the boundary (see Hecht and Saltel(1991) [15]). The resolution can be controlled by varying the spacing between the points that define the boundary and varying the rate of change of the mesh spacing in the interior of the domain. As an example, the mesh generated for an arbitrary shape and combination of electrode reservoirs is presented in figure 3-3. Since several subdomains can be created and meshed independently and then combined into the
Figure 3-3: Example of the mesh generated for an arbitrary shape and combination of electrode reservoirs

In the final computational domain, this mesh generator allows a high degree of control over the spatial discretization.

3.2 Electric field and pressure distributions

3.2.1 Governing equations

The basic equations used in the calculation of the electrostatic potential and pressure distributions were presented in detail in section 2.2. For the electrostatic potential it is equation 2.47

$$-\nabla \cdot (\sigma \nabla \phi) = \nabla \cdot \left( F \sum_{i=1}^{N} z_i \frac{D_i}{r^2} \nabla C_i \right)$$

where \(\sigma\) is the solution electrical conductivity, defined by equation 2.48

$$\sigma = \frac{F^2}{r^2} \sum_{i=1}^{N} z_i^2 v_i C_i + \sigma_s$$
while the basic expression for the pressure calculation is equation 2.54,

\[- \nabla \cdot (k_h \nabla p) = \nabla \cdot (k_e \nabla \phi)\]

where \(k_h\) and \(k_e\) are, respectively, the effective hydraulic and electroosmotic permeability coefficients.

As can be seen, in both cases the distributions result from the solution of an equilibrium problem of the form

\[- \nabla \cdot (\rho \nabla u) = f\]  \hspace{1cm} (3.15)

subject to essential boundary conditions at the electrode reservoirs and no-flux boundary conditions at the external boundary. In general, both \(\rho\) and \(f\) vary in space.

### 3.2.2 Finite-element formulation

The finite element formulation for this problem has been widely studied in the literature (see for example Ames(1992) [5]), so only a brief description will be presented here.

**Discrete equations**

Following Galerkin's approach, the weak form of the differential equation is obtained by multiplying equation 3.15 times a trial function \(v\), and integrating over the computational domain \(\Omega\), to get

\[- \int_\Omega v \nabla \cdot (\rho \nabla u) dA = \int_\Omega vf dA\]  \hspace{1cm} (3.16)

Note that

\[\nabla \cdot (v \rho \nabla u) = \nabla v \cdot (\rho \nabla u) + v \nabla \cdot (\rho \nabla u)\]  \hspace{1cm} (3.17)
so equation 3.16 can be rewritten, using Gauss’ divergence theorem, as

$$\int_{\Omega} \nabla v \cdot (\rho \nabla u) dA - \int_{\partial \Omega} v \rho \nabla u \cdot \hat{n} dS = \int_{\Omega} v f dA \quad (3.18)$$

Here, $\partial \Omega$ is the boundary of the computational domain and $\hat{n}$ is a unit normal to the boundary. The integral on the boundary vanishes for zero essential boundary conditions ($v = 0$ at the electrode reservoirs $\Gamma_{e}$) given the no-flux boundary conditions ($\nabla u \cdot \hat{n} = 0$) at the external boundary $\Gamma_{ext}$. In that case, the weak form of the equilibrium equation is

$$\int_{\Omega} \nabla v \cdot (\rho \nabla u) dA = \int_{\Omega} v f dA \quad (3.19)$$

The modifications for non-homogeneous boundary conditions can be easily implemented and are discussed in the context of the solution procedure.

By using the basis functions described in section 3.1, the trial and weighting functions in equation 3.19 can be discretized as

$$\bar{u} = \sum_{i=1}^{N} \bar{u}_i \psi_i \quad (3.20)$$

$$\bar{u} = \sum_{j=1}^{N} \bar{u}_j \psi_j \quad (3.21)$$

where $\bar{u}$ and $\bar{u}$ are the discretized functions, and $\bar{u}_i$ and $\bar{u}_j$ are the nodal values.

Including these discretizations in equation 3.19 results in

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \bar{u}_i \bar{u}_j A_{ij} = \sum_{i=1}^{N} \bar{u}_i f_i \quad (3.22)$$

where

$$A_{ij} = \int_{\Omega} \nabla \psi_i \cdot (\rho \nabla \psi_j) dA \quad (3.23)$$

and

$$f_i = \int_{\Omega} \psi_i f dA \quad (3.24)$$

Assuming piecewise linear variation of the variable property $\rho$ inside the domain,
the entries of the stiffness matrix $A$ are given by

$$A_{ij} = \sum_{l=1}^{N} \bar{\rho}_l \int_{\Omega} (\nabla \psi_i \cdot \nabla \psi_j) \psi_l \, dA \quad (3.25)$$

Then, the discrete version of equation 3.19 is, in vector form,

$$\tilde{\nu}^T A \tilde{\nu} = \tilde{\nu}^T f \quad (3.26)$$

which can be reduced to

$$A \tilde{\nu} = f \quad (3.27)$$

The system matrix $A$ is symmetric, positive definite, and sparse. It is not necessarily banded, though, since the mesh is not structured and no special node numbering system is in place. Also, it is time dependent since it depends on the variable property $\rho$ which varies with time. Under these conditions, the iterative procedures are certainly advantageous relative to direct solution methods. In fact, the conjugate gradient method (see Hestenes (1952) [16], Hestenes (1980) [17]) is especially well suited for this case. It is robust, has very good convergence characteristics, and takes advantage of the system matrix's sparsity. In addition, the conjugate gradient iteration uses the action of $A$ rather than $A$ itself, so it does not require the formation and storage of the system matrix. This is accomplished by decomposing the system matrix into elemental matrices, and accounting for the contribution of each computational element to the nodal equations through direct stiffness summation.

In the conjugate gradient iteration, non-homogeneous essential boundary conditions are handled by providing an initial guess that satisfies these conditions and preventing changes to the solution at the essential boundaries during the iteration through the use of a masking vector.

**Elemental stiffness matrix**

The integral in equation 3.23 describing the entries of the system stiffness matrix can be evaluated by integrating over each computational element and then adding the
results. That is,

\[ A_{ij} = \sum_{\kappa=1}^{\mathcal{K}} \int_{\Omega_{\kappa}} \nabla \psi_i \cdot (\rho \nabla \psi_j) \, dA \]  \hspace{1cm} (3.28)

Since the global basis functions equal the elemental basis functions inside each element, the integrals in this equation can be evaluated over the reference element using equation 3.13. This leads to

\[ A_{ij} = \sum_{\kappa=1}^{\mathcal{K}} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} \hat{A}_{\alpha\beta}^{\kappa} \]  \hspace{1cm} (3.29)

where \( i = g_\alpha^\kappa, \ j = g_\beta^\kappa, \) and

\[ \hat{A}_{\alpha\beta}^{\kappa} = \left\{ \frac{1}{3} \text{area}^\kappa \left( \sum_{\gamma=1}^{3} \hat{\rho}_\gamma^\kappa \right) \right\} \sum_{m=1}^{2} \hat{D}_{\alpha m}^{\kappa} \hat{D}_{\beta m}^{\kappa} \]  \hspace{1cm} (3.30)

In equation 3.30, \( \hat{\rho}_\gamma^\kappa \) is the value of the variable property \( \rho \) at the global node \( l = g_\gamma^\kappa, \) and \( \hat{D}^\kappa \) is the coordinate transformation matrix defined in equation 3.10.

Note that equation 3.29, suggests an efficient and simple way to store \( A \). The elemental stiffness matrices and the global index \( g \) contain the information required to produce the non-zero entries of the system matrix. The storage space required is \( O(9\mathcal{K}) \), which is about \( O(20\mathcal{N}) \) as opposed to the \( O(\mathcal{N}^2) \) required to hold \( A \) in a direct approach. This fact was used to modify the standard conjugate gradient iteration so the elemental stiffness matrices would not be recalculated at each iteration but determined once at the preamble. This single change produced a reduction of 50% in the overall execution time of the code, while still maintaining its ability to handle a large number of degrees of freedom.

**Force vector**

On the left hand side of the equilibrium equation, the only difference between the electrostatic potential and pressure calculations is the value of the variable property \( \rho \). However, to determine the force term two separate formulations are required:
• Electrostatic potential problem: In this case, the forcing function \( f \) is

\[
f = \nabla \cdot \left( F \sum_{i=1}^{N} z_i \frac{D_i}{r^2} \nabla C_i \right) \quad (3.31)
\]

Including this definition in equation 3.24 results in

\[
f_i = F \sum_{i=1}^{N} z_i \int_{\Omega} \psi_i \nabla \cdot \left( \frac{D_i}{r^2} \nabla C_i \right) dA \quad (3.32)
\]

Here, \( i \) refers to the node number and \( i \) to the species number. This notation will be used whenever the meaning of \( i \) is not clear from context.

Using

\[
\nabla \cdot \left( \psi_i \frac{D_i}{r^2} \nabla C_i \right) = \nabla \psi_i \cdot \left( \frac{D_i}{r^2} \nabla C_i \right) + \psi_i \nabla \cdot \left( \frac{D_i}{r^2} \nabla C_i \right) \quad (3.33)
\]

the integral in equation 3.32 can be rewritten, using Gauss's divergence theorem, as

\[
\int_{\Omega} \psi_i \nabla \cdot \left( \frac{D_i}{r^2} \nabla C_i \right) dA = \int_{\partial \Omega} (\mathbf{n} \cdot \nabla C_i) \psi_i \frac{D_i}{r^2} dS - \int_{\Omega} \left( \nabla \psi_i \cdot \nabla C_i \frac{D_i}{r^2} \right) dA \quad (3.34)
\]

The first term on the right hand side can be neglected. It is zero on the external boundary due to the no-flux boundary conditions \( (\mathbf{n} \cdot \nabla C_i = 0) \), and has no effect on the electrode boundaries since this equation is not used on essential boundaries.

Then, equation 3.32 is equivalent to

\[
f_i = -F \sum_{i=1}^{N} z_i \int_{\Omega} \left( \nabla \psi_i \cdot \nabla C_i \right) \frac{D_i}{r^2} dA \quad (3.35)
\]

Note that \( \nabla \psi_i \) and \( \nabla C_i \) are constant within each element (equation 3.14). Taking them out of the elemental integrals leads to

\[
f_i = -F \sum_{i=1}^{N} z_i \sum_{\kappa=1}^{K} \sum_{\alpha=1}^{3} \nabla \mathbf{h}^\kappa_\alpha \cdot \nabla C_i^\kappa \frac{\text{area}^\kappa}{3} \sum_{\beta=1}^{3} \frac{D_i(\mathbf{X}_\beta^\kappa)}{r^2(\mathbf{X}_\beta^\kappa)} \quad (3.36)
\]
Here, $D_i(\dot{X}_g)$ and $\tau(\dot{X}_g)$ are the diffusion coefficient of species $i$ and the tortuosity factor at the local node $\dot{X}_g$, $i$ is the global node corresponding to the local to global index $g_i^\kappa$, and $\nabla x^\kappa$ refers to the gradient of a scalar field $x$ in element $\kappa$.

- Pressure problem: In this case, the forcing function $f$ is

$$f = \nabla \cdot (k_e \nabla \phi)$$  \hspace{1cm} (3.37)

Including this definition in equation 3.24 and following the procedure described for the potential case results in

$$f_i = - \sum_{\kappa=1}^{K} \sum_{a=1}^{3} \nabla h^\kappa_a \cdot \nabla \phi^\kappa \frac{\text{area}^\kappa}{3} \sum_{\beta=1}^{3} k_e(\dot{X}_\beta^\kappa)$$  \hspace{1cm} (3.38)

### 3.2.3 Tests

The code was initially tested by selecting a solution satisfying the boundary conditions, plugging it into the differential equation to obtain a feasible forcing function and feeding the forcing function to the code. It was checked that the numerical solution approached the test function originally included in the differential equation. It was also verified that the numerical solution responded well to changes in the spatial distribution of the variable property $\rho$ (see figure 3-4), or changes in the boundary conditions and force terms. Multiple electrode or complex geometries are readily handled by the code due to the general nature of the formulation and the flexibility of the mesh generator. An example of this is the potential distribution shown in figure 3-5 which corresponds to the geometry presented in figure 3-3. In this example, uniform concentration distributions have been assumed.

A more stringent test of this section of the code and its integration with the rest of the program will be producing no accumulation of charge, either locally or globally, during transport. Such a test is presented in section 3.4.
Figure 3-4: Electrostatic potential for two different spatial distributions of the electrical.

Figure 3-5: Potential distribution for the geometry presented in figure 3-3
3.3 Concentration distributions

3.3.1 Transport equations

As was explained in chapter 2, determining the individual species concentration distributions in a system with \( N \) species and \( M \) conserved quantities involves solving a system of \( M \) transport equations of the form

\[
\frac{\partial T_k}{\partial t} + \sum_{i=1}^{N} \nu_{ik} (\nabla \cdot j_i) = 0 \tag{3.39}
\]

\( N \) adsorption isotherms, and \( r = N - M \) chemical equilibrium relationships. In the transport equations, \( T_k \) is the concentration of the conserved quantity \( k \), \( j_i \) is the flux of species \( i \), and \( \nu_{ik} \) is the stoichiometric coefficient of species \( i \) in the conserved quantity \( k \).

Since the concentration, and therefore the flux, of each individual species depends on the concentrations of all conserved quantities at a particular point, the set of transport equations in 3.39 can be written as

\[
\frac{\partial T_k}{\partial t} + \sum_{i=1}^{N} \nu_{ik} (\nabla \cdot G_i(T_1, \cdots, T_M)) = 0 \tag{3.46c}
\]

where the \( G_i \) functions include the solution to the chemical and adsorption equilibrium problem and the evaluation of the corresponding species flux. These functions will rarely be available in explicit form, but result from the numerical solution of the chemical equilibrium problem. Moreover, if a fully implicit time discretization is attempted, these functions also involve solving for the electric field and pressure distributions in order to calculate the convection and migration terms of the species flux. It is not difficult to imagine the complexity and tremendous computational load associated with this approach. In fact, preliminary trials of implicit schemes resulted in a much lower execution speed than that achieved using explicit schemes, even in very simple systems. Not included in this consideration are the convergence problems arising from the complex nature of the \( G_i \) functions. For example, these
functions may become discontinuous as the set of mass action equations changes due to the presence of solid species in the system. Under near-saturation conditions, an iterative procedure using these functions might jump continually from saturated to unsaturated conditions and vice versa, failing to find the solution.

One may also consider semi-implicit alternatives in order to partially relax the computational load. For example, using the convection and migration velocities from the previous time step would avoid solving for the electrostatic potential and pressure distributions at each iteration of the time integration scheme. Under these conditions, the scheme would involve iterating only on the concentration fields and would thus be similar to those proposed in the literature (see for example Walsh et al. (1984) [43] and Kirkner and Reeves (1988) [23]). However, the stability constraints related to the migration and convection terms are inherited and the extra work does not usually provide a significant benefit.

As will be seen in the next section, this coupling between the transport equations and especially the coupling with the electric potential becomes a serious obstacle when implementing fluctuation splitting schemes or any other method-of-characteristics-based algorithm.

