Electrokinetic Remediation Modeling Incorporating Geochemical Effects

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Abstract: Electrokinetic remediation technology is one of the developing technologies that offers great promise for the cleanup of soils contaminated with heavy metals. However, the performance of an electrokinetic remediation system depends on the interaction of a complex set of interrelated system variables and parameters. Many of these interactions were addressed in this study by incorporating geochemical reactions into electrokinetic remediation modeling. A one-dimensional transport model was developed to predict the transport and speciation of heavy metals (chromium, nickel, and cadmium) in soil during electrokinetic remediation as a function of time and space. The model incorporates: (1) pH-dependent adsorption of contaminants to the soil surface; (2) sensitivity of soil surface potential and electroosmotic flow to the pore water properties; and (3) synergistic effects of multiple chemical species on electrokinetic remediation. The model considers that: (1) Electrical potential in the soil is constant with time; (2) surface complexation reactions are applicable in the highly concentrated clay suspensions; (3) the effect of temperature is negligible; and (4) dissolution of soil constituents is negligible. The predicted pH profiles, electroosmotic flow, and transport of chromium, nickel, and cadmium in kaolin soil during electrokinetic remediation were found to reasonably agree with the bench-scale electrokinetic experimental results. The predicted contaminant speciation and distribution (aqueous, adsorbed, and precipitated) allow for an understanding of the transport processes and chemical reactions that control electrokinetic remediation.

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Introduction

Electrokinetic remediation is a developing remedial technology that has significant potential for in situ remediation of fine-grained soils contaminated with heavy metals. Electrokinetic remediation involves applying a low direct current or a low potential gradient to electrodes that are inserted into the ground. As a result, based on their charge, the contaminants are transported to either the cathode or anode, where they are extracted by one or more of the following methods: Electroplating, adsorption onto the electrode, precipitation or coprecipitation at the electrode, pumping and extracting water near the electrode, or complexing with ion-exchange resins (e.g., Acar and Alshawabkeh 1993; Probst and Hicks 1993; Lindgren et al. 1992).

Although the implementation of electrokinetic remediation is simple, the behavior of heavy metals in soils under the application of electric potential is complex and difficult to predict. The application of a direct electric current to soil results in several changes to the soil medium, such as pH, redox potential, and electrolyte concentration. These changes may impact the surface chemistry of clay particles, which in turn impacts the success of the electrokinetic remedial effort. The driving mechanisms for contaminant flux occur at interface between the soil particles and solution, therefore the nature of this interface affects the electrokinetic response of the system (Al-Hamdan and Reddy 2005). Moreover, the total system response depends on the interaction of a complex set of interrelated system variables and parameters. Electrokinetic modeling is conducted to better understand various changes within the soil-water system during electrokinetic remediation.

Several mathematical models have been developed to predict contaminant transport during electrokinetic remediation (Kim 1998; Haran et al. 1997; Alshawabkeh and Acar 1996; Yu and Neretnieks 1996; Menon 1996; Choi and Lui 1995; Yeung and Dalta 1995; Jacobs et al. 1994; Euykolt and Daniel 1994; Shapiro and Probst 1993; Alshawabkeh and Acar 1992; Bruehl et al. 1992; Corapcioğlu 1991). However, many of these models do not accurately account for the geochemistry of heavy metals and, as a result, the modeling results do not reflect experimental observations. Specific deficiencies in these models include: (1) they do not account for the sorption reactions or the pH-dependent contaminant adsorption to the soil; (2) they neglect the effect of pH changes and ionic strength of pore water on the surface potential of the solids; and (3) they focus only on a single contaminant and therefore do not account for the synergistic effects of multiple chemical species on the performance of electrokinetic remediation. In addition, these models are validated only for a specific simulation time (treatment duration). Most of these studies were concerned with determining the residual contaminant distribution in the soil and measuring the overall removal efficiency after the
electrokinetic treatment. In general, these models also showed low removal of heavy metals from soils using electrokinetic remediation. Unfortunately, these studies did not investigate a detailed chemical speciation of the contaminants, or did they investigate how the contaminants are held (retained and bounded) to the soil constituents. Some modeling studies did show speciation of contaminants in the soils during electrokinetic remediation, but these studies were often limited to a single contaminant (Alshawabkeh and Acar 1996; Yu and Neretnieks 1996; Jacobs et al. 1994). A more detailed assessment of the speciation and distribution of contaminants may provide reasons for the low contaminant removal during electrokinetic remediation. Further, understanding the contaminant-retaining mechanisms in soil-water systems during electrokinetic remediation will permit a more educated design approach to engineer the chemistry for enhanced contaminant remediation (Pamukcu et al. 2004).

This paper presents a one-dimensional transport model that predicts metal contaminant behavior in soil during electrokinetic remediation. The model calculates the concentration of any chemical species during electrokinetic remediation as a function of time and space. The benefit of this simulation is that it is capable of predicting the chemical speciation of the contaminants as well as the form that they would exist within the soils (i.e., aqueous, adsorbed, or precipitated). In addition, the model addresses the following contaminant-soil interactions that occur during electrokinetic remediation: (1) pH-dependent adsorption of contaminants to the soil surface; (2) sensitivity of soil surface potential and electroosmotic flow to the pore water properties such as pH, ionic strength, and presence of heavy metals; and (3) synergistic effects of multiple chemical species on electrokinetic remediation. Model predictions are compared with the laboratory bench-scale experimental results.

Modeling Approach and Model Development

The application of a DC electric field across a soil-water system causes a very complex set of phenomena to occur within the system. These phenomena are collectively referred to as electrokinetics. Electrokinetic modeling involves simulating the processes that induce contaminant transport as well as the geochemical processes that occur within the electrokinetic system. In this study, a FORTRAN 77 computer model EKGEOCHEM (ELECTROKINETIC GEOCHEMICAL) is developed to simulate electrokinetic remediation of soil contaminated with heavy metals. The general framework of the model consists of a two-step approach that separates the transport and chemical processes in the system. A solution to the transport governing equation provides an initial estimate of concentrations. A second step corrects these concentrations to account for the partitioning of mass due to a suite of chemical reactions. Fig. 1 shows the flowchart of the EKGEOCHEM model, which consists of two major components: (1) a contaminant transport submodel that takes into consideration the transport processes in soils under electric fields (namely diffusion, electromigration, hydraulic advection, and electroosmotic advection); and (2) a chemical speciation submodel (CHEMSPC) that takes into consideration the acid-base, precipitation-dissolution, oxidation-reduction, and adsorption-desorption reactions.