### 3.3.2 Solution Methods

**Standard Galerkin**

As in the electrostatic potential case, the weak form of the transport equations is obtained by multiplying equation 3.39 times a trial function \( v \) and integrating over the computational domain. That is,

\[
\int_\Omega \nu \frac{\partial T_k}{\partial t} dA = - \sum_{i=1}^{N} \nu_{ik} \int_\Omega \nu (\nabla \cdot j_i) dA
\]

(3.41)

Using

\[
\int_\Omega \nu (\nabla \cdot j_i) dA = \int_{\partial \Omega} j_i \cdot \hat{n} dS - \int_\Omega \nabla \nu \cdot j_i dA
\]

(3.42)

and noting that the first term on the right hand side is zero for non-reacting, imperme-
able, non-conducting walls and is not used on the essential boundaries, equation 3.41 can be written as

$$\int_{\Omega} v \frac{\partial T_k}{\partial t} dA = \sum_{i=1}^{N} \nu_{ik} \int_{\Omega} \nabla \cdot j_i dA \quad (3.43)$$

Upon discretization of the trial and weighting functions, this equation results in

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\partial T_k(X_j)}{\partial t} \int_{\Omega} \psi_i \psi_j dA = \sum_{i=1}^{N} \nu_{ik} \sum_{i=1}^{N} \int_{\Omega} \nabla \psi_i \cdot j_i dA \quad (3.44)$$

Including the definition of the species flux (equation 2.9)

$$j_i = ((k_e + k_{ei}) \nabla \phi + k_h \nabla p) C_i - \frac{D_i}{\tau^2} \nabla C_i$$

in the integral on the right hand side of equation 3.44 and realizing that the potential, pressure and concentration gradients are constant within each element, leads to

$$\int_{\Omega} \nabla \psi_i \cdot j_i dA = \sum_{\kappa=1}^{3} \sum_{\alpha=1}^{3} \left( \nabla h_{\alpha}^\kappa \cdot \nabla \phi^\kappa \int_{\Omega^\alpha} (k_e + k_{ei}) C_i dA + \nabla h_{\alpha}^\kappa \cdot \nabla p^\kappa \int_{\Omega^\alpha} k_h C_i dA - \nabla h_{\alpha}^\kappa \cdot \nabla C_i^\kappa \int_{\Omega^\alpha} \frac{D_i}{\tau^2} dA \right) \quad (3.45)$$

The integrals in this equation are easily evaluated in terms of the elemental mass matrix and the value of the variable properties $k_e, k_{ei}, k_h$ and $D_i$ at the local nodes.

The standard Galerkin formulation just presented has two important properties:

First, it produces a discretization with the same form of the discrete equilibrium equation used to determine the electrostatic potential distribution. That is, if the individual species transport equations were discretized using this formulation, multiplied times the species charge numbers and then added together, the set of discrete equations used to determine the electrostatic potential distribution would be recovered. This property is not common to all discretization schemes, but is crucial to maintain electroneutrality in the solution. Recall that the electrostatic potential distribution is obtained from a charge transport equation in which the accumulation
term has been set to zero. The second property is that, provided an explicit time discretization is used, this formulation allows solving the system of transport equations as it were uncoupled. This is so, because all the information required to evaluate the right hand side of the discrete equations is available at the previous time level.

A limitation of the scheme is that it requires solving for the boundary layers. That is, in order to avoid oscillations in the solution, the mesh resolution has to be set so the grid Peclet number (Peclet number based on the mesh spacing) is less than two. This usually implies very fine resolutions relative to the scale of the computational domain and, together with the stability requirements for explicit schemes, in most cases results in impractically high computational costs. As an example, figure 3-6 shows the initial distribution of the Peclet number of the chloride ions, based on the distance between the electrodes, for a case representative of typical electrorestoration applications. Note that the Peclet number reaches values in the order of $10^4$ even when the applied potential difference is moderate and no high, localized electric fields have developed. This result indicates that in order to solve for the boundary layers using the standard Galerkin approach, in this example the size of the computational elements must be about five thousand times smaller than the distance between the electrodes.

**Fluctuation-splitting schemes**

These methods were developed to solve the Euler equations describing inviscid compressible flows. In these flows, the transport of mass, momentum and energy is dominated by advection just in the same way that the transport of mass is dominated by convection and migration in electrorestoration applications. It is because of this that a significant effort was devoted at applying the fluctuation splitting and other upwind discretization schemes in the numerical implementation of the electrorestoration model.

These methods are based on the calculation of the residual or fluctuation accounting for accumulation of the modeled variable within a computational element [8]. This fluctuation is determined by integrating the transport equations over each computa-
Figure 3-6: Spatial distribution of the Peclet number in a typical electrorestoration application

The fluctuation $\Phi^\kappa$ over element $\kappa$ is determined from

$$\Phi^\kappa = \int_{\Omega^\kappa} \frac{\partial u}{\partial t} \, dA = - \int_{\Omega^\kappa} \nabla \cdot \vec{F}(u) \, dA$$  \hspace{1cm} (3.47)

Applying a standard Galerkin discretization to this equation results in the residual being distributed in equal proportion to each node. That is, the contribution of element $\kappa$ to the rate of change of the scalar $u$ at the local node $\hat{X}_\alpha^\kappa$ would be given by

$$\frac{1}{3} \text{area}^\kappa \frac{\partial u(\hat{X}_\alpha^\kappa)}{\partial t} = \frac{1}{3} \Phi^\kappa$$  \hspace{1cm} (3.48)

Instead, the fluctuation splitting schemes redistribute the residual so no update is
assigned to the upstream nodes. That is,

$$\frac{1}{3} \text{area}^\kappa \frac{\partial u(\hat{X}_a^\kappa)}{\partial t} = \beta_a^\kappa \Phi^\kappa$$  \hspace{1cm} (3.49)$$

with $\beta_a^\kappa = 0$ for the upstream nodes and $\sum_{a=1}^{3} \beta_a^\kappa = 1$. The various schemes differ in the way the distribution coefficients $\beta_a^\kappa$ are determined.

A common feature among the schemes is that they linearize the conservation law (3.46) as

$$\frac{\partial u}{\partial t} + \vec{\lambda} \cdot \nabla u = 0$$  \hspace{1cm} (3.50)$$

where $\vec{\lambda}$ is an average advection speed vector over each triangle, and then use the solution of a linear wave equation to calculate the distribution coefficients.

Implementing these schemes for systems of conservation equations in more than one space dimension is rather complex. In fact, even for the well studied system of Euler equations, the implementation of these schemes is the subject of active research (see for example Paillère et al. (1994) [29]). The main difficulty arising in the implementation of these methods to systems of equations is that they require a residual decomposition step in which the total fluctuation has to be divided into scalar components corresponding to individual waves. For example, considering a system of transport equations in conservative form

$$\frac{\partial U}{\partial t} + \nabla \cdot \vec{F} = 0$$  \hspace{1cm} (3.51)$$

the total residual over each triangle is [29]

$$\Phi^\kappa = - \int_{\Omega^\kappa} \nabla \cdot \vec{F} dA = - \int_{\partial \Omega^\kappa} (\vec{n} \cdot \vec{F}) dS = - \sum_{k=1}^{N_e} \phi^k r_U^k$$  \hspace{1cm} (3.52)$$

Here, $N_e$ is the number of non-zero waves used in the decomposition, $\phi^k$ is the contribution of the $k^{th}$ wave to the total residual and $r_U^k$ is a vector in $U$-space. After the individual wave fluctuations $\phi^k$ are determined, they are independently distributed to the three nodes of the triangle using scalar distribution schemes (equation 3.49) [9].
The problem resides in calculating the individual wave fluctuations.

The conservation equations are linearized using

\[
\frac{\partial U}{\partial t} + \bar{\mathbf{G}} \cdot \nabla U = 0
\]  

(3.53)

where \( \bar{\mathbf{G}} \) is the Jacobian vector \( (\partial \mathbf{F}_x/\partial U, \partial \mathbf{F}_y/\partial U) \) evaluated at the average state of the element. Determining the wave fluctuations \( \phi^k \) and the appropriate vector \( \mathbf{r}_U^k \) involves calculating the eigenvalues and eigenvectors of this Jacobian vector.

It can be seen from this discussion that applying the fluctuation splitting schemes to the system of transport equations presented in equation 3.40 involves an impractical amount of computational work, as the \( \mathbf{F}_i \) functions relating the individual species fluxes to the concentrations of the conserved quantities are not generally available in explicit form, but result from the numerical solution of the chemical equilibrium problem and the electrostatic potential and pressure distributions; and the formal implementation of these methods require evaluating the eigenvalues and eigenvectors of a Jacobian vector based on these functions.

As an alternative, the set of transport equations in 3.40 was decomposed back into the original set of individual species transport equations. The generation terms were set to zero, and the contribution of diffusion was not included but handled separately with a standard Galerkin formulation. The result was a set of \( N \) equations of the form

\[
\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{j}_i = 0
\]  

(3.54)

where \( \mathbf{j}_i = \mathbf{u}_i C_i \) and the total species velocities \( \mathbf{u}_i \) are given by \( \mathbf{u}_i = (k_e + k_{ei}) \nabla \phi + k_h \nabla p \).

Following an explicit time integration scheme, the total species velocities were calculated with the data at the previous time level and were assumed to remain constant during the time step. The fluctuation over each computational element was calculated separately for each species using

\[
\Phi_i^k = - \int_{\Omega^*} \nabla \cdot \mathbf{j}_i dA = -\text{area}^* (\mathbf{u}_i) \cdot \nabla C_i^* = - \sum_{\alpha=1}^{3} k_\alpha C_i (\hat{X}_\alpha^*)
\]  

(3.55)
where
\[
\langle u_i \rangle = \frac{1}{\text{area}^\kappa} \int_{\Omega^\kappa} u_i \, dA
\]
and
\[
k_\alpha = ((u_i) \cdot \nabla h_\alpha^\kappa) \text{area}^\kappa
\]

Individual distribution coefficients \((\beta_i)_{\alpha}^\kappa\) were then determined for each species, according to the specific scalar distribution scheme [29]. For example, using the Narrow-scheme,
\[
(\beta_i)_{\alpha}^\kappa \Phi_i^\kappa = -\max(0, k_\alpha)(C_i(\hat{X}_\alpha^\kappa) - C_{i}^{in})
\]
where
\[
C_{i}^{in} = \frac{\sum_{j=1}^{3} C_i(\hat{X}_j^\kappa) \min(0, k_j)}{\sum_{j=1}^{3} \min(0, k_j)}
\]

These distribution coefficients were used to get a temporary estimate of the species accumulation at each node, using
\[
\sum_{\kappa=1}^{3} \frac{1}{3} \text{area}^\kappa \frac{\partial C_i(X_i)}{\partial t} = \sum_{\kappa=1}^{3} \sum_{\alpha=1}^{3} (\beta_i)_{\alpha}^\kappa \Phi_i^\kappa
\]
where \(i = \Phi_i^\kappa\).

These estimates were superposed to those obtained for the diffusion terms and then combined according to the stoichiometry of the problem to determine the accumulation of the conserved quantities at each node. That is,
\[
\frac{\partial T_k(X_i)}{\partial t} = \sum_{i=1}^{N} \nu_{ik} \left( \left( \frac{\partial C_i(X_i)}{\partial t} \right)_{\text{mig}} + \left( \frac{\partial C_i(X_i)}{\partial t} \right)_{\text{diff}} \right)
\]

This implementation produced good results when modeling linear convection of neutral species. However, when modeling more complex systems, it resulted in significant accumulation of charge and mass in the solution. In effect, the link between the transport of mass and the transport of charge was lost. This is attributed to the non-symmetric effect introduced in the discrete equations by the upwind bias. Opposite to the standard Galerkin case, in this case the discrete equations used to
determine the electrostatic potential distribution are not recovered by summing the discrete transport equations according to the species charge numbers.

One might consider determining the electrostatic potential distribution by combining the discrete transport equations produced by this formulation and requiring the accumulation of charge to be zero. However, doing this destroys the symmetry of the system matrix $A$ in equation 3.27, and requires the use of alternative solution methods. Also, it is not clear whether the system is well posed and a unique solution can be found. This problems are expected to arise in other upwind formulations.

3.3.3 Modified Galerkin method

An important result of the analysis presented above is that the compatibility between the discrete equations used in the elliptic part of the problem and the discrete equations of transport is a crucial factor in maintaining the electroneutrality of the solution. The standard Galerkin formulation satisfied this critical requirement but resulted in high computational costs due to the high resolution requirements.

In most practical cases, the transport of contaminants in electrorestoration applications is dominated by convection and migration. Therefore, it was expected that increasing the diffusion coefficients would not have a significant effect on the global concentration distributions. This led to the use of artificial diffusivity to thicken the boundary layers and relax the resolution requirements.

The modified Galerkin method used in the code is similar to the Standard Galerkin method presented in the previous section. However, in this case an artificial diffusivity is added to the diffusion coefficients used in the transport equations so the maximum grid Peclet number $\max(R_g)$ is less than two. It has been shown [30] that for the linearized, one-dimensional version of the convection diffusion equation, this criterion is useful in determining whether oscillation or wiggles will appear in the steady state solution. Here, it has been applied to the transient case with the idea that the mesh, at any time during the simulation, must be fine enough to hold the steady state solution. Also, in the nonlinear, two-dimensional case in hand, the criterion is applied locally in time and space. The grid Peclet Number for species $i$ within one
element is defined by

\[(R_g)_i = \frac{\max(|u_i|)h}{D_i}\]  \hspace{1cm} (3.62)

where, \(\max(|u_i|)\) is the maximum of the species velocity within the element, \(h\) is the characteristic element size, defined as the length of the shortest side, and \(D_i\) is the diffusivity of the species.

The artificial diffusivity is selected so the maximum grid Peclet number over the computational domain, for any species included in the transport equations is less than 2. This results in a modified diffusivity

\[D_i^* = D_i + \frac{1}{2}\max(|u_i|)h\] \hspace{1cm} (3.63)

Initially, this modified diffusivity was determined locally and varied with time as needed. This, however, resulted in the development of nonsymmetrical solutions in cases where symmetry was expected. The reason for this is that the diffusivity calculated from equation 3.63 is significantly dependent on the local mesh size and thus permeates the unstructured nature of the mesh into the solution. To overcome this problem, a uniform diffusivity was used. For each species, the diffusivity used was the maximum over the computational domain of the modified diffusivity calculated in equation 3.63. This produced a symmetrical solution at the expense of increasing the local effect of diffusion in some areas beyond what was actually needed for stability.

The advantage of this approach is that a reasonable approximation to the global solution is obtained even when the inner solution at the boundary layers is not resolved. As more computational resources are available, the quality of the local solution can be improved by increasing the mesh resolution. Also, the scheme is amenable to improvement through the use of adaptive meshing.

Care should be taken, however, when interpreting the results near the electrode reservoirs where boundary layers typically develop. Some aspects of the solution at the boundaries depend on the concentration gradients in the boundary layers and are therefore more sensitive to the mesh resolution. More details on the effect of the added diffusivity on the accuracy and reliability of the model predictions are presented in
\[
\begin{array}{c|cc}
\text{Metals} & \text{Ligands} & \text{Species} \\
\hline
H^+ & OH^- & \text{H}^+ \quad C_1 \\
Na^+ & Cl^- & \text{OH}^- \quad C_2 \\
 & & \text{Na}^+ \quad C_3 \\
 & & \text{Cl}^- \quad C_4 \\
\end{array}
\]

Table 3.1: Chemical species in the NaCl system

section 3.5.