In the EKGEOCHEM model, the CHEMSPC submodel is initially used to calculate the speciation of each contaminant (mobile or fixed) as well as the soil surface potential. The contaminant transport submodel then incorporates the mobile contaminant data as initial conditions used to calculate the new aqueous concentrations of each contaminant at each space increment. The transported portion of the contaminant at each space increment is then added to the previously retained portion at the same space increment in order to determine the total contaminant concentration profile. CHEMSPC then repeats the same process using the new total concentration to find the contaminant speciation and potential of the soil surface for each space increment at time step \( t_m \). The new mobile concentrations for the time step \( t_m \) are the initial conditions for the next time step \( t_m + \Delta t \).

Modeling of Transport Processes

The multispecies transport model developed by Alshawabkeh and Acar (1992) was adapted as the transport model for this study. This model takes into consideration the transport mechanisms of the contaminants in soil during electrokinetic remediation: (1) advection due to the movement of water under hydraulic and electrical potential gradients; (2) diffusion due to concentration gradients; and (3) electromigration due to the ionic mobility of charged ions toward oppositely charged electrodes. In the presence of hydraulic, electrical, and chemical gradients, the one-dimensional total flux of species \( j \) per unit area of the soil medium is given by Alshawabkeh and Acar (1992) as follows:

\[
J_j = -D_j \frac{\partial C_j}{\partial x} - C_j (u_j^* + K_x) \frac{\partial E}{\partial x} - C_j K_h \frac{\partial h}{\partial x}
\]

(1)

\[
D_j^* = D_j \tau n
\]

(2)
where $C_j$ = concentration of species $j$; $D_j^*$ = effective diffusion coefficient of species $j$ in free solution at infinite dilution; $\tau$ = tortuosity factor; $n$ = soil porosity; $u^*_j$ = effective ionic mobility of species $j$; $F$ = Faraday constant; $T$ = absolute temperature; $R$ = ideal gas constant; $\zeta$ = charge of species $j$; $K_e$ = electroosmotic permeability; $\varepsilon$ = permittivity of the medium; $\varepsilon_0$ = permittivity in vacuum ($8.854 \times 10^{-12}$ C/N m); $\eta$ = viscosity of the pore water, $E$ = electrical potential; $K_h$ = hydraulic conductivity; and $h$ = hydraulic head.

The one-dimensional time-dependent equation for the transport of solute based on the conservation of mass, presented by Alshawabkeh and Acar (1992), is

$$\frac{\partial nC_j}{\partial t} = -\frac{\partial J_j}{\partial x} + nR_j$$

(5)

where $R_j$ = production rate of the aqueous species $j$ per fluid volume due to chemical reactions. Without the chemical reaction portion of the equation, the transport equation is given as

$$\frac{\partial nC_j}{\partial t} = D_j^* \frac{\partial^2 C_j}{\partial x^2} + (u^*_j + K_e) \frac{\partial E}{\partial x} + (u^*_j + K_e) \frac{\partial C_j}{\partial x} \frac{\partial E}{\partial x}$$

$$+ K_h \frac{\partial h}{\partial x} + K_e \frac{\partial C_j}{\partial x} \frac{\partial E}{\partial x}$$

(6)

In this study, the following simplifying assumptions were made in the transport model: (1) the transport processes can be described by a one-dimensional model; (2) the flux due to hydraulic gradient is negligible as it is very small in low permeability soils; and (3) the electrical field ($\partial E/\partial x$) is assumed to be constant with time across the specimen. This assumption may not entirely be valid because the electrical potential drop through the soil starts linear, but becomes increasingly nonlinear over time (Eykholt 1992). However, this assumption is considered valid in order to provide a first-order approximation to the chemical gradients; (4) the soil porosity and hydraulic conductivity are constant in time and space; and (5) no chemical reactions are involved in the transport model (all chemical reactions involving the contaminants and their adsorption processes to the soil are implemented in the chemical submodel). These conditions simplify the governing transport model of the contaminant to the following:

$$\frac{\partial nC_j}{\partial t} = D_j^* \frac{\partial^2 C_j}{\partial x^2} = V_j \frac{\partial C_j}{\partial x}$$

(7)

where

$$V_j = -(u^*_j + K_e) \frac{\partial E}{\partial x}$$

(8)

The Crank-Nicholson implicit finite difference technique (Carnahan et al. 1969) is used to solve the main transport equations. This method is used because it is unconditionally stable and provides a second-order accuracy. The finite difference approximation of the governing transport equation is expressed as

$$C_j^{t+\Delta t} - C_j^t = \frac{D_j^*}{2n} \left( \frac{C_{j+1} - 2C_j + C_{j-1}}{\Delta x^2} \right)^{t+\Delta t} + \frac{C_{j+1} - 2C_j + C_{j-1}}{\Delta x^2} \right)^t$$

$$- V_j \left( \frac{C_{j+1} - C_j}{\Delta x} \right)^{t+\Delta t} + \left( \frac{C_j - C_{j-1}}{\Delta x} \right)^t$$

(9)

**Modeling of Chemical Reactions**

The important chemical reactions that occur in soils during electrokinetic treatment are: acid-base reactions (reaction of an acid or a base with water), adsorption-desorption (the interaction of a contaminant between the liquid phase and the solid phase/solid surface), precipitation-dissolution reactions (reactions in which a contaminant precipitates or dissolves based on its solubility and concentration), and oxidation-reduction reactions (reactions in which a contaminant loses/donates or gains/accepts electrons). For detailed background on these chemical reactions, refer to Snoeyink and Jenkins (1980). In this study, a chemical speciation submodel (CHEMSPC) is developed to account for these chemical reactions.

One of the difficult problems in electrokinetic modeling is the coupling of different chemical reactions and mass transport processes because they take place at different rates. For example, if the reaction rate is fast relative to the transport process, it is valid to assume that the system is at chemical equilibrium and to calculate the concentrations of all species in solution. On the other hand, when reactions are slow, one may assume that chemical equilibrium applies only as a limiting case; in other words, the system is tending toward equilibrium. Acid-base and complexation reactions are usually fast relative to transport reactions, whereas redox reactions are generally slow. Dissolution and precipitation reactions are variable (sometimes they are quite slow). Even in the case of slow redox reactions, we can achieve an understanding of where the system is tending by computing the chemical equilibrium speciation. Therefore, for the purposes of this study, the chemical submodel assumes that the system is at equilibrium.