### 3.4 Test case: The NaCl system

Starting with the simplest system that involves all major sections of the code, let us consider a dilute solution of sodium chloride in an inert, non-conducting soil. Following the general approach outlined in chapter 2, the list of metals, ligands and chemical species assumed to exist in the system are presented in Table 3.1. The only reactions assumed to be taking place are dissociation of water in the bulk liquid,

\[
\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \quad (3.64)
\]

and water electrolysis at the electrodes

\[
\begin{align*}
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2(g) & \quad \text{(cathode)} \\
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2(g) + 4e^- & \quad \text{(anode)}
\end{align*} \quad (3.65)
\]

It can be seen in equation 3.64 that the generation rates of the hydrogen and hydroxyl ions in the bulk liquid are equal. This leads to the definition of the following conserved quantities for which the generation terms will be zero:

\[
\begin{align*}
T_1 &= C_1 - C_2 \\
T_2 &= C_3 \\
T_3 &= C_4
\end{align*} \quad (3.66, \ 3.67, \ 3.68)
\]
Combining the individual species transport equations according to the definition of the conserved quantities (equations 3.66 to 3.68) results in

\[
\frac{\partial T_1}{\partial t} + \nabla \cdot (j_1 - j_2) = 0 \tag{3.69}
\]

\[
\frac{\partial T_2}{\partial t} + \nabla \cdot j_3 = 0 \tag{3.70}
\]

and

\[
\frac{\partial T_3}{\partial t} + \nabla \cdot j_4 = 0 \tag{3.71}
\]

Following the solution procedure, the concentration of the individual species are determined from the value of the conserved quantities by solving for chemical equilibrium. In this case, the equilibrium calculation is very simple. There is only one chemical equilibrium relationship, given by

\[
C_1 C_2 = K_W \tag{3.72}
\]

Including this equation in equation 3.66 results in either

\[
T_1 = C_1 - \frac{K_W}{C_1} \tag{3.73}
\]

or

\[
T_1 = \frac{K_W}{C_2} - C_2 \tag{3.74}
\]

To minimize numerical round off errors, equation 3.73 is used for acidic conditions \( T_1 > 0 \) and equation 3.74 is used for basic conditions \( T_1 < 0 \). This leads to the solution

\[
\begin{cases}
    C_1 = b, & C_2 = K_W/b \quad \text{if } T_1 \geq 0 \\
    C_1 = K_W/b, & C_2 = b \quad \text{if } T_1 < 0
\end{cases} \tag{3.75}
\]

where

\[
b = \frac{|T_1| + \sqrt{T_1^2 + 4K_W}}{2} \tag{3.76}
\]

The code will be tested by simulating species transport in the sodium chloride
system for two different cases: diffusion with no applied electric field, and transport under an applied electric field. In both cases, the major sections of the code are involved. The first example focuses on the interplay between the transport of mass and charge, while the second example incorporates the simulation of electrochemical reactions in the boundary conditions. Further tests of the reliability and accuracy of the model are presented in chapter 4 where the model predictions are compared with experimental data.

3.4.1 Apparently pure diffusion of NaCl

In this case there are no electrodes. However, an electric field is expected to develop due to the difference in the diffusion coefficients of the electrolyte constituents (see Probst (1994) [31]). It has been observed that the anion and cation in a binary electrolyte (chloride and sodium in this example) apparently diffuse at the same rate despite any difference in the individual ion diffusivities. This is an interesting effect resulting from the interdependence between the transport of mass and charge. Therefore, this example is a good test of the ability of the code to model the link between the transport of mass and charge and thus maintain electroneutrality in the solution. Note that in the formulation above electroneutrality is not imposed a priori, but results from modeling the species transport in a self-consistent manner.

Numerical simulation

The numerical simulation of this phenomenon was carried out using the transport equations (equations 3.69 to 3.71) and the solution to the chemical equilibrium problem (equations 3.75 and 3.76) presented above. The mesh resolution was selected so the grid Péclet Number based on the molecular diffusion coefficients was less than two. Thus, no artificial diffusivity was required.

The species mobilities and diffusion coefficients used in the simulation were taken from published electrochemical data (See Vanýsek [41]), and are presented in Table 3.2.
<table>
<thead>
<tr>
<th>Species</th>
<th>Name</th>
<th>Mobility ( (m \text{ mol})/(N \text{ s}) )</th>
<th>Diffusion coefficient ( (m^2/s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H(^+)</td>
<td>(3.756 \times 10^{-12})</td>
<td>(9.311 \times 10^{-9})</td>
</tr>
<tr>
<td>2</td>
<td>OH(^-)</td>
<td>(2.127 \times 10^{-12})</td>
<td>(5.273 \times 10^{-9})</td>
</tr>
<tr>
<td>3</td>
<td>Na(^+)</td>
<td>(5.379 \times 10^{-13})</td>
<td>(1.334 \times 10^{-9})</td>
</tr>
<tr>
<td>4</td>
<td>Cl(^-)</td>
<td>(8.197 \times 10^{-13})</td>
<td>(2.032 \times 10^{-9})</td>
</tr>
</tbody>
</table>

Table 3.2: Mobilities and diffusion coefficients used in the simulation of the NaCl system

The simulation was carried out in a square domain of \(0.05m \times 0.05m\), and intended to reproduce the diffusion of the electrolyte after the introduction of an instantaneous line source. However, since a delta function cannot be accurately represented with linear finite elements, the calculation does not start right at the introduction of the line source but a finite time later. At \(t = 0\), the sodium and chloride concentrations are equal, and correspond to a delta function of strength \(Q = 10^{-3} \text{ mol} \) per unit depth at \(t_0 = -600 \text{ s}\), passing through the point \((x', y') = (0.025, 0.025)\) and diffusing with a diffusivity \(D = 1.611 \times 10^{-9} \text{ m}^2/\text{s}\) (see equation 3.83 in the next section). This concentration distribution can be evaluated using (see e.g. Carslaw and Jaeger (1948) [6])

\[
C(x, y) = \frac{Q}{4\pi D(t - t_0)} \exp(-r^2/4D(t - t_0))
\]  

where \(r^2 = (x - x')^2 + (y - y')^2\). The initial hydrogen and hydroxyl concentrations are equal and uniform throughout the domain.

The results from the numerical simulation of this system are presented in figures 3-7 to 3-13. As expected, an electric field developed as the chloride ions tended to diffuse away from the source insertion point at a faster rate than the sodium ions. As can be seen in figure 3-7, the electrostatic potential was axisymmetric with respect to the source insertion point and had a negative curvature. The migration velocities resulting from this electric field enhanced the transport of the slower diffusing sodium ions and delayed the transport of the faster moving chloride ions relative to the insertion point, as illustrated in figure 3-8. As a result, the sodium and chloride ions ended up diffusing at essentially the same rate. This is shown in figure 3-9 which presents the sodium concentration distribution and the difference between the sodium and chloride
concentrations at two different times during the simulation. Note that the difference between the sodium and chloride concentrations is several orders of magnitude smaller than either concentration throughout the area spanned by the diffusion front.

The total mass of sodium and chloride in the system remained constant during the simulation, demonstrating the mass conservation properties of the numerical formulation. This is shown in figure 3-10 which presents the difference between the total mass of sodium at time t and the initial mass. The error is of order $10^{-9}$ mol, compared with a total mass of about $10^{-3}$ mol. The oscillations in the curve indicate that the error is comparable to the computer's precision.

The diffusion-induced electric field also caused the hydrogen and hydroxyl ions to migrate in opposite directions with respect to the source insertion point. This resulted in pH changes within the area spanned by the diffusion front, as shown in
Figure 3-8: Effect of a convex potential distribution on the transport of sodium and chloride

Figure 3-11. This is an interesting effect not typically mentioned in the literature, as the hydrogen and hydroxyl ions are commonly neglected in the analysis of binary electrolytes (see e.g. Newman (1991) [28]). Nevertheless, the numerical results support this approximation since they show that the variation of the hydrogen and hydroxyl ions distributions inside the diffusion front is small. Observe that the pH remained near-neutral throughout the diffusion process and that the changes in the maximum and minimum pH were smaller as time progressed, indicating an asymptotic behavior.

Figure 3-12 presents the net charge distributions produced by the model. Note that the net charge is small compared to the ionic strength of the solution. The error near the center of the cell corresponds to numerical imprecision when subtracting two large numbers. Note that the spatial pattern of the net charge near the center of the cell is very similar to the spatial pattern of the difference between the sodium and chloride concentrations (compare figure 3-12 and figure 3-9 (right)). As in the total mass case, the total accumulation of charge in the system is negligible (See figure 3-13).

As mentioned in chapter 2, the electroneutrality condition can be used to replace one of the transport equations. Doing this typically results in a much simpler
Figure 3-9: Sodium concentration distributions (left) and difference between sodium and chloride concentrations (right) at $t=900$ and $3600$ s during the simulation of diffusion in the NaCl system.
Figure 3-10: Difference between the total mass of sodium at time $t$ and at time=0 during the simulation of diffusion in the NaCl system. The initial mass of sodium is about $10^{-3}$ mol

numerical solution to the transport problem. For example, in this case, using the electroneutrality condition allows determining $T_1$ at any time from $T_2$ and $T_3$. That is,

$$T_1 = T_3 - T_2$$  \hspace{1cm} (3.78)

So, if the electroneutrality condition had been used explicitly, calculating the transport of hydrogen and hydroxyl ions would have been unnecessary. Since these are the fastest moving ions, they impose the most severe constraints on the mesh resolution and the time step for numerical stability. Therefore, eliminating these species from the transport equations, would have allowed solving the problem with approximately one tenth of the computational effort.

Analytical solution

The development of the diffusion-induced electric field presented above can be inferred from the equation of current continuity (equation 2.43), which in terms of the species
Figure 3-11: pH distributions at t=0, 900, 1800 and 3600 s during the simulation of diffusion in the NaCl system
Figure 3-12: Net charge distributions at t=0, 900, 1800 and 3600 s during the simulation of diffusion in the NaCl system
Figure 3-13: Total net charge during the simulation of diffusion in the NaCl system.

The fluxes are

\[ F \nabla \cdot \left( \sum_{i=1}^{N} z_i \mathbf{j}_i \right) = 0 \]  \hspace{1cm} (3.79)

In this example, this equation yields

\[ F (\nabla \cdot (\mathbf{j}_1 - \mathbf{j}_2) + \nabla \cdot \mathbf{j}_3 - \nabla \cdot \mathbf{j}_4) = 0 \]  \hspace{1cm} (3.80)

Examining the transport equations 3.69 to 3.71, it can be seen that equation 3.80 is equivalent to

\[ - \frac{\partial T_1}{\partial t} - \frac{\partial T_2}{\partial t} + \frac{\partial T_3}{\partial t} = 0 \]  \hspace{1cm} (3.81)

This is a clear indication of the coupling between the transport of mass and charge. It shows that equations 3.69 to 3.71 are not independent, but coupled through the equation of current continuity.

Considering that the concentrations and concentration gradients of the sodium and chloride ions are much larger than those of the hydrogen and hydroxyl ions, and that there are no chemical or electrochemical sources of hydrogen or hydroxyl, it is assumed that the rate of change of these ions is small compared to the rate of change.
of the electrolyte constituents. That is,

\[ \frac{\partial T_1}{\partial t} \ll \frac{\partial T_2}{\partial t}, \frac{\partial T_3}{\partial t} \]  \hspace{1cm} (3.82)

Then, neglecting \( \partial T_1/\partial t \) in equation 3.81, we have

\[ - \frac{\partial T_2}{\partial t} + \frac{\partial T_3}{\partial t} = 0 \]  \hspace{1cm} (3.83)

or

\[ \nabla \cdot (j_3 - j_4) = 0 \]  \hspace{1cm} (3.84)

and to satisfy electroneutrality \( C_3 \approx C_4 \equiv C \).

Including the definition of the species fluxes and the migration velocities in equation 3.84 leads to, assuming \( \tau = 1 \),

\[ - \nabla \cdot ((v_3 + v_4) F \nabla \phi C) = \nabla \cdot ((D_3 - D_4) \nabla C) \]  \hspace{1cm} (3.85)

which allows determining the electrostatic potential from the electrolyte concentration distribution. Here, \( v_i \) is the mobility of species \( i \), related to the diffusivity through the Nernst-Einstein relationship \( v_i = D_i / RT \).

The electrolyte concentration \( C \) can be determined from the transport equations involving \( C_3 \) or \( C_4 \). For example, using the transport equation for \( C_3 \) (equation 3.70), we have

\[ \frac{\partial C}{\partial t} = \nabla \cdot (v_3 F \nabla \phi C - D_3 \nabla C) \]  \hspace{1cm} (3.86)

Isolating \( \nabla \cdot (F \nabla \phi C) \) from equation 3.85 and including it in this equations yields

\[ \frac{\partial C}{\partial t} = D \nabla^2 C \]  \hspace{1cm} (3.87)

where \( D \) is the apparent diffusivity of the electrolyte, defined by

\[ D = D_3 \left( 1 - \frac{D_3 - D_4}{D_3 + D_4} \right) = \frac{2D_3D_4}{D_3 + D_4} \]  \hspace{1cm} (3.88)
Including the data presented in table 3.2 in this equation results in an apparent diffusivity \( D = 1.611 \times 10^{-9} \text{ m}^2/\text{s}. \)

This result confirms that, through the interaction with the induced electric field, the ionic species in the binary electrolyte behave as a single neutral species diffusing with an apparent diffusivity \( D \). In fact, equation 3.88 is consistent with the more general expression presented in the literature (See e.g. Probststein (1994) [31], Vanýsek (1993) [41]) for calculating the apparent diffusivity of electrolytes from the diffusivities of the ionic constituents. This equation is

\[
D_{\text{salt}} = \frac{(z_+ + |z_-|)D_+D_-}{z_+D_+ + |z_-|D_-} \tag{3.89}
\]

Going back to equation 3.85, it can be seen that in the region spanned by the diffusion front \( (C > 0) \), the electrostatic potential is related to the electrolyte concentration by

\[
\nabla^2 \phi + \nabla \phi \cdot \nabla (\ln C) = -\frac{RT(D_3 - D_4)}{FD(D_3 + D_4)} \frac{\partial}{\partial t} (\ln C) \tag{3.90}
\]

The analytical solution to the electrolyte concentration distribution for the case of an instantaneous line source of strength \( Q \) at \( t = t_0 \), was given in equation 3.77. Rewriting 3.90 in cylindrical coordinates, including the spatial and time derivatives of the electrolyte concentration,

\[
\frac{\partial}{\partial r} (\ln C) = -\frac{2r}{4D(t - t_0)}
\]

\[
\frac{\partial}{\partial t} (\ln C) = \frac{r^2}{4D(t - t_0)^2} - \frac{1}{t - t_0}
\]

in it, and multiplying both sides times \( r \), results in

\[
\frac{\partial \theta}{\partial r} - \frac{2r \theta}{E} = -\frac{RT(D_3 - D_4)}{FD(D_3 + D_4)E(t - t_0)} \left[ r^3 - Er \right] \tag{3.91}
\]

where \( \theta = r \partial \phi / \partial r \) and \( E = 4D(t - t_0) \).
Setting $\theta(0) = 0$, the solution to this differential equation is

$$\theta(r) = \frac{1}{2} AEr^2$$  \hspace{1cm} (3.92)

where

$$A = \frac{RT(D_3 - D_4)}{FD(D_3 + D_4)E(t - t_0)}$$  \hspace{1cm} (3.93)

Finally, integrating with respect to $r$, we get the potential distribution inside the diffusion front ($C > 0$)

$$\phi(r) = \frac{1}{4} AEr^2 + K$$  \hspace{1cm} (3.94)

where $K$ is an arbitrary constant. Outside the diffusion front, all concentrations are uniform, so the potential distribution satisfies Laplace’s equation. In between these, there is a transition region where the two solutions match.