**Chemical Model Framework**

The chemical speciation submodel (CHEMSPC) is developed to calculate the speciation of each contaminant, including the mobile (i.e., aqueous) and fixed (i.e., precipitated and/or adsorbed) portions, as well as the soil surface zeta potential. Similar to other chemical models (i.e., MINTEQA2 and MINEQL*), CHEMSPC operates on the principles of the Newton-Raphson root-finding solution technique to mass law equilibrium. However, MINEQL and MINTEQA2 are more comprehensive than CHEMSPC in that they contain a vast thermodynamic database with the capability to create new databases and incorporate several adsorption models (including both electrostatic and nonelectrostatic models). CHEMSPC is developed based on the mass balance of the species of interest that exist within the electrokinetic remediation system. Fig. 2 shows the flow chart of CHEMSPC submodel. CHEMSPC reads the total concentrations of all components existing in the system from the EKGEOCHEM simulation. This submodel also has the option to implement oxidation-reduction (redox) reactions to calculate the activity (i.e., concentration) ratio between two members of the redox couple (such as Cr(VI)/Cr(III) couple). The oxidation reaction and reduction reaction must always be coupled because free electrons...
cannot exist in solution, and electrons must be conserved (i.e., the potentials of both half-reactions are the same at equilibrium). Therefore, the redox reactions during electrokinetic remediation were modeled in this study by defining the activity ratio between the two members of a redox couple when the system is at equilibrium with either another redox couple in the presence of reducing or oxidizing agents, or with dissolved oxygen (i.e., O₂/H₂O couple) in the absence of oxidizing or reducing agents (i.e., the pore water is oxygenated or oxygen-bearing as the oxygen gas is generated at the anode due to the electrolysis reactions).

The resulting mass balance equations of the species in the soil system form a set of algebraic equations of activity for each species in terms of independent variables called components. The Newton-Raphson iterative solution technique is used to solve the resulting nonlinear set of mass balance equations to determine the concentrations of all chemical species existing in the system. In order to organize the mass balance equations in matrix notation, the chemical system is presented in tabular form. Table 1 represents a systematic relationship between the components and all species existing in a heavy metal-contaminated kaolin system (i.e., chemical reactions) consisting of trivalent and hexavalent chromium, nickel, cadmium, chlorine, potassium, and soil kaolin). In Table 1, the first row represents the components, the first column shows the species, the last row gives the total concentration of each component in the system, and the last column shows the logarithmic values of the equilibrium constants between the species and the components. The values entered in Table 1 represent the stoichiometric coefficients. The equilibrium constants of the chemical reactions (except for the adsorption-desorption reactions) between the species and the components were obtained from the MINQUEL thermodynamic database (Schecher and McAvoy 1994).

The mass balance equations for the system described in Table 1 are given in the following:

\[
\begin{align*}
\text{TOT[Cd}^{2+}] &= \{\text{Cd}^{2+}\} + \{\text{CdOH}^+\} + \{\text{Cd(OH)}_2\text{aq}\} + \{\text{Cd(OH)}_3\} \\
&+ \{\text{Cd(OH)}_4^-\} + 2\{\text{Cd}_2\text{O}_3\text{Cl}^-\} + \{\text{CdOHCl}_\text{aq}\} \\
&+ \{\text{CdCl}^+\} + \{\text{CdCl}_2\text{aq}\} + \{\text{CdCl}_3\} + \{\text{SOCl}^+\} \\
\text{(10a)}
\end{align*}
\]

\[
\begin{align*}
\text{TOT[Ni}^{2+}] &= \{\text{Ni}^{2+}\} + \{\text{NiOH}^+\} + \{\text{Ni(OH)}_2\text{aq}\} + \{\text{Ni(OH)}_3\} \\
&+ \{\text{NiCl}^+\} + \{\text{NiCl}_2\text{aq}\} + \{\text{SONi}^+\} \\
\text{(10b)}
\end{align*}
\]

\[
\begin{align*}
\text{TOT[Cr}O_2^3^-] &= \{\text{CrO}_4^{2-}\} + 2\{\text{Cr}_2\text{O}_3^+\} + \{\text{H}_2\text{CrO}_4\} + \{\text{H}_2\text{CrO}_6\text{aq}\} \\
&+ \{\text{CrO}_3\text{Cl}^-\} + \{\text{KCrO}_4\} + \{\text{SO}_2\text{H}_2\text{CrO}_4\} \\
\text{(10c)}
\end{align*}
\]

\[
\begin{align*}
\text{TOT[Cr}O_3^2^-] &= \{\text{CrO}_4^{3-}\} + \{\text{Cr(OH)}_2^+\} + \{\text{Cr(OH)}_3^+\} \\
&+ \{\text{Cr(OH)}_3\text{aq}\} + \{\text{Cr(OH)}_4^+\} + \{\text{Cr}_2\text{O}_3\text{Cl}^-\} \\
&+ \{\text{CrCl}_2^+\} + \{\text{CrCl}_3^+\} + \{\text{CrOHCl}_2\text{aq}\} \\
\text{(10d)}
\end{align*}
\]

\[
\begin{align*}
\text{TOT[C}^-] &= \{\text{Cl}^-\} + \{\text{CdOHCl}_\text{aq}\} + \{\text{CdCl}^-\} + 2\{\text{CdCl}_2\text{aq}\} \\
&+ 3\{\text{CdCl}_3\} + \{\text{NiCl}^+\} + 2\{\text{NiCl}_2\text{aq}\} + \{\text{Cr}_2\text{O}_3\text{Cl}^-\} \\
&+ 2\{\text{Cr}_2\text{Cl}_4^+\} + \{\text{CrOHCl}_2\text{aq}\} + \{\text{CrO}_3\text{Cl}^-\} \\
\text{(10e)}
\end{align*}
\]

\[
\text{TOT[K}^+] = \{\text{K}^+\} + \{\text{KCrO}_3\} \\
\text{(10f)}
\]

\[
\begin{align*}
\text{TOT[SO}^2\text{-}] &= \{\text{SO}^2\text{-}\} + \{\text{SO}_3\text{H}^+\} + \{\text{SO}_2\text{C}d^+\} + \{\text{SONi}^+\} \\
&+ \{\text{SO}_2\text{H}_2\text{CrO}_4\} + \{\text{SOCl}(\text{O})_2\text{H}_2\text{O}\} \\
\text{(10g)}
\end{align*}
\]

The charge balance equations for the same system described in Table 1 are given in the following:

\[
\begin{align*}
2\{\text{Cd}^{2+}\} + \{\text{CdOH}^+\} + \{\text{Cd}_2\text{O}_3\text{Cl}^-\} + \{\text{CdCl}^-\} + 2\{\text{Ni}^{2+}\} \\
+ \{\text{NiOH}^+\} + \{\text{Cr(OH)}_2^+\} + 3\{\text{Cr}^{3+}\} + 2\{\text{Cr}_2\text{O}_3^+\} + \{\text{K}^+\} + \{\text{H}^+\} \\
+ \{\text{SO}_2\text{H}^+\} + \{\text{SOCl}^+\} + \{\text{SONi}^+\} = \{\text{Cd(OH)}_3\} \\
+ 2\{\text{Cd(OH)}_4^-\} + \{\text{CdCl}^-\} + \{\text{Ni(OH)}_3^+\} + \{\text{NiCl}^-\} \\
+ \{\text{Cr(OH)}_2^+\} + \{\text{Cr}_2\text{O}_3^+\} + 2\{\text{Cr}_2\text{O}_3\text{Cl}^-\} + \{\text{H}_2\text{CrO}_4\} \\
+ \{\text{Cr}_2\text{O}_3\text{Cl}^-\} + \{\text{KCrO}_4\} + \{\text{Cl}^-\} + \{\text{OH}^-\} + \{\text{SO}^-\} \\
\text{(11)}
\end{align*}
\]

The surface charge of kaolin (SOH) is expressed as

\[
\sigma_o = -\frac{F}{A_i C_i} \{\text{SOH}^2\} + \{\text{SOCl}^+\} + \{\text{SONi}^+\} - \{\text{SO}^-\} \\
\text{(12)}
\]
where \( A_s \) = solid surface area and \( C_s \) = weight of solid in contact with a liter of solution (g/L). For details about the mathematical description of a chemical equilibrium problem, refer to Schnoor (1995).