With this result in hand, we can attempt to verify the assumption that the rate of change of $T_1$ is negligible compared to the rate of change of the other conserved quantities (expression 3.82). Recall that

$$\frac{\partial T_1}{\partial t} = -\nabla \cdot (j_1 - j_2) = -\nabla \cdot (-F \nabla \phi(v_1 C_1 + v_2 C_2) - D_1 \nabla C_1 + D_2 \nabla C_2))$$

Finding an analytical solution to this equation requires considerable work due to the nonlinear relationship between the hydrogen concentration $C_1$ and the conserved quantity $T_1$. However, it can be shown with ease that at $t = 0$, when $C_1 = C_2$, the rate of change of $T_1$ is not zero, but given by

$$\frac{\partial T_1}{\partial t} = \frac{(D_1 + D_2)(D_3 - D_4)C_1}{2D_3D_4(t - t_0)} \approx -2 \frac{C_1}{(t - t_0)}$$  \hspace{1cm} (3.95)

The initial rate of change of the other conserved quantities, $T_2$ and $T_3$, can be evaluated from the electrolyte concentration distribution to be

$$\frac{\partial T_2}{\partial t} \approx \frac{\partial T_3}{\partial t} = C \frac{r^2}{(t - t_0)} \left( \frac{r^2}{E} - 1 \right)$$

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so well inside the diffusion front, where \( r \ll \sqrt{E} = 2\sqrt{D(t - t_0)} \),

\[
\frac{\partial T_1}{\partial t} / \frac{\partial T_2}{\partial t} \approx 2C_1/C \ll 1
\]

these results indicate that neglecting \( \partial T_1/\partial t \) in equation 3.81 is a good approximation inside the diffusion region at early times, but that since the rate of change is not strictly zero, a moderate change in pH should be expected.

**Comparison of numerical results and analytical solution**

Since the initial conditions for the numerical simulation correspond to a delta function of strength \( Q = 10^{-3} \text{ mol} \) introduced at \( t_0 = -600 \text{ s} \) and diffusing with a diffusivity \( D = 1.611 \times 10^{-9} \text{ m}^2/\text{s} \), a direct comparison can be made between the numerical results and the analytical solution just presented. This is done in figures 3-14 to 3-16.

Figure 3-14 shows the analytical and numerical electrolyte concentration profiles at \( t = 3600 \text{ s} \). In both cases, the concentration of sodium and chloride ions are approximately equal, so they are shown with the same curve. To demonstrate the sensitivity of the solution to the diffusivity, the analytical concentration profile is plotted for three different cases: diffusion of a neutral species with diffusivity equal to that of the sodium ions (dotted line), diffusion of a neutral species with diffusivity equal to that of the chloride ions (dash-dotted line) and diffusion of the NaCl electrolyte including the effect of the diffusional electric field (thick solid line). The two short vertical lines labeled 1 and 2 indicate the location of the reference nodes used in figure 3-15 to show the time evolution of the concentration profile.

Figure 3-16 presents the electrostatic potential distribution at \( t = 3600 \text{ s} \), predicted by the numerical code, and calculated using equation 3.94. The two are in close agreement in the region of validity of the analytical expression. The numerical solution shows the transition from the parabolic behavior inside the diffusion front to a constant value outside.
Figure 3-14: Comparison of analytical and numerical results at $t=3600$ s for the electrolyte concentration distribution during the simulation of diffusion in the NaCl

Figure 3-15: Time evolution of the numerical results and the analytical solution for the sodium concentration at two different points of the domain during the simulation of diffusion in the NaCl system. (Node 1 corresponds to the point $(0.0264, 0.0249)$ and node 2 corresponds to the point $(0.0277, 0.0238)$)
Figure 3-16: Comparison of analytical and numerical results at \( t=3600 \) s for the electrostatic potential distribution during the simulation of diffusion in the NaCl system

The excellent agreement between the model predictions and the analytical solution as demonstrated in these figures, confirms the accuracy of the numerical implementation and its ability to effectively represent the coupling between the transport of mass and charge.

3.4.2 Transport under an applied electric field

In this case, a fixed potential difference is applied across a single electrode pair in a system containing a dilute NaCl solution and an inert, uncharged soil. In this example, as in the diffusion case, the transport of all chemical species is included in the simulation, and the electroneutrality condition is not imposed \textit{a priori} but expected to result from the calculations. The set of transport equations and equilibrium relationships used was presented in section 3.4. This example involves simulating the transport of all species, the dissociation of water in the interior of the cell and the electrolysis reactions at the electrodes.
<table>
<thead>
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<th>Parameter</th>
<th>Units</th>
<th>Symbol</th>
<th>Values</th>
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<td></td>
<td>0.025</td>
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<tr>
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<td>( \phi_1 )</td>
<td>3.0</td>
</tr>
<tr>
<td>Potential at the cathode well</td>
<td>V</td>
<td>( \phi_2 )</td>
<td>0.0</td>
</tr>
<tr>
<td>Porosity</td>
<td></td>
<td>( n )</td>
<td>1.0</td>
</tr>
<tr>
<td>Tortuosity</td>
<td></td>
<td>( \tau )</td>
<td>1.0</td>
</tr>
<tr>
<td>Soil conductivity</td>
<td>( S/m )</td>
<td>( \sigma_s )</td>
<td>0.0</td>
</tr>
<tr>
<td>Dissociation constant of water</td>
<td></td>
<td>( K_W )</td>
<td>( 10^{-14} )</td>
</tr>
</tbody>
</table>

Table 3.3: Parameters used in the simulation of transport in the NaCl system

The parameters used in the simulation are presented in table 3.3. Initially, the sodium and chloride ions are uniformly distributed at a concentration of 5 mol/m³. The initial pH is 7.

**Numerical solution**

The numerical results for this case are presented in figures 3-17 to 3-20.

Under the action of the applied electric field, the sodium ions migrate toward the cathode and accumulate in and near the cathode reservoir. This is shown in figure 3-17 which presents the sodium concentration distributions at different times during the simulation.

Similarly, the negatively charged chloride ions migrate toward the anode and accumulate in and near the anode reservoir. At the same time, hydrogen ions are produced at the anode, and hydroxyl ions at the cathode by the water electrolysis reactions. These ions also move through the medium under the action of the electric field, but meet at an intermediate region between the electrodes and mutually annihilate to form water.

The rate of production of hydrogen and hydroxyl ions at the electrodes is related to the current by Faraday's law (equation 2.27)

\[
V_w R_i^e = \frac{\nu_{ie}}{F} I
\]

where \( \nu_{ie} \) is the number of moles of species \( i \) produced in the electrochemical reactions
Figure 3-17: Sodium concentration distributions at $t=0$, 1, 3, and 6 hrs during the simulation of transport under an applied electric field in the NaCl system.
Figure 3-18: pH distribution at t=0, 1, 3, and 6 hrs during the simulation of transport under an applied electric field in the NaCl system

per mole of electrons circulated in the external circuit. In this case, it is 1 for both the hydrogen and hydroxyl ions. It can be seen from this relation that the electrochemical reactions represent sources and sinks of charge, and that the rate of electrochemical production of hydrogen and hydroxyl ions is consistent with the electroneutrality condition.

The electric-field-driven transport of all four species, and the chemical transformation of hydrogen and hydroxyl ions into water result in the development of a pH jump in the interior of the cell. This pH jump can be seen in figure 3-18 which shows the calculated pH distribution at different times during the simulation.

At any point in space, the charge differential created by unequal concentrations
Figure 3-19: Relative charge distribution at t=6 hrs in the simulation of transport under an applied electric field in the NaCl system of sodium and chloride is balanced by an equal and opposite differential between the concentrations of hydrogen and hydroxyl ions. This results naturally from the electrostatic potential distribution. Due to numerical round off errors, the net charge of the solution is not exactly zero. However, it can be shown that the net charge is small compared to the concentration differential between sodium and chloride or between hydrogen and hydroxyl ions. That is,

\[ q = C_1 - C_2 + C_3 - C_4 \ll |C_1 - C_2| \text{ or } |C_3 - C_4| \]

This is demonstrated in figure 3-19 which shows that ratio between the net charge \( q \) and the sum of the hydrogen and hydroxyl concentrations in the cell is about \( 10^{-4} \). This is a representative measure because the \( H^+ \) and \( OH^- \) concentrations are constrained by \( C_1C_2 = 10^{-8} \), so the difference between the concentrations is of the same order as the sum. It is a convenient measure because it does not lose its meaning when the pore solution is at a neutral pH.

The pH distribution presented above gives a good indication of the shape of the
Figure 3-20: Electric field distribution in the NaCl system at t=0, 1, 3, and 6 hrs

electric field distribution. The hydrogen and hydroxyl ions are about one order of magnitude more mobile than the other ions, and therefore give the largest contribution to the electrical conductivity of the solution. These ions reach relatively high concentrations at both sides of the pH jump but maintain very low concentrations at the point of neutral pH in the middle of the jump. This results in a sudden decrease in the electrical conductivity of the solution at the location of the pH jump. This effect is accentuated by the accumulation of background ions near the electrodes because the conductivity of the solution at both sides of the pH jump is further increased. This uneven distribution of the electrical conductivity causes the electric field to spike at the location of the pH jump, as illustrated in figure 3-20.

Due to the severe spatial variation of the electric field, and the use of linear basis
functions in the formulation, in this case there was a cumulative error in the mass balance of about 1.8% of the original mass in the system. As will be discussed in the next section, this error is attributed to a loss of precision in the evaluation of the mass fluxes in and out of the electrode reservoirs and to flux discontinuities across element boundaries, brought about by the use of linear basis functions.

In this case, the complex nature of the phenomena prevented obtaining an analytical solution to the transport problem. However, the numerical results are consistent with theoretical and experimental studies carried out on one-dimensional systems dominated by the transport of the background electrolyte (see e.g. Probstein and Hicks (1993) [32], Hicks and Tondorf (1994) [18] or Jacobs et al. (1994) [21]).

3.5 Limitations

The results presented in the previous section demonstrate that the code produces a realistic representation of the contaminant removal processes. However, there are some limitations which affect the accuracy of the model predictions, the most important being the use of linear elements and the inclusion of artificial diffusivity.

The linear basis functions used in the finite element formulation of the problem provide a good estimate of the value of the solution at the nodes, but not of the gradients. This affects the accuracy of the concentration boundary conditions which use the approximated potential, pressure and concentration gradients to calculate the fluxes of the different species into the electrode reservoirs. Also, since the potential and pressure gradients are constant within each element, the total species velocities calculated from equation 2.5,

$$u_i = (k_e + k_{ei}) \nabla \phi + k_h \nabla p$$

are discontinuous across the element boundaries. This is one of the reasons why the fluctuation splitting schemes, which depend on an accurate representation of the element residuals, resulted in an significant loss or accumulation of mass. The effect
on the formulation used in the code is less severe, due to the optimal properties of the finite element method. However, an error in the mass balance is still obtained when comparing the rate of change of the total mass inside the domain with the fluxes through the boundaries. As will be seen below, and in the last part of chapter 4, an inaccurate representation of the boundary layers near the electrode reservoirs is a contributing factor.

Another aspect of the numerical code that affects the accuracy of the solution is the introduction of artificial diffusivity. In most practical cases, the dominant contaminant removal processes are convection and electromigration. Under these conditions, the global concentration distributions predicted by the model are not expected to be significantly affected by the artificial diffusivity. However, some of the model predictions, especially those based on the local conditions at the electrode reservoirs can be affected by an inaccurate representation of the boundary layers. To evaluate the impact of the artificial diffusivity on the solution, a sensitivity analysis to the mesh resolution was performed on a representative transport problem.

Following the formulation and solution procedure presented in the study of the NaCl system, a series of simulations with varying mesh resolution was run on a system conformed of a single electrode pair in an inert soil matrix saturated with a dilute sodium chloride solution. In this case, the development of a normal boundary layer was forced by imposing fixed concentration boundary conditions at the cathode electrode. This is consistent with the washed electrode operating mode, considered to be representative of typical conditions at the field.

In this case, a low pH front develops as hydrogen ions are produced at the anode by the electrolysis reactions, this signal travels through the medium towards the cathode as a result of the applied electric field. At the cathode, a boundary layer develops where the species concentrations accommodate to the boundary conditions imposed. This boundary layer is clearly visible in figure 3-21 which shows the pH distribution at several times during the simulation.
Figure 3-21: Sensitivity to mesh resolution. pH distribution at $t=0$, 2, 6, and 12 hrs during the simulation of transport in a NaCl system with washed cathode
Figure 3-22: Sensitivity to mesh resolution. Total current based on the local conditions at the cathode electrode

Figures 3-22 and 3-23 show the total current based on the local conditions at the cathode and the anode reservoirs calculated using different mesh resolutions. As mentioned above, this variable is very sensitive to the mesh resolution due to its dependence on the species fluxes at the boundary. It can be seen that the total current based on the conditions at the anode, where no boundary layer develops, suffers a much smaller variation with the mesh resolution.

Figure 3-24 shows the current density distribution at $t=12$ hrs, calculated using different mesh resolutions. Note that the current density distribution away from the cathode suffers no significant variation with the mesh resolution.

These results suggest that a way to minimize the effect of the mesh resolution on this variable is to use the current continuity equation to calculate the total current at a certain distance from the electrodes, where the effect of the mesh resolution is small.

Similarly, the effect of the mesh resolution on the global concentration distributions is small. This is shown in figure 3-25 which presents the pH distributions at $t=12$ hrs, for different mesh resolutions. The pH was selected as an indicator of the
Figure 3-23: Sensitivity to mesh resolution. Total current based on the local conditions at the anode electrode

solution because it is a very sensitive variable, and typically is the determinant factor on the chemical speciation of the system. It can be seen in the figure that the general features of the solution do not change significantly between the different cases. This is expected to be the case in most practical applications.
Figure 3-24: Sensitivity to mesh resolution. Current density distribution at $t=12$ hrs for different mesh spacing.
Figure 3-25: Sensitivity to mesh resolution. pH distribution at t=12 hrs for different mesh spacing
3.6 Summary

This chapter presented the numerical code developed to simulate the removal of contaminants from soil by electric fields in two-dimensional geometries.

Different discretization schemes were studied with the aim of providing the best possible approximation to the solution given the constraints in the computational resources available. Contrary to what was initially expected, it was found that the Galerkin finite element formulation provided a better platform for the discretization of the differential equations of the problem than the fluctuation splitting schemes and other upwind techniques typically used in modeling convection dominated flows. A key factor in favor of the Galerkin formulation were that the discrete equations for determining the electrostatic potential distribution resulted in a positive definite matrix solvable with robust, fast, and well established solution methods such as the conjugate gradient iteration. More importantly, the equations resulting from the discretization of the transport equations were compatible with the discrete electrostatic potential equations, allowing the code to successfully model the coupling between the transport of mass and the transport of charge.

Due to the convergence and numerical stability requirements of the Galerkin formulation, it was necessary to introduce artificial diffusivity in order to approximate the solution for cases with high migration or convection velocities. However, since the main features of the solution are dominated by convection and migration, doing this had little effect on the global concentration distributions predicted by the model. Care should be taken, however, when interpreting the model predictions near the electrode reservoirs, since the variables that depend on an estimate of the species fluxes at the boundary are sensitive to the mesh resolution. When required, the quality of the local solution can be improved by reducing the local mesh spacing.

The results from the test cases demonstrated that the numerical code provides a realistic description of the mass transfer processes taking place when a multicomponent system is subject to an applied or induced electric field and illustrated the usefulness of the model in gaining insight on complicated and typically counterintu-
itive phenomena. In the next chapter the scrutiny of the model and its numerical implementation will be taken to a new level with the simulation of a real system and the comparison of the model predictions with experimental data.
Chapter 4

Comparison of model predictions and experimental data

In this chapter, the electrorestoration model presented in chapters 2 and 3 is used to simulate the removal of phenol from kaolin clay in a two-dimensional setup. Three different cases of increasing complexity are considered in the description of the phenol system: a neutral species description which only includes the role of convection and diffusion, a more complex model which adds electromigration and chemical transformations in the pore liquid, and a third representation which incorporates the soil acid/base chemistry. Comparison of the model predictions for these three cases with the experiment data illustrates the role of the different transport mechanisms and chemical processes on the removal of phenol from kaolin clay and tests the ability of the model to provide a realistic description of the relevant phenomena.

4.1 Experimental measurements

This section presents a summary of the experimental procedure followed and the data obtained in the laboratory. A more detailed description is provided in Jacobs(1993) [20].
4.1.1 Experimental setup

The experiment was conducted in a closed rectangular cell 0.28 m long, 0.13 m wide and 0.07 m deep, containing a single anode/cathode pair separated about 0.12 m along the centerline. The electrode reservoirs were made of PVC tubes of about 0.03 m in diameter and 0.15 m in length with a perforated section of about 0.06 m extending into the clay area. Both electrode wells were open at the top to vent the electrolysis gases. Graphite rods used as active electrodes were submerged in the liquid filling the wells.

An array of passive electrodes made of 1/8" stainless steel tube extended about 0.03 m from the top section of the cell in the area between the electrodes to measure the electrostatic potential distribution during the experiment. The passive electrodes were regularly spaced in columns and rows approximately 0.025 m apart from each other. The identification code and specific location of the passive electrodes in the test cell are presented in figure 4-1. In this experiment, the passive electrodes at points C2 and C6 were not installed, so direct measurements of the potential at the walls of the electrode reservoirs are not available. For modeling purposes, the potential at the periphery of the electrode reservoirs was estimated by interpolating the measured data at the surrounding sampling points. This procedure is explained in more detail in section 4.2.

The test cell was filled with a contaminated sample prepared by mixing dry Albion Sperse 100 kaolin clay with a 4.782 mM solution of phenol in distilled water in a weight proportion of 38% of liquid and 62% of clay. The electrode wells were filled with tap water, and a voltage of 40 V was applied to the active electrodes and maintained throughout the experiment. During the experiment, a 10 mM NaOH purge solution was introduced at the anode well while the effluent spilling over a certain level in the cathode well was collected for analysis. A schematic representation of the whole setup is shown in Figure 4-2.

The value of important parameters and the initial conditions of the experiment are summarized in table 4.1.
Figure 4-1: Identification and location of passive electrodes in 2-D test cell

Figure 4-2: Experimental setup
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test cell dimensions</td>
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<td>$0.28 \times 0.13 \times 0.0683$</td>
</tr>
<tr>
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<td></td>
<td>0.62</td>
</tr>
<tr>
<td>Liquid mass fraction</td>
<td></td>
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</tr>
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<td>Dry solid density</td>
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</tr>
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</tr>
<tr>
<td>Pore volume</td>
<td>$m^3$</td>
<td>$1.524 \times 10^{-3}$</td>
</tr>
<tr>
<td>Applied potential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distance between active electrodes</td>
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</tr>
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<td>Phenol concentration in the cell</td>
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<td>4.782</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.1: Initial conditions and important parameters in the phenol removal experiment

### 4.1.2 Electrostatic potential distributions

The electrostatic potential showed moderate changes during the experiment, with the largest variations occurring near the cathode. Figures 4-3 and 4-4 show the maximum, minimum and mean of the electrostatic potential observed at each sampling point. In the figures, the shaded area indicates the region occupied by the clay sample and the nodes of the mesh plots correspond to the passive and active electrodes. In figure 4-4, the mean is indicated by thick lines, and the maximum and minimum values (included for reference) are indicated by dotted lines.

The transient behavior of the potential is better described in terms of its variation along a line. Figure 4-5 shows the initial potential distribution and the maximum and minimum values observed along the line $x = 0.04$ m (column B). The value of the potential at points B1, B4 and B7 throughout the experiment is shown in figure 4-6. Note that changes occurred mainly during the first 18 days of the treatment, with the values gradually leveling off after that. At the end of the experiment, the potential distribution had returned almost to its initial state, as is evidenced in figure 4-7.
Figure 4-3: Maximum and minimum values of the electrostatic potential observed during the experiment.

Figure 4-4: Mean electrostatic potential observed during the experiment. Mean values indicated by thick lines, maximum and minimum values indicated by dotted lines.
Figure 4-5: Observed electrostatic potential along the line $x = 0.04$ m (Column B)

Figure 4-6: Potential at points B1, B4 and B7 during the experiment
Figure 4-7: Potential distribution at the beginning (dotted lines) and end (solid lines) of the experiment
4.1.3 Final pH and concentration distributions

At the end of the experiment, the sample was split in 35 sections arranged in a rectangular array with 5 columns and 7 rows covering the whole test module. The pore liquid was pressed out of each section and split into two samples. The first sample was analyzed for phenol content using high pressure liquid chromatography and the pH of the second sample was measured using pH strips. This analysis was carried out column by column and spanned a period of about 6 days.

The concentration distribution obtained is shown normalized with respect to the initial concentration in figure 4-8. In the figure, the nodes of the mesh plot correspond to the midpoint of each section. Note that very high contaminant removal was achieved in most of the cell, with the largest remaining concentrations being less than 12% of the initial concentration and the average level of removal being about 96%.

The pH measured at the end of the experiment is shown in figure 4-9. The relatively uniform distribution obtained suggests that the buffering capacity of the system was large compared with the amount of hydrogen and hydroxyl ions produced at the electrodes during the experiment. This hypothesis will be confirmed in section 4.4.

4.1.4 Electroosmotic flow rate and contaminant removal

In spite of changes in the electrostatic potential distribution, the electroosmotic flow rate observed throughout the experiment was quite steady, with small variations around an average value of 201.5 ml/day. The concentration of phenol in the effluent increased very quickly and then decayed more or less exponentially with the amount of effluent displaced, as is shown in figure 4-10.
Figure 4-8: Phenol concentration distribution at the end of the experiment, normalized with respect to the initial concentration. The nodes of the plot correspond to the midpoint of each section.

Figure 4-9: pH distribution at the end of the experiment.
Figure 4-10: Concentration of phenol in effluent as a function of pore volumes displaced

The amount of contaminant removed was calculated multiplying the concentration in the effluent times the volume of effluent displaced. Figure 4-11 shows the fraction of contaminant removed as a function of the number of pore volumes displaced. The high correlation between the fraction of contaminant removed and the number of pore volumes displaced suggests that convection is the dominant contaminant removal process in this system. Note that the final level of contaminant removal determined by this method was 80%, which indicates an error of about 16% in the mass balance when compared with the amount of phenol measured at the end of the experiment. This gap is attributed to evaporation losses as well as chemical degradation occurred in both the effluent and the soil samples during the period previous to analysis.
4.2 Neutral species model

4.2.1 Description

In the neutral species model, no charged species are assumed to exist in the system and all chemical transformation and sorption processes are neglected. The electrostatic potential and pressure distributions are determined assuming uniform electrical conductivity and uniform hydraulic and electroosmotic permeabilities.

Governing equations

In this case, the general equation for determining the electrostatic potential distribution described in chapter 2 (equation 2.47)

$$ -\nabla \cdot (\sigma \nabla \phi) = \nabla \cdot \left( F \sum_{i=1}^{N} z_i \frac{D_i}{\tau^2} \nabla C_i \right) $$

reduces to Laplace's equation

$$ \nabla^2 \phi = 0 $$

(4.1)
since there are no charged species and the electrical conductivity is assumed to be uniform. Also, equation 2.54 describing the pressure distribution

$$-\nabla \cdot (k_h \nabla p) = \nabla \cdot (k_e \nabla \phi)$$

has the trivial solution

$$p(x, y) = p_{wells}$$

if both electrode wells are subjected to the same pressure (atmospheric pressure in this case), so the convection velocity can be determined from

$$u_c = k_e \nabla \phi$$

With no chemical transformations, the concentration of phenol is a conserved quantity and the corresponding transport equation for a medium of uniform porosity is

$$\frac{\partial C_{phenol}}{\partial t} + \nabla \cdot j_{phenol} = 0$$

where the molar flux $j_{phenol}$ is only due to convection and diffusion and is expressed by

$$j_{phenol} = u_c C_{phenol} - \frac{D}{\tau^2} \nabla C_{phenol}$$

Model parameters

A complicating factor affecting all the simulations presented in this chapter is that the code was designed to simulate fixed potential conditions at the walls of the electrode reservoirs, while the experiment was run with constant potential at the active electrodes and lacked direct measurements of the potential at the electrode walls. To circumvent this obstacle, the mean effective potential at the boundary of the electrode wells was estimated by interpolating the measured data at the surrounding electrodes. Figure 4-12 shows a finite-element mesh used in the model and a reference mesh whose nodes correspond to the passive electrodes used in the experiment. The effective potential at the reservoirs is calculated by first interpolating the mean
observed potential (shown in figure 4-4) at the intersection of the reference mesh with the electrode wells and then averaging the results.

Figures 4-13 and 4-14 show enlargements of the areas near the electrode reservoirs. The mean values of the measured potential at the sampling points close to the electrode reservoirs are indicated in large font numbers and the interpolated values at the walls are shown in small font numbers. Averaging the interpolated values at the anode reservoir, shown in figure 4-13, results in an effective potential of 35.0 V. Following the same procedure at the cathode reservoir (see figure 4-14) results in an effective potential of 6.2 V or in other words, an effective potential difference of 28.8 V. These are the values used as fixed boundary conditions in the model.

As it was mentioned above, the convection velocity is calculated assuming uniform electroosmotic permeability. Without a description of the ionic environment or the functional dependence of the zeta potential on the concentration distributions, the coefficient of electroosmotic permeability is an empirical parameter selected to match the mean measured flow rate during the experiment. As it is evidenced in figure 4-15,
Figure 4-13: Interpolated potential at the wall of the anode reservoir (small font numbers) based on the mean observed potential at the sampling points (large font numbers).

Figure 4-14: Interpolated potential at the wall of the cathode reservoir (small font numbers) based on the mean observed potential at the sampling points (large font numbers).
Figure 4-15: Measured and calculated flow rates in neutral species model

the flow rate in the experiment was quite steady and could be well represented by a constant electroosmotic permeability coefficient. Also, the uniform pH observed at the end of the experiment suggests that a uniform zeta potential was likely.

The porosity of the medium was calculated in terms of the mass fraction of liquid and the reported densities of the dry clay [3] and water using

$$n = \frac{x \rho_c}{(1 - x) \rho_w + x \rho_c}$$  \hspace{1cm} (4.2)

where $n$ is the porosity, $x$ is the mass fraction of liquid, $\rho_c$ is the density of the dry clay and $\rho_w$ is the density of water. The porosity was 0.6144 and the pore volume of the mixture was 1.524 l.

The tortuosity can be evaluated from one-dimensional conductivity measurements as explained in [38]. In this procedure, the conductivity of a uniform mixture of clay and a known solution, $\sigma_{mix}$, is measured as a function of the conductivity of the pore solution $\sigma_{sol}$ in

$$\sigma_{mix} = n\left(\sigma_{sol}\frac{1}{\tau^2} + \sigma_s\right)$$  \hspace{1cm} (4.3)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Symbol</th>
<th>Values</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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<td>k_h</td>
<td>10^{-15}</td>
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<td>Zeta potential</td>
<td>V</td>
<td>\zeta</td>
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</tr>
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<td>F/m</td>
<td>\epsilon</td>
<td>7.0 × 10^{-10}</td>
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<td>Pore liquid viscosity</td>
<td>Pa s</td>
<td>\mu</td>
<td>10^{-3}</td>
</tr>
<tr>
<td>Effective hydraulic permeability</td>
<td>m^2/(Pa s)</td>
<td>k_h</td>
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<td>Effective electroosmotic permeab.</td>
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<td>k_e</td>
<td>-2.4 × 10^{-9}</td>
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<tr>
<td>Initial concentration in wells</td>
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<tr>
<td>Diffusion coefficient of phenol</td>
<td>m^2/s</td>
<td>D</td>
<td>10^{-9}</td>
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</table>

Table 4.2: Parameters and initial conditions in the neutral species model

The parameter \( n/\tau^2 \) is calculated from the slope of the curve and the value of the tortuosity \( \tau \) isolated using the porosity determined from equation 4.2. The value of 1.25 reported by Shapiro in [38] was used in the simulation.

The hydraulic permeability was determined from permeability measurements to be about 10^{-15} \( m^2 \) [10]. A diffusion coefficient of 10^{-9} \( m^2/s \) was assumed for phenol. A summary of the parameters and initial conditions used in the neutral species simulation is presented in table 4.2.

### 4.2.2 Results

**Electrostatic potential distribution**

The calculated electrostatic potential distribution is presented in figure 4-16. The triangular mesh indicates the calculated potential and the thick-line mesh indicates the average of the measured values at the sampling points. The corresponding electric field strength distribution is shown in figure 4-17. Note that the two-dimensional nature of this system brings about an amplification factor in the electric field strength.
Figure 4-16: Calculated electrostatic potential distribution (triangular mesh) in neutral species model. The thick-line mesh indicates the average values observed at the sampling points.

In one-dimension, the electric field strength corresponding to a 28.8 V potential difference across 0.092 m in a medium of uniform conductivity would be 314 V/m, while the peak electric field strength obtained for the two-dimensional configuration is nearly 455 V/m; that is, an increase of about 45%. This results from the fact that in 1-dimension the current density is constant along the length of the specimen while in this two-dimensional case with cylindrical electrodes the current density must increase near the electrodes.

**Concentration distributions**

The calculated concentration distributions at several times during the experiment are presented in figures 4-18 and 4-19. Figure 4-18 shows contour plots of the calculated concentration distribution at t=0 and after 1, 3, 7, 15 and 33 days of treatment. Note the advancement of the clean front due to convection as the purge solution is introduced into the system and the slower rate of contaminant removal once the purge solution has begun to emerge at the cathode reservoir. This effect is also
Figure 4-17: Calculated electric field strength distribution in the neutral species model apparent in figure 4-19 which shows surface plots of the concentration distribution. The concentration near the corners of the test module decreases at a much slower rate than the concentration in the area between the electrodes where purging is most effective.
Figure 4-18: Calculated concentration distributions at $t = 0, 1, 3, 7, 15$ and $33$ days using the neutral species model
Figure 4-19: Calculated concentration distributions at $t=1$, 3, 15 and 33 days using the neutral species model
Figure 4-20: Comparison of measured concentration of phenol in the effluent and the calculated values using the neutral species model.

Concentration in the effluent and contaminant removal

The concentration of phenol in the effluent calculated using the neutral species model is compared with the measured values in figure 4-20. The model overestimates the concentration of phenol in the effluent during the first five days of the experiment, and after that predicts that it drops slightly faster than observed. However, the general agreement of the model predictions with the experimental data is very good. This agreement is also evident in figure 4-21 which shows the fraction of contaminant removed, calculated by integrating the amount of contaminant leaving the test module in time, as a fraction of the pore volumes displaced. The error accumulated during the first 5 days of experiment is balanced out during the last part of the experiment, bringing the level of contaminant removal very close to the measured values. This close agreement between the model predictions and the experimental data confirms that the phenol system actually behaves as a neutral species system under the conditions of the experiment.
4.2.3 Discussion

This model was not initially expected to provide a realistic representation of the phenol removal experiment described in section 4.1 because it does not include chemical transformations, the effect of other ions on the electric field distribution or the electromigration of charged species. However, the phenol concentration in the effluent and removal rate predicted by this model resulted in close agreement with the experiment. This close agreement between the model predictions and the experimental data confirms that the phenol system actually behaved as a neutral species system under the conditions of the experiment. As will be discussed in section 4.4, this fact is attributed to the high buffering capacity of the clay with respect to the amount of acid and base generated at the electrodes, which contributed to maintaining a uniform pH of about 5.5. Considering that the hydrogen ions carry most of the current, and that the zeta potential depends strongly on the pH of the pore solution, it can be inferred that this uniform pH distribution probably resulted in uniform electrical conductivity and electroosmotic permeability distributions as was assumed in the
calculation. In addition, the pH in the cell remained well below the pKa of phenol, so the contaminant was actually neutral in most of the domain.