Unlike MINEQL+, CHEMSPEC ignores the effect of the temperature on the equilibrium constant values of the chemical reactions and assumes that the system’s temperature is constant at 22°C. On the other hand, CHEMSPEC takes into consideration the effect of the species concentrations on the equilibrium constant values. As a first approximation, CHEMSPEC calculates the concentrations of all species by solving the resulting nonlinear set of mass balance equations. It then calculates the corrected

<table>
<thead>
<tr>
<th>Species</th>
<th>Components</th>
<th>( \text{Log } K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(^{2+} )</td>
<td>0 0 1 0 0 0 0 0 0 0 0 0</td>
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</tr>
<tr>
<td>CdOH(^+ )</td>
<td>1 -1 1 0 0 0 0 0 0 0 0</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
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</tr>
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<td>3 -3 0 0 0 1 0 0 0 0</td>
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<td>NiCl(^- )</td>
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</tr>
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<td>NiCl(<em>2) (</em>{aq} )</td>
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<td>0.96</td>
</tr>
<tr>
<td>Cr(OH)(<em>2) (</em>{aq} )</td>
<td>0 0 0 0 0 0 1 0 0 0 0</td>
<td>0.0</td>
</tr>
<tr>
<td>Cr(_2)OH(<em>2) (</em>{aq} )</td>
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<td>9.62</td>
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<tr>
<td>Cr(OH)(<em>3) (</em>{aq} )</td>
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</tr>
<tr>
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</tr>
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</tr>
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<td>Cl(^- )</td>
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<td>0.0</td>
</tr>
<tr>
<td>K(^\oplus )</td>
<td>0 0 0 0 0 0 1 0 0 0 0</td>
<td>0.0</td>
</tr>
<tr>
<td>H(^+ )</td>
<td>0 1 0 0 0 0 0 0 0 0 0</td>
<td>0.0</td>
</tr>
<tr>
<td>OH(^- )</td>
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<tr>
<td>SOH(<em>2) (</em>{aq} )</td>
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<td>0.0</td>
</tr>
<tr>
<td>SO(<em>2) (</em>{aq} )</td>
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<tr>
<td>SO(_2)H(<em>2) (</em>{aq} )</td>
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<td>3.8</td>
</tr>
<tr>
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<td>0 -1 1 0 0 0 0 0 0 0 0</td>
<td>-3.3</td>
</tr>
<tr>
<td>SOn(^\oplus )</td>
<td>0 -1 -1 0 0 0 0 0 0 0 0 0</td>
<td>-2.6</td>
</tr>
<tr>
<td>SO(_3)CrO(<em>4) (</em>{aq} )</td>
<td>0 0 0 0 1 0 0 0 0 0</td>
<td>5.0</td>
</tr>
<tr>
<td>SO(_2)CrO(<em>4) (</em>{aq} )</td>
<td>0 2 0 1 0 0 0 0 0 0</td>
<td>12.5</td>
</tr>
<tr>
<td>Coul(^\oplus )</td>
<td>0 0 0 0 0 0 1 0 0 0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\(^a\)Chromium redox half-reaction is: Cr\(_2\)O\(_7\)\(^-2\) + 14H\(^+\) + 6e\(^-\) \(\rightarrow\) 2Cr\(^{3+}\) + 7H\(_2\)O, \(p_e^\circ = +22.5\).

\(^b\)Coul=exp(\(-\Delta \bar{E}^\circ/F/RT\)).
equilibrium constants of the reactions (i.e., ‘$K_i$’ based on the calculated activity coefficients of the species (i.e., ionic strength of the system). The adjusted equilibrium constants are then returned to the mass balance equations and solved for new concentrations.

After CHEMSPC determines the concentrations of the species for the corrected equilibrium constants of the reactions, it checks for the precipitation of the contaminants. CHEMSPC implements the precipitation reactions by comparing the solubility of the contaminant, or the ion activity product, with the total aqueous form of the contaminant or its solubility constant, respectively. For each contaminant, the amount of precipitation is subtracted from its concentration in the aqueous state. The adjusted contaminant concentrations are returned to the mass balance equations and solved for new activities.

The resulting values of the concentrations from CHEMSPC are returned to the main EKGEOCHEM program. The EKGEOCHEM model considers that the resulting aqueous form of the contaminant from CHEMSPC is the mobile portion in the transport model [i.e., Eq. (9)]. Even though each charged ion (i.e., species of the same contaminant) has its own ionic mobility, the resulting positively charged aqueous species of the same contaminant from the chemical submodel are lumped together in the transport submodel as a positively charged ion, whereas the negatively charged aqueous species are lumped together as a negatively charged ion. This assumption may be considered valid because it is very difficult to separate the mobility of different species of the same contaminant. However, the mobility of $H^+$ and $OH^-$ ions are treated separately as they have a significant influence on the geochemistry of the system.

CHEMSPC Specific Implementations

Specific implementations were employed in CHEMSPC in order to address the following contaminant-soil interactions during electrokinetic remediation: (1) pH-dependent adsorption of contaminants to the soil surface; (2) the effects of system conditions such as pH, ionic strength, and the presence of heavy metals on the soil surface potential, and therefore on the electroosmotic flow; and (3) the synergistic effects of multiple chemical species on electrokinetic remediation.

In order to address the pH-dependent adsorption process in electrokinetic remediation, adsorption has been implemented in CHEMSPC in terms of a set of surface complexation reactions (i.e., electrostatic models). With the concept of complexation, it is possible to deal with the adsorption equilibria in the same manner as aqueous equilibria. In other words, electrostatic adsorption reactions consider simultaneously the impact of important system properties such as changes in pH, aqueous complex formation, and solution ionic strength (i.e., solution speciation) on the contaminant adsorption and electroosmotic flow, which depends on the surface potential [Eq. (4)].