4.3 Weak acid model

4.3.1 Description

The neutral species model described in the previous section presented a very effective representation of the phenol system in hand in predicting the location and shape of the cleaned areas and the rate and level of contaminant removal. However, it has two very important limitations: first, it is not general because it does not include important phenomena known to affect and in some cases even dominate the electrorestoration process; and second, it does explain why this phenol system behaves the way it does.

In order to address these issues, a new description of the system was required. The description of the phenol system presented in this section, includes the acid/base reactions of water and phenol in the pore liquid and the water electrolysis reactions at the electrodes. It describes the coupled transport of mass and charge due to convection, electromigration and diffusion and considers the role of the ionic environment and the contribution of diffusion to the current density when determining the electrostatic potential distribution.

The effect of adsorption was not included in this analysis. Laboratory measurements of phenol adsorption on Kaolin-clay indicated a linear adsorption isotherm with slope \( K_d = 0.075 \) (see Shapiro(1990)[38]). This resulted in a retardation factor of 1.075 which was not considered to significatively affect the the phenol concentration distributions or the time scale for removal.

A background electrolyte solution (0.1 \( mM \) NaCl) is included to model salts put into solution when mixing the dry clay and the pore solution. Also, the effect of the 10 \( mM \) NaOH solution introduced at the anode is considered in the simulation.

The pressure distribution, as in the neutral species model, is determined assuming uniform hydraulic and electroosmotic permeability distributions.
<table>
<thead>
<tr>
<th>Metals</th>
<th>Ligands</th>
<th>Species</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>OH⁻</td>
<td>1</td>
<td>H⁺</td>
</tr>
<tr>
<td>Na⁺</td>
<td>A⁻</td>
<td>2</td>
<td>OH⁻</td>
</tr>
<tr>
<td>Cl⁻</td>
<td></td>
<td>3</td>
<td>HA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>A⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>Na⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>Cl⁻</td>
</tr>
</tbody>
</table>

Table 4.3: Chemical species in the weak acid description of the phenol system

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
<th>Conserved Quantity</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>(C_1)</td>
<td>TOT(Charge)</td>
<td>(T_0)</td>
</tr>
<tr>
<td>OH⁻</td>
<td>(C_2)</td>
<td>TOT(Phenol)</td>
<td>(T_1)</td>
</tr>
<tr>
<td>C₆H₅OH</td>
<td>(C_3)</td>
<td>TOT(Na)</td>
<td>(T_2)</td>
</tr>
<tr>
<td>C₆H₅O⁻</td>
<td>(C_4)</td>
<td>TOT(Cl)</td>
<td>(T_3)</td>
</tr>
<tr>
<td>Na⁺</td>
<td>(C_5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>(C_6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Nomenclature used in the weak acid description of the phenol system

The chemical species assumed to exist in this description of the phenol system are presented in table 4.3. In selecting this list of species, it has been assumed that the dissociation of HCl, NaOH and NaCl proceed to completion, and that the amount of sodium-phenol compounds is negligible.

**Governing equations**

The mathematical formulation for this chemical system is very similar to the one presented in example 2.1 (page 37). Based on the nomenclature indicated in table 4.4, the system of equations and unknowns in this case is:

- 6 Unknowns: \(\{C_1, \ldots, C_6\}\)
- 6 Equations:
- 4 conservation equations:

\[
T_0 = C_1 - C_2 - C_4 + C_5 - C_6 \\
T_1 = C_3 + C_4 \\
T_2 = C_5 \\
T_3 = C_6
\]

(4.4)

with \( T_0 = 0 \) and \{T_1, \ldots, T_3\} determined from the transport equations,

- and 2 mass action equations

\[
K_1 = C_1 C_2 \\
K_2 = C_1 C_4 / C_3
\]

(4.5)

The transport equations for the conserved quantities \{T_1, \ldots, T_3\} are:

\[
\frac{\partial T_1}{\partial t} + \nabla \cdot (j_3 + j_4) = 0 \\
\frac{\partial T_2}{\partial t} + \nabla \cdot j_5 = 0 \\
\frac{\partial T_3}{\partial t} + \nabla \cdot j_6 = 0
\]

(4.6)

The individual species concentrations are determined from the conserved quantities by solving the electroneutrality condition

\[
T_0 = C_1 - \frac{K_1}{C_1} - \frac{T_1}{1 + C_1 / K_2} + T_2 - T_3 = 0
\]

(4.7)

for the hydrogen concentration \( C_1 \) and then replacing it in the mass action equations. This equation can be also written in terms of the alkalinity of the solution as

\[
-C_1 + \frac{K_1}{C_1} + \frac{T_1}{1 + C_1 / K_2} = \text{Alk} = T_2 - T_3
\]

(4.8)

It can be seen that if the local alkalinity is much larger than the total amount of phenol \( (T_1) \), the equilibrium hydrogen concentration can be determined from equation 2.62.
<table>
<thead>
<tr>
<th>Species</th>
<th>Name</th>
<th>Mobility $((m \text{ mol})/(N \text{ s}))$</th>
<th>Diffusion coef. $(m^2/s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$^+$</td>
<td>$3.756 \times 10^{-12}$</td>
<td>$9.311 \times 10^{-9}$</td>
</tr>
<tr>
<td>2</td>
<td>OH$^-$</td>
<td>$2.127 \times 10^{-12}$</td>
<td>$5.273 \times 10^{-9}$</td>
</tr>
<tr>
<td>3</td>
<td>C$_6$H$_5$OH</td>
<td>$4.036 \times 10^{-13}$</td>
<td>$1.000 \times 10^{-9}$</td>
</tr>
<tr>
<td>4</td>
<td>C$_6$H$_5$O$^-$</td>
<td>$4.395 \times 10^{-13}$</td>
<td>$1.089 \times 10^{-9}$</td>
</tr>
<tr>
<td>5</td>
<td>Na$^+$</td>
<td>$5.379 \times 10^{-13}$</td>
<td>$1.334 \times 10^{-9}$</td>
</tr>
<tr>
<td>6</td>
<td>Cl$^-$</td>
<td>$8.197 \times 10^{-13}$</td>
<td>$2.032 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Table 4.5: Mobility and diffusion coefficients used in the weak acid description of the phenol system

That is,

$$C_1 = \begin{cases} 
-\text{Alk} & \text{if Alk} < 0 \\
K_1/\text{Alk} & \text{if Alk} > 0 
\end{cases} \quad (4.9)$$

Otherwise, the equilibrium hydrogen concentration is determined by solving equation 4.8.

**Model parameters**

Some of the parameters used in this simulation are the same as in section 4.2. This is the case for the effective potential and pressure at the boundary of the electrode reservoirs, the porosity, tortuosity, hydraulic permeability and the electroosmotic permeability of the medium.

The mobilities of the chemical species are calculated from ion conductivity data published in [41] with the exception of the phenol and phenolate ions for which a mobility of about $4 \times 10^{-13}$ $(mol \text{ m})/(N \text{ s})$ is assumed. The diffusion coefficients are calculated from the mobilities using the Nernst-Einstein relation

$$D_i = \nu_i RT \quad (4.10)$$

The values of the mobility and diffusion coefficients used in the simulation are presented in table 4.5.

A 0.1 $mM$ NaCl solution is included to model the salts dissolved from the soil into the pore liquid and a 1 $mM$ NaCl solution is used to model the initial conditions.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Symbol</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell dimensions</td>
<td>m</td>
<td></td>
<td>$0.28 \times 0.13 \times 0.0683$</td>
</tr>
<tr>
<td>Distance between active electrodes</td>
<td>m</td>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>Diameter of electrode wells</td>
<td>m</td>
<td></td>
<td>0.0283</td>
</tr>
<tr>
<td>Pressure at electrode wells</td>
<td>Pa</td>
<td>${p_1, p_2}$</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Potential at the anode well</td>
<td>V</td>
<td>$\phi_1$</td>
<td>35.0</td>
</tr>
<tr>
<td>Potential at the cathode well</td>
<td>V</td>
<td>$\phi_2$</td>
<td>6.2</td>
</tr>
<tr>
<td>Porosity</td>
<td></td>
<td>$n$</td>
<td>0.6144</td>
</tr>
<tr>
<td>Tortuosity</td>
<td></td>
<td>$\tau$</td>
<td>1.25</td>
</tr>
<tr>
<td>Hydraulic permeability</td>
<td>$m^2$</td>
<td>$k'_h$</td>
<td>$10^{-15}$</td>
</tr>
<tr>
<td>Zeta potential</td>
<td>V</td>
<td>$\zeta$</td>
<td>$-5.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Pore liquid electrical permittivity</td>
<td>$F/m$</td>
<td>$\epsilon$</td>
<td>$7.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>Pore liquid viscosity</td>
<td>$Pa$</td>
<td>$\mu$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Effective hydraulic permeability</td>
<td>$m^2/(Pa \ s)$</td>
<td>$\kappa_h$</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>Effective electroosmotic permeab.</td>
<td>$m^2/(V \ s)$</td>
<td>$\kappa_e$</td>
<td>$-2.4 \times 10^{-9}$</td>
</tr>
<tr>
<td>Soil conductivity</td>
<td>$S/m$</td>
<td>$\sigma_s$</td>
<td>0.001</td>
</tr>
<tr>
<td>Dissociation constant of water</td>
<td></td>
<td>$K_1$</td>
<td>$10^{-14}$</td>
</tr>
<tr>
<td>Dissociation constant of phenol</td>
<td></td>
<td>$K_2$</td>
<td>$1.28 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Table 4.6: Parameters used in the weak acid description of the phenol system at the electrode reservoirs.

A summary of the parameters and initial conditions used in the simulation is presented in tables 4.6 and 4.7.

### 4.3.2 Results

The new phenomena included in this description of the phenol system greatly increase the amount of information available about the transient response of the system, and as it can be expected, also increase the complexity of the results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Symbol</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentrations in test cell</td>
<td>$mol/m^3$</td>
<td>$T_1$</td>
<td>4.782</td>
</tr>
<tr>
<td>TOTAL(phenol)</td>
<td></td>
<td>$T_1$</td>
<td>4.782</td>
</tr>
<tr>
<td>TOTAL(Na)</td>
<td></td>
<td>$T_2$</td>
<td>0.1</td>
</tr>
<tr>
<td>TOTAL(Cl)</td>
<td></td>
<td>$T_3$</td>
<td>0.1</td>
</tr>
<tr>
<td>Initial concentrations in the wells</td>
<td>$mol/m^3$</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>TOTAL(phenol)</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>TOTAL(Na)</td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>TOTAL(Cl)</td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 4.7: Initial conditions in the weak acid description of the phenol system
**pH distribution**

The electrolysis reactions occurring at the electrodes together with the transport of the background ions Na\(^+\) and Cl\(^-\) play a major role in the response of the system. As time progresses, the sodium ions originally present in the system and those introduced in the purge solution migrate toward the cathode and accumulate in and near the cathode reservoir. This accumulation occurs because the electromigration flux of the sodium ions into the cathode reservoir is initially one to two orders of magnitude larger than the convective flux out of the cathode reservoir and into the effluent collector. At the same time, hydroxyl ions are produced at the cathode electrode by the water electrolysis reaction and migrate toward the anode. Eventually, the concentration of sodium ions in the cathode reservoir reaches a steady state value at which the net flux into the reservoir equals the discharge rate in the effluent. The concentration of hydroxyl ions also reaches a steady state at which the generation rate at the electrode equals the transport of these ions toward the anode.

The excess charge of the sodium ions over the chloride ions is balanced mainly by the hydroxyl ions and in a lower proportion by the phenolate ions. Recall that the transport of mass and the transport of charge are coupled through the condition of electroneutrality, so at any point in space, the concentrations resulting from the transport are such as to maintain a neutral solution. This coupling, as it was mentioned in chapters 2 and 3, is in the core of the electrostatic potential calculation.

Figure 4-22 shows the calculated concentration distribution of sodium at different times during the simulation. The high concentrations near the anode well result from the introduction of the 10 \(mM\) NaOH purge solution.

A similar scenario occurs near the anode electrode. The negatively charged chloride ions initially present in the system migrate toward the anode well at a faster rate than the convection flow from anode to cathode and accumulate in and near the anode reservoir. Meanwhile, hydrogen ions are produced at the anode by electrolysis and migrate toward the cathode. At an intermediate region between the electrodes, the hydrogen and hydroxyl ions meet to form water.
Figure 4-22: Calculated Na concentration distributions at $t = 0$, 6 hrs, 1 day and 3 days using the weak acid model
Figure 4-23: Calculated pH distribution at t = 0, 6 hrs, 1 day and 3 days using the weak acid model

The transport of ions in this way and the chemical transformation of hydrogen and hydroxyl ions into water result in the development of a pH jump in the interior of the cell. This pH jump can be seen in figure 4-23 which shows the calculated pH distribution at different times during the simulation.

**Electrostatic potential distribution**

The pH distribution presented in the previous section, as well as the accumulation of the background ions near the electrodes have a dramatic effect on the electrostatic potential distribution. The hydrogen and hydroxyl ions are about one order of magnitude more mobile than the other ions, and therefore give the largest contribution
to the electrical conductivity of the solution. Note that in most of the domain the concentration of sodium approximates the concentration of hydroxyl ions and the concentration of chloride approximates the concentration of hydrogen ions. The hydrogen and hydroxyl ions reach relatively high concentrations at both sides of the pH jump but maintain very low concentrations at the point of neutral pH in the middle of the jump. This results in a sudden decrease in the electrical conductivity of the solution at the location of the pH jump. This effect is accentuated by the accumulation of background ions near the electrodes because the conductivity of the solution at both sides of the pH jump is further increased. This is illustrated in figure 4-24 which shows the calculated electrical conductivity distribution at several times during the simulation.

The uneven distribution of the electrical conductivity is the major factor affecting the electrostatic potential distribution. As can be seen in figures 4-25 and 4-26 the electric field reaches very high values at the location of the pH jump and becomes very weak everywhere else as time progresses.

**Phenol concentration distribution**

The dissociation state of phenol, that is, the fraction of phenol in charged form, can be readily calculated by including the mass action equation of phenol in the corresponding conservation equation to get

\[
x = \frac{\text{phenolate}}{\text{total phenol}} = \frac{C_4}{T_1} = \frac{1}{1 + 10^{(pK_a - pH)}}
\]

where \( pK_a = -log(K_2) \). It can be seen from this equation that the pH has a large effect on the transport of phenol in the system. At the high pH side of the pH jump the pH is larger than the pKa, so a significant fraction of phenol is dissociated into the negatively charged phenolate ion and migrates from cathode to anode. On the other hand, at the low pH side of the jump the pH is much smaller than the pKa and virtually all phenol is neutral and moves with the pore liquid from anode to cathode. This effect prevents the phenol from being removed from the cell but results in the
Figure 4-24: Calculated electrical conductivity distribution at t = 0, 6 hrs, 1 day and 3 days using the weak acid model
Figure 4-25: Calculated electrostatic potential distribution at t= 0, 6 hrs, 1 day and 3 days using the weak acid model.
Figure 4-26: Calculated electric field distribution at $t=0$, 6 hrs, 1 day and 3 days using the weak acid model
accumulation of the contaminant in a narrow band of the soil at the location of the pH jump.