The major advancement of electrostatic adsorption reactions is the consideration of charges on both the adsorbate ion (metal) and the adsorbent (soil) surface (SO$^+$), taking into consideration corrections for the activities of the adsorbate ion between the charged soil surface and the bulk solution. Moreover, in electrostatic models, a charge ($\sigma$) associated with the surface is assumed to be balanced by charge ($\sigma_j$) associated with a diffuse layer of counter ions. These charges are such that $\sigma + \sigma_j = 0$. The presence of electrostatic potentials arising from the surface charge of soil grains affects the behavior of ions in solution and near the surface (Allison et al. 1991). The activity difference between ions near the surface and those far away is the result of electrical work in moving the ions across the potential gradient between the charged surface and the bulk solution (Langmuir 1997). The activity change between these zones is related to the ion charge ($z$) and the electrical potential ($\psi$) near the surface and can be expressed using the exponential Boltzmann expression:

$$\{X^z\} = \{X^z\} e^{-z\psi/RT};$$  \hspace{1cm} (13)

$$\text{where } z = \text{charge of ion } X; \{X^z\} = \text{activity of ion } X \text{ of charge } z \text{ near the surface}; \{X^z\}' = \text{corresponding activity of } X \text{ in bulk solution outside the influence of the charged surface}; e^{-z\psi/RT} \text{ is the Boltzmann factor (Coulombic correction)}; F=\text{Faraday constant}; R=\text{ideal gas constant}; \text{ and } T=\text{absolute temperature.}$$

The drawback of the surface complexation models is that they are developed from dilute suspensions and may not be applicable in highly concentrated clay suspensions. James and Parks (1982) suggest that these models will not be directly applicable unless thin double layers are present in the soil. However, the surface complexation models are more representative of the surface charge and the pH-dependent adsorption behavior than the non-electrostatic models (Zachara et al. 1988). Therefore, they fit better for electrokinetic models than regular adsorption models.

The constant capacitance model is the electrostatic model that is implemented in this study. This model treats the metal surface reactions as complexation reactions analogous to the formation of complexes in solution. Surface sites are represented as SOH groups where S’s are metals associated with the solid structure and located at the solid-liquid interface. In the constant capacitance model, the total surface charge $\sigma_0$ is related to the surface potential $\psi_0$ as $T \sigma_0 = C \psi_0$, where $C=\text{constant capacitance term}$ (Langmuir 1997). The protonation and dissociation reactions of the surface functional group, SOH, are represented by

$$\text{SOH} + H^+ \leftrightarrow \text{SOH}H_2^+ \hspace{1cm} (14)$$

$$\text{SOH} - H^+ \leftrightarrow \text{SO}^- \hspace{1cm} (15)$$

where $H^+$=hydronium ion near the surface, and the intrinsic equilibrium constants for these reactions are

$$K_\sigma(\text{int}) = \frac{[\text{SOH}H_2^+]}{[\text{SOH}][H^+]} \exp[F\psi/RT] \hspace{1cm} (16)$$

$$K_\phi(\text{int}) = \frac{[\text{SO}^-][H^+]}{[\text{SOH}]} \exp[-F\psi/RT] \hspace{1cm} (17)$$

Typical surface complexation reactions for specific ion adsorption used in the constant capacitance model are

$$\text{SOH} + M^{m+} \leftrightarrow \text{SOM}^{(m-1)} + H^+ \hspace{1cm} (18)$$

$$2\text{SOH} + M^{m+} \leftrightarrow (\text{SOH})_2M^{(m-2)} + 2H^+ \hspace{1cm} (19)$$

$$\text{SOH} + H_2L \leftrightarrow \text{SH}_nL^{(1-n)} + H_2O + (i-1)H^+ \hspace{1cm} (20)$$

$$\text{SOH} + H_nL \leftrightarrow \text{SH}_nL^{(2-n)-j} + 2H_2O + (j-1)H^+ \hspace{1cm} (21)$$

where $M=\text{metal ion}; m=\text{charge on the metal ion}; L=\text{ligand}; n=\text{number of protons present in the undissociated form of the ligand}; i=1 \leq i \leq n; \text{and } j=1 \leq j \leq n=\text{number of proton dissociations undergone by a ligand.}$ The intrinsic equilibrium constants describing the above-mentioned reactions are
\[ K_M^j (\text{int}) = \frac{[\text{SOM}^{m-1}] [\text{H}^+]}{[\text{SOH}][M^{m+}]} \exp((m-1)F\psi/RT) \]  

(22)

\[ K_M^2 (\text{int}) = \frac{[(\text{SO})_2 M^{m-2}] [\text{H}^+]^2}{[\text{SOH}]^2 [M^{m+}]} \exp((m-2)F\psi/RT) \]  

(23)

\[ K_L^j (\text{int}) = \frac{[(\text{SH}_{m-j}) L^{1-i}] [\text{H}^+]^{-i}}{[\text{SOH}]^2 [H_2 L]} \exp((1-i)F\psi/RT) \]  

(24)

\[ K_L^j (\text{int}) = \frac{[(\text{SH}_{m-j}) L^{2-i}] [\text{H}^+]^{-2}}{[\text{SOH}]^3 [H_2 L]} \exp((2-j)F\psi/RT) \]  

(25)

In this study, the adsorption of Na\(^+\) and K\(^+\) to the solid surface and their adsorption competition with the studied metals (i.e., Ni, Cd, and Cr) are ignored. The relative affinity of adsorption for a free metal cation will increase with the tendency of the cation to form inner-sphere surface complexes (Sposito 1989). For a series of metal cations of a given valence, this tendency has a positive correlation with the ionic radius. The monovalent cations such as K\(^+\) and Na\(^+\) have relatively large ionic radii and do not form inner-sphere surface complexes, and therefore are located exclusively in the diffuse layer and bulk aqueous phase (Jenne 1998). As a result, their competition with the metals to be adsorbed by solid surfaces is negligible. Also, the metal adsorption in CHEMSPC is considered to be free metal (M\(^{m+}\)) adsorption. This assumption is not valid because the metal hydroxo-complexes (MOH\(^+\)) are significantly more adsorbable than free metal cations (Elliott et al. 1986). However, because of the lack of adsorption data for metals and their hydroxo-complexes to solid surfaces, this assumption may be considered valid for a first-order approximation in electrokinetic remediation.

In order to address the synergistic effects of multiple chemical species on electrokinetic remediation, the species activity corrections have been implemented in CHEMSPC. Ideally, one could assume that the thermodynamic activities of the ions are the same as their concentrations because the ions behave independently of one another in infinitely dilute solutions. However, as the concentration of ions in solution increases, electrostatic interactions between the ions also increase, making the thermodynamic activities of the ions less than their measured or assumed concentrations (Snoeyink and Jenkins 1980). The relation between the activity of an ion and its concentration is given by

\[ a_i = \gamma_j C_j \]  

(26)

where \( a_i \) = thermodynamic activity of aqueous species \( j \); \( \gamma_j \) = activity coefficient of aqueous species \( j \); and \( C_j \) = concentration of aqueous species \( j \).