In studying this effect it is useful to determine the effective velocity of phenol. This velocity includes the effect of chemical transformations on the net transport of a conserved quantity, and in general can be determined from

$$u_{eff}^k = \frac{\sum_{i=1}^N \nu_{i,k} u_i C_i}{\sum_{i=1}^N \nu_{i,k} C_i}$$  \hspace{1cm} (4.12)

In the phenol system case, the effective velocity can be determined from

$$u_{eff} = \frac{u_3 C_3 + u_4 C_4}{T_1}$$  \hspace{1cm} (4.13)

or, in terms of the dissociation parameter $x$

$$u_{eff} = (1 - x) u_3 + x u_4$$  \hspace{1cm} (4.14)

A convenient way to compare the relative strengths of convection and migration in the transport of phenol is to determine a relative speed defined by

$$u_{rel} = \frac{u_{eff} \cdot \hat{u}_c}{|u_c|}$$  \hspace{1cm} (4.15)

where $\hat{u}_c$ is a unit vector in the direction of the convection velocity. A relative speed close to 1 indicates that convection dominates the transport, a relative speed larger than 2 indicates that migration dominates the transport and occurs in the same direction as convection, and a relative speed less than zero indicates that migration dominates the transport and acts opposite to the convection velocity. The relative speed calculated by the weak acid model at different times during the simulation is presented in figure 4-27. At $t=0$, the relative velocity is close to one in the entire domain indicating that the phenol is in neutral form and its transport is dominated by convection. At $t=6$ hrs, the focusing effect is in progress, with the phenol moving in the direction of the flow in the low pH region close to the anode and opposite to
Figure 4-27: Relative magnitude of the effective phenol velocity with respect to the convection velocity in the weak acid simulation of the phenol system.

The flow in the high pH region close to the cathode. At t=1 and 3 days the dominance of migration is readily apparent. The relative speed is negative all over the domain and reaches values at low as -17, indicating that phenol moves opposite to the flow at a speed that can be up to 17 times larger than the convection velocity.

The impact of this phenomenon is illustrated in figure 4-28, which shows the concentration distribution of phenol at several times during the simulation. As was mentioned before, the contaminant accumulates in a narrow band at the location of the pH jump.

This focusing effect was described in the setting of one-dimensional metal removal experiments by Probsttein and Hicks (1993) [32]. Details of the experimental procedure.
Figure 4-28: Calculated phenol distribution at $t = 0$, 6 hrs, 1 day and 3 days using the weak acid model
and further analysis of the phenomenon were presented by Hicks and Tondorf in [18]. The process has been successfully reproduced with a mathematical model by Jacobs et al. [21]. In the metal removal case, the focusing effect involved metal species migrating in converging directions at each side of the pH jump and precipitating just at the point of minimum solubility inside the pH jump. In this case, the phenomenon is shown to occur without the participation of precipitation reactions.

4.3.3 Discussion

This description of the phenol system predicted very interesting phenomena such as the development of the pH shock and the consequent development of a high localized electric field and focusing of the contaminant in a narrow band. These phenomena are likely to occur in a system in which the buffer capacity is small compared to the acid and base generated at the electrodes. The experimental data, however, did not show the development of a pH jump but a uniform pH distribution, and the observed potential distribution was smooth, without the sudden changes observable in the model calculations. This discrepancy between the model predictions and the experimental data suggests that the buffer capacity of the system was not small compared with the acid and base generated at the electrodes, and that an important element was left out in the description of the phenol system.

The buffer capacity of the system is a measure of its resistance to change the pH after the addition of strong acids or bases. It is affected by the amount of weak acid and bases present which would react with the added hydrogen or hydroxyl ions and prevent their accumulation. In the weak acid description of the system, the buffer capacity was determined only by the amount of phenol present at a specific point, not including any acid/base reactions occurring at the surface of the clay particles. This, as will be discussed in the next section, seemed to be the missing piece in the puzzle.
4.4 Weak acid + soil chemistry model

4.4.1 Description

From the results presented in the previous section, it was clear that the description of the phenol system had to be upgraded to include at least the acid/base characteristics of the soil. The important role that the kaolin clay used in the experiments played in the acid/base chemistry of the system was identified and characterized by Dzenitis in [11].

In this section, Dzenitis' acid/base characterization of the clay used in the experiments is incorporated into the weak acid model to provide a more complete description of the phenol system. This soil chemistry model is not intended to provide an accurate representation of all the physical and chemical processes taking place at the soil surface. Instead, it aims at capturing the effect of those processes on the acid/base chemistry of the system. A detailed description of kaolinite chemistry can be found in Grim (1968) [12]. It is important to note, though, that the ion exchange capacity and the titration data observed at a particular case are very dependent on factors such as the presence of impurities, the particle size distribution and the degree of crystallinity. It is because of this that the use of direct measurements on the soil of interest may not be avoided even in relatively simple cases.

The acid/base chemistry of kaolin clay is represented here in terms of a combination of immobile weak acids and bases. The total amount of these compounds, and the equilibrium constants associated with their acid/base reactions are selected to fit measured acid/base titration data. This is a likely approach in engineering applications due to the complexity of natural soils. The clay particles are assumed to consist of an amphiprotic compound HL representing the edge sites and a weak acid HE representing the face behavior. This description is consistent with some generally accepted characteristics of kaolinite such as having amphoteric edge surface sites and a typically negative face surface charge (see e.g. Zhou and Gunter (1992) [45], Williams and Williams (1978) [44]). The titrations were carried out under constant and varying ionic strength conditions. The results from the two sets of titration data
<table>
<thead>
<tr>
<th>Metals</th>
<th>Ligands</th>
<th>Species</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>OH⁻</td>
<td>1</td>
<td>H⁺</td>
</tr>
<tr>
<td>Na⁺</td>
<td>A⁻</td>
<td>2</td>
<td>OH⁻</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>L⁻</td>
<td>3</td>
<td>HA</td>
</tr>
<tr>
<td>E⁻</td>
<td></td>
<td>4</td>
<td>A⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>Na⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>Cl⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>H₂L⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>HL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>L⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>HE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11</td>
<td>E⁻</td>
</tr>
</tbody>
</table>

Table 4.8: Chemical species in the weak acid + soil chemistry description of the phenol system

were similar except in the small alkalinity range. However, the effect of ionic strength is not explicitly modeled, and the curve fit corresponding to a fixed ionic strength of 100 eq/m³ is used here.

Incorporating this characterization of the acid/base chemistry of kaolin clay into the weak acid description of the phenol system implies including 5 new species:

- 3 species corresponding to the amphiprotic compound: H₂L⁺, HL, and L⁻, and
- 2 species associated with the weak acid: HE and E⁻

The chemical description of the system will now include 11 species as presented in table 4.8.

**Governing equations**

Two new conserved quantities and three new mass conservation equations are added to the set of equations described in section 4.3. Since the new species are immobile, no new transport equations are required.

The nomenclature used in this description of the system is presented in table 4.9. Based on this nomenclature, the system of equations and unknowns in this case is

- 11 Unknowns: \( \{C_1, \ldots, C_{11}\} \)

- 11 Equations:
\begin{table}
\centering
\begin{tabular}{|l|c|c|c|}
\hline
Species & Concentration & Conserved Quantity & Symbol \\
\hline
H\(^+\) & \(C_1\) & TOT(Charge) & \(T_0\) \\
OH\(^-\) & \(C_2\) & TOT(Phenol) & \(T_1\) \\
C\(_6\)H\(_5\)OH & \(C_3\) & TOT(Na) & \(T_2\) \\
C\(_6\)H\(_5\)O\(^-\) & \(C_4\) & TOT(Cl) & \(T_3\) \\
Na\(^+\) & \(C_5\) & TOT(L) & \(T_4\) \\
Cl\(^-\) & \(C_6\) & TOT(E) & \(T_5\) \\
H\(_2\)L\(^+\) & \(C_7\) & & \\
HL & \(C_8\) & & \\
L\(^-\) & \(C_9\) & & \\
HE & \(C_{10}\) & & \\
E\(^-\) & \(C_{11}\) & & \\
\hline
\end{tabular}
\caption{Nomenclature used in the weak acid + soil chemistry description of the phenol system}
\end{table}

- 6 conservation equations:

\[
\begin{align*}
T_0 &= C_1 - C_2 - C_4 + C_5 - C_6 + C_7 - C_9 - C_{11} \\
T_1 &= C_3 + C_4 \\
T_2 &= C_5 \\
T_3 &= C_6 \\
T_4 &= C_7 + C_8 + C_9 \\
T_5 &= C_{10} + C_{11}
\end{align*}
\tag{4.16}
\]

with \(T_0 = 0\), \(\{T_1, \ldots, T_3\}\) determined from the transport equations and \(\{T_4, T_5\}\) fixed by the characterization of the clay's acid/base chemistry,

- and 5 mass action equations

\[
\begin{align*}
K_1 &= C_1C_2 & K_2 &= C_1C_4/C_3 \\
K_3 &= C_1C_8/C_7 & K_4 &= C_1C_9/C_8 & K_5 &= C_1C_{11}/C_{10}
\end{align*}
\tag{4.17}
\]

where the transport equations for the conserved quantities \(\{T_1, \ldots, T_3\}\) are the same.
as in the weak acid case

\[
\frac{\partial T_1}{\partial t} + \nabla \cdot (j_3 + j_4) = 0 \\
\frac{\partial T_2}{\partial t} + \nabla \cdot j_5 = 0 \\
\frac{\partial T_3}{\partial t} + \nabla \cdot j_6 = 0
\]

In this case, the chemical equilibrium calculation is a little more complex. The equilibrium hydrogen concentration \( C_1 \) is determined by solving

\[
-C_1 + \frac{K_1}{C_1} + \frac{T_1}{1 + C_1/K_2} - \frac{T_4}{1 + K_3/C_1 + K_3K_4/C_1^2} + \frac{T_4}{1 - C_1/K_3 + K_4/C_1} + \frac{T_5}{1 + C_1/K_5} = \text{Alk} \tag{4.18}
\]

where \( \text{Alk} = T_2 - T_3 \). Then, the concentration of the other species are determined by including the equilibrium hydrogen concentration in the conservation and mass action equations.

**Model parameters**

Most of the model parameters used in this case are the same as in section 4.3. The new parameters required in this case are the total amount of the amphiprotic compound and weak acid describing the acid/base chemistry of the clay and the corresponding equilibrium constants. These values are indicated in table 4.10. The total site concentrations are normalized with respect to the volume of liquid in a mixture of 1.5 kg solid per liter of liquid. The Total(L) concentration corresponds to a density of about \( 10^{19} \) sites/m\(^2\) edge, with an edge area of 0.14 m\(^2\) per m\(^2\) of total area and an area density of \( 10^4 \) m\(^2\) total area per kilogram of solid. All these values are typical of kaolinite (see *e.g.* Zhou and Gunter (1992) [45], Williams and Williams (1978) [44]). Using the conversion factor of 15 eq/m\(^3\) liquid for 1 meq/100g solid for this mixture, the observed exchange capacity of the clay (about 4 meq/100g solid) falls within the range of 3 to 15 meq/100g solid reported in Grim (1978) [12].
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Symbol</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation constant of $H_2L$</td>
<td>$K_3$</td>
<td></td>
<td>$2.897 \times 10^{-5}$</td>
</tr>
<tr>
<td>Dissociation constant of HL</td>
<td>$K_4$</td>
<td></td>
<td>$2.178 \times 10^{-6}$</td>
</tr>
<tr>
<td>Dissociation constant of HE</td>
<td>$K_5$</td>
<td></td>
<td>$3.311 \times 10^{-3}$</td>
</tr>
<tr>
<td>Total(L)</td>
<td>$mol/m^3$ (liquid)</td>
<td>$T_4$</td>
<td>33.037</td>
</tr>
<tr>
<td>Total(E)</td>
<td>$mol/m^3$ (liquid)</td>
<td>$T_5$</td>
<td>25.119</td>
</tr>
</tbody>
</table>

Table 4.10: Parameters used in the soil chemistry description of the phenol system. (These parameters are additional to those indicated in table 4.6)

### 4.4.2 Results

**pH distribution**

The role of the clay's acid/base chemistry on the pH response of the system is clearly illustrated by comparing the calculated pH distribution presented in section 4.3 (figure 4-23) with the pH distribution presented in figure 4-29 which includes the buffering effects of the soil. In the latter case, no pH jump develops inside the cell. Instead, the pH distribution remains almost uniform in the cell, with changes only occurring in the electrode reservoirs. This result suggests that the buffering capacity of the system is indeed large compared to the acid and base generated at the electrodes.

To better understand this effect, it is convenient to perform a numerical titration of the chemical system and note the change in the dissociation state of the soil compounds as the alkalinity is varied. The results from such a titration are presented in figures 4-30 to 4-32.

Figure 4-30 shows the calculated equilibrium pH as a function of the alkalinity for a 4.78 $mM$ solution of phenol and no clay (dotted line) and a mixture of clay and the same phenol solution in a mass ratio of 40% liquid and 60% clay (solid line) based on Dzenitis' characterization of the clay's acid/base chemistry. The effect of the clay is clearly represented in the departure of the mixture's behavior from that of the solution alone.

The buffering effect of the soil is illustrated in figures 4-31 and 4-32. At zero alkalinity, the weak acid compound is mostly dissociated into the E form. As acid is
Figure 4-29: pH distribution at t = 0, 1, 5 and 10 days calculated using the weak acid + soil chemistry description of the system
Figure 4-30: Calculated equilibrium pH as a function of alkalinity for a 4.78 mM phenol solution alone (dotted line) versus a mixture of kaolin clay and a 4.78 mM phenol solution in a 1.5:1 solid to liquid mass ratio (solid line).

added to the system, the E-sites take hydrogen ions according to

$$
E^- + H^+ \rightarrow HE
$$

thus buffering the decrease in pH. Similarly, as base is added to the system, the amphiprotic compound $H_2L^+$ dissociates into the $HL$ and $L^-$ forms, releasing hydrogen ions which slow the accumulation of hydroxyl ions and thus buffer the increase in pH.

Electrostatic potential distribution

As it was mentioned in section 4.3 the pH distribution has a major effect on both the electrostatic potential distribution (through its relationship with the electrical conductivity of the solution) and the dissociation state of phenol. Thus, the calculated pH distribution translates into a relatively uniform electrical conductivity distribution in the interior of the cell and a much higher conductivity at the electrode reservoirs, especially the cathode's. As a consequence, the electric field strength in the prox-
Figure 4-31: Calculated concentrations of the weak acid compounds representing the clay’s face sites as a function of alkalinity

Figure 4-32: Calculated concentration of the amphiprotic compounds representing the clay’s edge sites as a function of alkalinity
Figure 4-33: Calculated conductivity, electrostatic potential and electric field distributions at $t=10$ days produced by the weak acid + soil chemistry description of the system

Imity of the electrode reservoirs is very low. This is illustrated in figure 4-33 which shows the calculated potential, conductivity and electric field strength distributions at $t=10$ days. Because of the low electric field strength, the relative contribution of convection to the species flux is more important in the immediate vicinity of the electrode reservoirs.