In this study, the activity coefficient of aqueous species \( j \) is calculated by the following (Stumm and Morgan 1996):

\[ \log \gamma_j = -0.5C_j^2 \left( \frac{1 + \sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu \right) \]  

(27)

where \( \mu \) = ionic strength of the aqueous solution, defined by

\[ \mu = 0.5 \sum_{j=1}^{n} (C_j z_j^2) \]  

(28)

where \( C_j \) = concentration of ion species \( j \) and \( z_j \) = charge of species \( j \).

In order to verify the accuracy of the EKGEOCHEM model, its two components (i.e., transport and chemical components) were validated individually. The transport component of EKGEOCHEM model was validated by comparing the simulation results with those of the analytical solution of the one-dimensional nonreactive advective-dispersive mass transport equation, given by

\[ \frac{\partial C}{\partial t} = D_{hd} \frac{\partial^2 C}{\partial x^2} + v_x \frac{\partial C}{\partial x} \]  

(29)

where \( v_x \) = average seepage velocity; \( D_{hd} \) = hydrodynamic dispersion (=\( \tau D + \alpha_x v_x \)); \( \alpha_x \) = dispersivity; \( D \) = ion diffusion coefficient at infinite dilution in water; and \( \tau \) = tortuosity of the porous medium. The analytical solution of Eq. (29) for a continuous source in one dimension is given by (Bear 1961)

\[ \frac{C(x,t)}{C_0} = \frac{1}{2} \left[ \text{erfc} \left( \frac{x - v_x t}{2 \sqrt{D_{hd} t}} \right) + \exp \left( \frac{v_x t}{D_{hd}} \right) \text{erfc} \left( \frac{x + v_x t}{2 \sqrt{D_{hd} t}} \right) \right] \]  

(30)

The initial condition used for the above-presented analytical solution is \( C(x,t=0)=0 \) and the boundary conditions are \( C(x=0,t)=1.0 \) and \( C(x=\infty,t)=0 \). For validation purposes, the initial and boundary conditions for EKGEOCHEM were assumed to be the same as those for the analytical solution except for \( C(x=L,t)=0 \). The difference in boundary conditions at \( x=L \) for
the analytical and EKGEOCHEM solutions results in good comparison for the short time durations and slight difference in results is seen for long time durations. Fig. 3(a) shows such a comparison of the simulation results of the transport model of EKGEOCHEM to those of the analytical solution of the one-dimensional non-reactive advective-dispersive mass transport equation for nickel ($D=6.79 \times 10^{-6}$ cm/s) in kaolin of 0.46 porosity value and of 0.44 tortuosity value. The result shows for different elapsed times: 1, 4, and 8 months. The results show that the prediction of EKGEOCHEM model and analytical model are in good agreement for short-term simulations (1 and 4 months). However, there is a slight difference for 8-month simulation when $x/L$ approaches 1 because of the differences in the boundary conditions at $x=L$ in the analytical and EKGEOCHEM solutions.

On the other hand, the chemical model is validated by comparing the surface charge results of CHEMSPC for kaolin suspension of 100 mg/L as a function of pH with the Gouy-Chapman model combined with the Nernst equation that correlates the surface charge density ($\sigma_0$) to the system pH by (Mitchell 1993)

$$\sigma_0 = \left( \frac{2nek}{\pi} \right)^{0.5} \sinh \left( 1.15w(p_H0 - pH) \right)$$

(31)

where $k=$Boltzmann constant; $w=$counter ion valence; and $p_H0=pH$ at which the surface potential is zero. For kaolin, Al-Hamdan and Reddy (2005) reported $p_H0$ value of 2.8±0.5 at temperature 22°C. Fig. 3(b) shows that the predictions of CHEMSPC model and Gouy-Chapman model combined with the Nernst equation are in reasonably good agreement. However, for high pH values (i.e., $pH>10$) the resulting surface charges using Gouy-Chapman model combined with the Nernst equation were negatively higher than those using EKGEOCHEM model. In EKGEOCHEM, the surface charge is determined using the mass and charge balance equations of all species in the system using surface complexation models (see Table 2). On the other hand, the theoretical Gouy-Chapman model combined with the Nernst equation correlates the surface charge to the solution pH in a hyperbolic function as seen in Eq. (28). For a given counter ion valance and $p_H0$, the negative charge using Eq. (28) dramatically increases when the value of ($p_H0-pH$) is negatively high (i.e., high pH). Thus, the surface charges using Gouy-Chapman model combined with the Nernst equation were negatively higher than those using EKGEOCHEM model for pH higher than 10.

### Table 2. Kaolin Surface Complexation Reactions Used in EKGEOCHEM [Af-Handan (2002), with Permission]

<table>
<thead>
<tr>
<th>Surface charge</th>
<th>$\sigma_0 = C \phi_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_o =$surface potential</td>
<td></td>
</tr>
<tr>
<td>$C =$constant capacitance</td>
<td></td>
</tr>
<tr>
<td>$C=1.0 F/m^2$ if water ionic strength, $\mu=0.1$ M</td>
<td></td>
</tr>
<tr>
<td>$C=0.7 F/m^2$ if $\mu=0.01$ M</td>
<td></td>
</tr>
<tr>
<td>$C=0.5 F/m^2$ if $\mu=0.001$ M</td>
<td></td>
</tr>
<tr>
<td>Intrinsic constants</td>
<td></td>
</tr>
<tr>
<td>Ion</td>
<td>Intrinsic constant expression</td>
</tr>
<tr>
<td>H$^+$</td>
<td>SOH$^+ + H^+ \rightarrow SOH_2^+$</td>
</tr>
<tr>
<td>SOH$^+ + SO^- \rightarrow SOH^- + SO^-$</td>
<td>3.3±1.0</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>SOH$^+ + Cd^{2+} \rightarrow SOCd^+ + H^+$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>SOH$^+ + Ni^{2+} \rightarrow SOni^+ + H^+$</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>SOH$^+ + Cr^{3+} \rightarrow SOCr^2+ + H^+$</td>
</tr>
<tr>
<td>CrO$_4^{2-}$</td>
<td>SOH$^+ + CrO_4^{2-} + 2H^+ \rightarrow SOH_2CrO_4$</td>
</tr>
</tbody>
</table>

### Table 3. Initial and Boundary Conditions Used in EKGEOCHEM

<table>
<thead>
<tr>
<th>Ion</th>
<th>Initial condition at $x=0$</th>
<th>Boundary condition at $x=L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$^{2+}$</td>
<td>$2.092 \times 10^{-2}$</td>
<td>$\frac{\partial C_{Ni}}{\partial t} = 0.0$</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>$5.46 \times 10^{-3}$</td>
<td>$\frac{\partial C_{Cd}}{\partial t} = 0.0$</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>$0.0$</td>
<td>$\frac{\partial C_{Cr}}{\partial t} = 0.0$</td>
</tr>
<tr>
<td>CrO$_4^{2-}$</td>
<td>$2.117 \times 10^{-2}$</td>
<td>$\frac{\partial C_{Cr}}{\partial t} = 0.0$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>$4.920 \times 10^{-2}$</td>
<td>$\frac{\partial C_{K}}{\partial t} = 0.0$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>$6.130 \times 10^{-2}$</td>
<td>$\frac{\partial C_{Cl}}{\partial t} = 0.0$</td>
</tr>
<tr>
<td>H$^+$</td>
<td>$1.349 \times 10^{-7}$</td>
<td>$10^{-(-0.4177 \ln(i)+3.997)} \approx 10^{0.468 \ln(i)+11.095}$</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>$7.413 \times 10^{-8}$</td>
<td>$10^{-14+(-0.4177 \ln(i)+3.997)} \approx 10^{0.468 \ln(i)+11.095}$</td>
</tr>
</tbody>
</table>

The time $t$ is in hours.