**Phenol concentration distribution**

Figure 4-34 shows the calculated phenol concentration distributions obtained for this case. As can be expected from the previous discussion, these distributions are very similar to the ones presented in figure 4-18 for the neutral species case. In most of
the test module the pH is well below the pKa of phenol, so the contaminant remains
in its neutral form and moves with the pore liquid. In this case, however, a very
interesting phenomenon is shown to occur near the cathode. As the pH increases in
the cathode reservoir, the phenol transforms into the negatively charged phenolate
form and migrates upstream toward the anode. It soon reaches the low pH region
of the soil, transforms back into the neutral form and resumes its travel toward the
cathode. This process results in the rejection and subsequent accumulation of phenol
at the interface between the soil and the electrode well where the pH change occurs.
This accumulation can be observed in figure 4-34 in the concentration distributions
at t=6 hrs, 1 day and 3 days.

At the same time, the accumulation of sodium and hydroxyl ions in the cathode
reservoir results in the increase of the electrical conductivity and the reduction of the
local electric field strength, so as time progresses, convection becomes more important
near the cathode and the focusing effect weakens.

Eventually, a quasi-equilibrium condition is reached in which the upstream mi-
grational flux of the phenolate ions is balanced by the net favorable diffusional flux
of phenol into the reservoir. At this point, accumulation of phenol stops and the
convective flux at the low pH side of the region appears to go through the pH jump
unaffected. At later times, convection becomes dominant near the cathode reservoir
and the neutral species behavior is recovered. This transition can be observed in the
predicted concentration distributions at t=3, 5 and 10 days.

The phenomenon thus described would explain the close agreement between the
model predictions for the neutral species case and the observed phenol concentrations
in the effluent. Unfortunately, there is not enough experimental data at the time to
either confirm or disprove its occurrence.

The phenomenon also highlights an important limitation of the numerical code.
As it was discussed in chapter 3, the aim of the code is to produce the best possible
approximation to the global solution of the transport problem, subject to given con-
straints in mesh resolution, even when the inner solution of the boundary layers is
not resolved. In order to accomplish this, artificial isotropic diffusivity is introduced
Figure 4-34: Calculated phenol concentration distributions at different times during the 10-day simulation period, obtained using the weak acid + soil chemistry description of the system.
which, in effect, thickens the boundary layers to make them fit in one computational element. As a result, when thin boundary layers develop in the solution, the code produces inaccurate descriptions of the concentration gradients at the boundary. This, while minimally affecting the solution outside of the boundary layer, may have a significant effect on the local solution.

In this case, this limitation is reflected in the predicted phenol concentrations in the effluent. It can be seen in figure 4-35 that although the model predicts the right behavior (i.e. sudden increase, short plateau, then slow decrease) of the phenol concentration in the effluent, it fails to reproduce the experimental observations. Another factor influencing these results is the severe strain imposed on the code by the sudden change of soil properties at the boundary. In this case, the system has a large buffering capacity (due to the clay) on the soil side of the reservoir wall and a negligible buffering capacity inside the reservoir. As a result, the pH change and all the processes described above occur over one single layer of computational elements. These elements, being linear, cannot appropriately accommodate to the conditions at both sides and cause an increased error.

Another parameter that can be affected by the inaccurate concentration gradients at the boundary is the total current. In this case, the total current calculated at the cathode reservoir wall differed from the experimental observations. However, the total current calculated at the anode, where no thin boundary layers developed, showed very good agreement with the experiment. This is shown in figure 4-36. This problem can be overcome by using the fact that $\nabla \cdot i = 0$ to calculate the total current at a safe distance from the boundary where the contribution of diffusion to the current density is typically small.

As more computational resources are available, the magnitude of these errors can be reduced by increasing the mesh resolution.
Figure 4-35: Comparison of measured concentration of phenol in the effluent and the calculated values using the weak acid + soil chemistry model.

Figure 4-36: Comparison of measured and calculated current using the data at the anode reservoir.
4.5 Summary

In this chapter, the experimental data obtained in the removal of phenol from kaolin clay was compared with model predictions for three different cases: one that only included convection and diffusion of phenol, identified as "neutral species"; one in which electromigration and chemical transformations in the pore liquid were considered, denoted "weak acid"; and a third which incorporated the soil acid/base chemistry, denoted "weak acid + soil chemistry".

The neutral species case produced very good agreement with the observed concentrations of phenol in the effluent and the overall level and rate of contaminant removal. This close agreement between the model predictions and the experimental data confirmed that the phenol system actually behaved as a neutral species system under the conditions of the experiment. However, more sophisticated descriptions were necessary to explain these results.

In the next step, the acid/base reactions of water and phenol in the pore liquid and the water electrolysis reactions at the electrodes were included. Also, the new model described the coupled transport of mass and charge due to convection, electromigration and diffusion and considered the role of the ionic environment and the contribution of diffusion to the current density when determining the electrostatic potential distribution. This description of the phenol system predicted very interesting phenomena such as the development of the pH shock and the consequent development of a high localized electric field and focusing of the contaminant in a narrow band. These phenomena are likely to occur in a system in which the buffer capacity is small compared to the acid and base generated at the electrodes. The experimental data, however, did not show the development of a pH jump but a uniform pH distribution, and the observed potential distribution was smooth, without the sudden changes observable in the model calculations. This discrepancy between the model predictions and the experimental data suggested that the buffer capacity of the system was not small compared with the acid and base generated at the electrodes, and that an important element was left out in the description of the phenol system.
The answer to the problem materialized when the acid/base chemistry of the kaolin clay was added to the model. This provided a more complete description of the system and confirmed that the buffer capacity was indeed large relative to the electrochemical acid/base generation. This third description explained the neutral species behavior observed in the experiment, and indicated that a solute rejection process similar to that occurring in membranes probably took place in the vicinity of the cathode reservoir at some time during electrorestoration process.

The successful explanation of the experimental observations in terms of the modeled transport and chemical processes confirmed the theoretical arguments behind the model.

The complex phenomena occurring near the cathode electrode also highlighted some of the limitations of the numerical code. The most important is that while the code provides a realistic description of the contaminant removal processes and a good approximation of the global concentration distributions during the electrorestoration process, care should be taken in interpreting results near the electrode reservoirs where the local solution can be affected by inadequate mesh resolution.
Chapter 5

Conclusions and future work

This work presented the mathematical model and numerical code developed to simulate the removal of contaminants from soils by electric fields in two-dimensional geometries. The model describes the coupled transport of mass and charge as well as the chemical speciation of a multicomponent system subject to an electric field. The transport mechanisms considered are electroosmosis, pressure-driven convection, electromigration and diffusion. The model can also describe homogeneous chemical reactions in the bulk fluid, heterogeneous reactions and sorption processes, and electrochemical reactions.

The chemical reactions and sorption processes were assumed to be fast compared with the transport processes, so chemical and adsorption equilibria were assumed. The solution procedure was based on the use of conserved quantities which remain constant during chemical reactions and sorption processes. This allowed replacing the individual species transport equations, with transport equations based on the conserved quantities and a set of chemical equilibrium relationships. The resulting system of differential and algebraic equations was much more amenable to numerical integration since the reaction terms canceled out and only the time scale of the transport processes needed to be resolved.

Another benefit of the conserved quantities approach and of the explicit time integration of the transport equations was the effective decoupling between the transport and the chemical equilibrium calculations. This allowed handling the chemical and
sorption equilibrium as a separate module or functional unit within the main electrorestoration program. As a result, different chemical systems can be described with minimum change to the numerical code; the customized models of the chemical systems can be easily verified by comparing them with standard equilibrium programs; and even commercial equilibrium programs can be used as part of the electrorestoration code.

Different discretization schemes were studied with the aim of providing the best possible approximation to the solution given the constraints in the computational resources available. Contrary to was initially expected, it was found that the Galerkin finite element formulation provided a better platform for the discretization of the differential equations of the problem than the fluctuation splitting schemes and other upwind techniques typically used in modeling convection-dominated flows. The key factors in favor of the Galerkin formulation were that the discrete equations for determining the electrostatic potential distribution resulted in a positive definite matrix solvable with robust, fast, and well established solution methods such as the conjugate gradient iteration; and more importantly, that the equations resulting from the discretization of the transport equations were compatible with the discrete electrostatic potential equations, allowing the code to successfully model the coupling between the transport of mass and the transport of charge.

Due to the convergence and numerical stability requirements of the Galerkin formulation, it was necessary to introduce artificial diffusivity in order to approximate the solution in cases with high migration or convection velocities. However, since the main features of the solution are dominated by convection and migration, doing this had little effect on the global concentration distributions predicted by the model. Care should be taken when interpreting the model predictions near the electrode reservoirs, since the variables that depend on an estimate of the species fluxes at the boundary are very sensitive to the mesh resolution. When required, the quality of the local solution can be improved by reducing the local mesh spacing. This suggests that using adaptive meshing techniques can significantly improve the solution without increasing the computational costs of the simulation.
It was determined that a crucial parameter to evaluate when assessing the treatability of a site by electric fields is the value of the system buffer capacity relative to the expected acid/base generation at the electrodes. This parameter can be estimated from the ratio between the ionic strength of the background or indifferent electrolytes and the change in charge allowable by the acid/base transformation of the weak acids and bases and the minerals in the system. In systems with a small relative buffer capacity, the pH and electrostatic potential responses are greatly influenced by the transport of the background electrolytes. The response in such systems is very similar to the response of a binary electrolyte (see chapters 3 and 4). On the other hand, in systems with a large relative buffer capacity, the pH remains relatively uniform and the potential suffers little variation in the time scale of the contaminant removal.

During the simulation of the removal of phenol from kaolin clay, it was found that under certain conditions a focusing effect similar that described by Probstein and Hicks [32] for metals removal can occur when removing weak acids (even soluble, weakly dissociated compounds) from soils by electroosmotic purging. If the pH rises above a certain level at an intermediate region between the electrodes, a significant fraction of the contaminant can be dissociated into a negatively charged form. Since the migration velocities are much larger than the convection velocities in typical electrorestoration applications, a small fraction of the negatively charged form of the contaminant can offset any convection flux towards the cathode. Under these conditions, the contaminant is not removed from the soil but accumulates at the region of pH change. The critical value of the pH at which this phenomenon occurs depends on the mobility of the charged species, the pKa of the contaminant and the magnitude of the convection velocity.

This result suggests an alternative strategy for the removal of soluble weak acids from soils by electric fields in cases where the buffer capacity of the system is small or comparable to the acid/base generation at the electrodes. Instead of relying on electroosmotically purging the undissociated form of the contaminant, the dissociation reaction could be enhanced by imposing basic conditions on the soil. This could be done, for example, by washing or conditioning the anode electrode. Establishing a
pH higher than the pKa of the contaminant would cause a significant fraction to be in the negatively charged form. This species would migrate towards the anode at a typically much faster velocity than the convection velocity, resulting in a faster removal process.

The numerical simulation of the phenol removal experiment also showed that the clay acid/base chemistry was a determinant factor for the successful removal of phenol in the experiment. The high buffer capacity of the clay relative to the acid/base generation at the electrodes prevented the development of a pH jump in the interior of the test module. This inhibited the accumulation of the contaminant in the interior of the cell. This result highlights the important role that the soil chemistry may play in the electrorestoration process.

The results from the test cases and the successful explanation of the experimental observations in terms of the modeled transport and chemical processes confirmed the theoretical arguments behind the model. Also, the large amount of information obtained from the numerical simulations illustrated the usefulness of the model in gaining insight on complicated and frequently counterintuitive phenomena.

Although the code developed constitutes a significant advancement in the field, there are still important areas for improvement. One of the most important issues to address in future work is the use of higher order basis functions that result in continuous gradients across computational elements. This should improve the conservation properties of the formulation and the quality of the solution at the electrode reservoirs. A good example is the hermite cubic element (see e.g. [5]). This element interpolates the value of the function, as well as the x and y derivatives at four different points. In evaluating these elements, careful consideration must be given to the effect of shocks in the solution. Also, as hinted above, the use of adaptive meshing has the potential of significantly improving the solution by making a better use of the computational resources available.

Preliminary theoretical studies of the effect of electrode placement on the effectiveness of contaminant removal where carried out by Jacobs [20] for convection-dominated systems. In that work it was determined that, contrary to the usual
expectations, radial electrode arrays generating outward flow produced significantly higher degree of removal per pore volume displaced than comparable arrays in which the effluent was collected at the center. The code developed here will allow studying other aspects of multielectrode systems such as power consumption, time scales for removal or pH and chemical speciation distributions. As an example, figures 5-1 to 5-4 show several multielectrode configurations, the corresponding potential and concentration distributions and the cumulative contaminant removal versus time for conditions similar to those of the phenol removal experiment.

The basic cell shapes are indicated by dotted lines in figure 5-1. Array 1 is a parallel electrode configuration with alternating rows of anodes and cathodes. Array 2 tiles the target area with square cells containing a central anode and a cathode at each corner and array 3 tiles the area using triangular cells. Array 4 is a combination of triangular and hexagonal cells.

Figure 5-2 shows the electric field strength distributions for each array. Dark shades indicate the areas with low electric field. The effect of these electric field distributions on the electrophoretic velocity and thus on the shape and size of the purged area are visible in figure 5-3. Although all arrays produced a high degree of contaminant removal within the target area, there were significant differences in the flow rate and in the shape of the contaminant concentration distribution. Array 2 produced a compact purged area affecting mostly the region within the electrodes, while the other configurations affected a significant region of the domain outside the periphery of the electrode array. Array 3 produced the highest flow rate.

Figure 5-4 shows the fraction of contaminant removed versus time for each of the electrode arrays in the example. The fraction removed is normalized with respect to the total mass in the domain and therefore reflects the size of the purged area. Array 3 produced that fastest contaminant removal due to its high flow rate.

This example illustrates how the electrode placement may affect the rate and level of contaminant removal in a particular application and how the numerical code can be used as a tool in the study of multiple-electrode configurations.

It is of particular interest to extend the analysis of multiple-electrode systems
and the effect of electrode placement on the level and rate of contaminant removal. This analysis should be complemented with further experimental study to verify the model predictions for multiple-electrode configurations, and with the study of other chemical systems.

Another research opportunity is the study of the effect of spatially varying hydraulic permeability and zeta potential on the removal of contaminants in convection-dominated systems. These parameters may significantly affect the convection velocity distribution and be key factors for the successful removal of neutral or weakly dissociated compounds. The development of a three-dimensional code which includes the effect of anisotropy in the medium may be required for this task. This is so because many natural soils are anisotropic and suffer significant variations of the material properties with depth.
Figure 5-2: Electric field strength distributions for the electrode arrays shown in figure 5-1. Note the wide variations in electric field strength within the target area.
Figure 5-3: Contaminant concentration distributions after 9 months for the multi-electrode examples. This figure illustrate the effect of electrode placement on the size and shape of the purged area.
Figure 5-4: Cumulative contaminant removal versus time for the multielectrode examples. The curves reflect the size and shape of the purged areas, so in this plot the time evolution is more significant than the final value.

Also of interest is the study of thermal effects during the electrorestoration process and the development of appropriate treatment strategies for the case of severe variation of the medium conductivity, as for example in the presence of large underground metal objects illustrated in figure 5-5.

In summary, the code developed will allow us to study many features of the contaminant removal processes as well as to examine the effects of varying key parameters on the overall effectiveness and efficiency of the electrorestoration process at a specific site. Thus, it will serve as a useful tool for both improving our understanding of the relevant physical phenomena and developing field applications of the technology.
Figure 5-5: Electrostatic potentials, electric field and current density distributions for a case with severe spatial variation of the soil conductivity.
Bibliography


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