### Modeling Results

In order to assess whether the developed model EKGEOCHEM presented in this study predicts the transport, speciation, and distribution of multiple contaminants under an electric field, the predictions of the model were compared with the results from a series of bench-scale electrokinetic experiments conducted by Al-Hamdan (2002). Four electrokinetic experiments, evaluating 1, 2, 4, and 10 days of treatment time, were conducted to assess the transient behavior of chromium, nickel, and cadmium in kaolin soil during electrokinetic remediation. In all of these tests, the soil was spiked with Cr(VI), Ni(II), and Cd(II) at initial concentrations of 1,000, 500, and 250 mg/kg, respectively. The sources of chemicals used in these tests were potassium dichromate ($K_2CrO_4$) for Cr(VI); nickel chloride ($NiCl_2 \cdot 6H_2O$) for Ni(II); and cadmium chloride ($CdCl_2 \cdot 2H_2O$) for Cd(II). The contaminated kaolin was placed in cylindrical electrokinetic cells. Each cell had an inside diameter of 6.2 cm and a total length of 19.1 cm. The applied constant voltage gradient in all tests was 1 VDC/cm. Deionized water was used as the reservoir fluid at each electrode for all tests. The water flow and pH in both the anode and cathode reservoirs were measured at different time periods throughout the duration of the experiments. At the end of the test duration, the soil was extruded and divided into five sections, and the pH of each section was measured. Contaminants in each section were extracted by performing acid and alkaline digestions, and the concentrations of chromium, nickel, and cadmium in each soil section were then determined by analyzing the extracted solution using an atomic absorption spectrophotometer (Al-Hamdan 2002).

### EKGEOCHEM Input Parameters

The EKGEOCHEM model is used to predict contaminant concentrations, pH, and electroosmotic flow profiles. EKGEOCHEM input parameters were selected to mimic the initial conditions of the bench-scale electrokinetic experiments (Al-Hamdan 2002). The known chemical components in the electrokinetic system
were Ni²⁺, Cd²⁺, Cr³⁺, CrO₄²⁻, K⁺, Cl⁻, H⁺, and OH⁻, and the electrical potential was 1.0 VDC/cm with a total treatment time of 240 h. The length of the contaminated soil sample was 19.1 cm, and it was divided into a total of 40 space elements (i.e., space increment was 0.4475 cm and total number of nodes was 41). The time increment for all simulations was 10 s, and the resulting concentrations profiles were printed every 8,640 time steps (i.e., every 24 h).

The input soil properties (i.e., porosity and tortuosity factor), as well as chemical properties, (i.e., ion diffusion coefficient) were obtained from literature. Kaolin was assumed to have a porosity value of 0.46 (Reddy et al. 2001). In literature, the tortuosity factor for kaolinite varies over a range of 0.12–0.5 (Alshawabkeh 1994). Alshawabkeh and Acar (1994) and Acar et al. (1994) used a tortuosity factor of 0.35 for kaolinite and showed reasonable predictions of acid/base transport. Shapiro and Probstein (1993), used a different definition for tortuosity, which is equivalent to a factor of (1/1.24)², or a tortuosity factor equivalent to 0.65 for kaolinite. Eykholt (1992), similar to Shapiro and Probstein (1993), used a value equivalent to a tortuosity factor of (1/1.5)²=0.44 for kaolinite. The tortuosity factor value used in this study for kaolin is 0.44. The model input values of the diffusion coefficient of charged ions at infinite dilution (Dj) were also obtained from literature (Lide 1993). Adsorption-desorption model input values for contaminants in kaolin are shown in Table 2, and were based on the potentiometric (titration) and adsorption batch experiments conducted using kaolin and the heavy metals Cr(VI), Cr(III), Ni(II), and Cd(II) at temperature 22°C (Al-Hamdan 2002).

The total number of initial and boundary conditions needed to solve the transport equation depends upon the number of the components existing within the soil system. As the model is one dimensional, each component needs one initial condition and two boundary conditions. Initial and boundary conditions used in this study are presented in Table 3. The initial condition for each ion

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**Fig. 4.** Predicted and experimental pH profiles in kaolin during electrokinetic remediation

**Fig. 5.** EKGEOCHEM model predictions during electrokinetic remediation: (a) zeta potential profiles; (b) electroosmotic flow volume

**Fig. 6.** Predicted and experimental concentrations of nickel in kaolin during electrokinetic remediation: (a) concentrations at each space increment; (b) averaged concentrations of consequent eight space increments
The boundary conditions were also selected to represent the laboratory experiments. For a positively charged component, the Dirichlet boundary condition was used at the anode, while the Neumann condition was used at the cathode. If the component was negatively charged, the Dirichlet condition was used at the cathode and the Neumann condition was used at the anode. For H\(^+\) and OH\(^-\) ions, the boundary conditions were assumed to be exponentially changing as a function of time. This assumption was based on the measured pH in the electrode reservoirs of the electrokinetic experiments (Al-Hamdan 2002).

**Model Predictions**

**Prediction of pH Profiles**

Comparisons between the predicted and experimental pH profiles for kaolin after 1, 2, 4, and 10 days of electrokinetic treatment are depicted in Fig. 4. A reasonable agreement between the predicted and the experimental results is observed. Due to the formation of H\(^+\) and OH\(^-\) ions at the anode and the cathode, respectively, an acid front is generated at the anode whereas a base front is generated at the cathode. As H\(^+\) is cationic in nature, it tends to move toward the cathode. On the other hand, the OH\(^-\) is anionic and it tends to move toward the anode. The predicted pH profiles across the kaolin specimen show that the rate of advance of the acid front toward the cathode is faster than that of the rate of advance of the base front toward the anode (i.e., ionic mobility of H\(^+\) is greater than that of OH\(^-\)). The predicted pH profiles also show that the acid front meets the base front within 2 to 4 days at a distance \(x\) between 60 and 70% of the soil length \(L\) from the anode (i.e., \(0.6 < x/L < 0.7\)). Consequently, the acid front drives the base front back toward the cathode. The simulation results showed that after 6 days the pH profile reached a steady state (i.e., the advancing rates of the acid and the base fronts are the same at \(x/L = 0.74\)). Also, a sharp gradient in the pH was generated at the location where the acid and base fronts meet.

**Prediction of Zeta Potential and Electroosmotic Flow**

Although it is difficult to accurately predict the rate of electroosmotic flow because of constantly changing zeta potential and voltage distribution in the specimen during electrokinetic remediation, it is still possible to estimate the electroosmotic flow volume based on the spatial average of the zeta potential and constant voltage gradient. The model predictions for zeta potential profiles across the soil during electrokinetic remediation are presented in Fig. 5(a). The zeta potential values vary across the soil from positive values in the middle to negative values in the region close to the cathode. This variation is attributed to the fact that zeta potential is dependent on the pore water pH, ionic strength, and the specific adsorption of metal ions on the solid particle surface. Small peaks are observed in the zeta potential profiles, and these peaks or wave fronts of zeta potential are formed as a result of the specific adsorption of the partially hydrolyzed metal ions onto the solid particles. Fig. 5(a) shows that at early stages in the process (less than 4 days) the zeta potential...
wave front advances with time toward the cathode. At later stages (more than 4 days), the zeta potential values diminish (i.e., zero or slightly positive) in approximately two-thirds of the soil near the anode, and increase to more negative values in the last third of the soil near the cathode. Also, it was observed that the peak in the zeta potential profiles [Fig. 5(a)], the sharp gradients in the pH profiles (Fig. 4), and the peak in the total metal concentration profiles (as presented in the next section), all occur almost at the same location. Therefore, the location and the magnitude of the zeta potential peak is dependent on the properties of the adsorbed hydrolyzable metal ion, the underlying adsorbing particle surface, pH, and the ionic strength.

A comparison between the model prediction and experimental results for the electroosmotic flow volume is shown in Fig. 5(b). Experimental results and predicted results show some agreement. A better correlation does not exist between the experiment results and the predicted results because the electroosmotic flow volume was estimated based on the spatial average of zeta potential. In addition, the voltage gradient is assumed to be constant across the soil whereas the actual voltage drop near the cathode region becomes steeper with time (Eykholt 1992).

The electroosmotic flow volume variation between the model and experimental results could also be attributed to the fact that EKGEOCHEM neglects the dissolution reaction of kaolin and its electrokinetic implications. The dissolution of kaolin may have electrokinetic implications because of the presence of dissolved species such as aluminum ions, which could generate additional electroosmotic flow or affect the charge on the mineral surface.

Carroll-Webb and Walther (1988) and Eykholt (1992) showed that the dissolution rate of kaolinite at 25°C is a pH-dependent process.

**Prediction of Metals Migration**

The EKGEOCHEM model predicts the distribution, form (i.e., aqueous, adsorbed, or precipitated), and species of metal contaminants in the soil. The modeling results showed that cadmium and nickel species profiles in kaolin during electrokinetic remediation.
nickel have similar behavior in kaolin during electrokinetic remediation (Al-Hamdan 2002). Therefore, only nickel and chromium results are presented herein. As each form of the contaminant affects the total contaminant profile separately, the model results provide a sense of the contribution of each. It is noted that transport occurs only when metal exists in the aqueous form, whereas the adsorbed and precipitated forms of metal remain immobilized in the soil.

Fig. 6 presents a comparison between the model predictions and the experimental results for nickel during electrokinetic remediation. The model predictions show that nickel migrates from the anode toward the cathode in kinematic wave fronts during electrokinetic remediation. Fig. 6 shows that the model results, however, do not directly correlate with the experimental results. This is attributed to the fact that the experimental results were based on five sections of the soil, whereas the model results were based on 40 sections. In other words, the experimental results represent only an average concentration of nickel in each section. Therefore, for a better representation and fair comparison between the model predictions and experimental results for nickel, the predicted values of the 40 space increments were combined to determine average concentration of nickel at five locations i.e., the average concentration of eight consecutive space increments in the model. Fig. 6(b) shows that the average predicted and experimental results of nickel are in agreement. However, any variation between the model predictions and experimental results could be attributed to the simplifications and assumptions made in the developed model such as: (1) assuming that the electrical field (∂E/∂x) is constant with time across the soil; (2) assuming that the surface complexation reactions are applicable in the highly concentrated clay suspensions; (3) neglecting the effect of temperature on the position of the equilibrium; (4) neglecting the Na⁺ and K⁺ adsorption and their adsorption competition with the studied metals (i.e., Ni, Cd, and Cr) over the solid surface; and (5) neglecting the dissolution reaction of kaolin and its electrokinetic implications.

The predicted aqueous (dissolved), adsorbed, and precipitated fractions of nickel in the soil during electrokinetic remediation are shown in Fig. 7. The aqueous nickel in the pore fluid is continuously transported from the anode toward the cathode in the soil. However, during the early stages (less than 4 days), adsorbed nickel existed in the center of the soil cell and precipitated nickel was present in the zone closer to the cathode. Moreover, as the acid front advanced from the anode into the soil over time, desorption and dissolution processes for nickel occurred, resulting in nickel transport toward the cathode. At later stages (10 days), nickel was completely precipitated in the soil region close to the cathode. In addition, it can be seen from Figs. 4 and 7 that the sharp gradients in pH and the peaks in the total metal concentration profiles all occur at the same location (the acid-base interface). The steepness of the pH jump and its influence on the metal distribution of nickel can be clearly seen in Fig. 7. At later stages, approximately 30–40% of the original nickel was found precipitated in a narrow band at the position of the pH jump, where the concentrations reach approximately 10 to 25 times the original concentration (i.e., the isoelectric focusing effect).
species of nickel that existed in the soil during electrokinetic remediation were Ni$^{2+}$ and NiOH$^+$, and the speciation of nickel changes significantly from the anode to the cathode, and also varies with treatment time. The amount and charge of different nickel species affect the transport processes (electromigration) and surface speciation (sorption/desorption), and ultimately control the extent of transport toward the electrodes.

A comparison between the model predictions and experimental results for hexavalent chromium in the soil during electrokinetic remediation is shown in Fig. 9. Unlike the predicted results of nickel, the predicted results of hexavalent chromium showed that it is transported from the cathode toward the anode. Although the general trends are similar, variations between the predicted concentrations of Cr(VI) and experimental results are observed. These variations are mainly attributed to the assumptions and simplifications in the model as stated earlier. In addition, some natural iron existed in the soil (i.e., kaolin used in the experiments was commercial soil and contained 6 ppm of iron), leading to partial reduction of Cr(VI) into Cr(III) under the low pH conditions. Further, Cr(VI) that exited from the soil into the anode reservoir may have reduced to Cr(III) because of the changed redox potential in the anode reservoir (Reddy et al. 2001). However, the model did not account for such reduction of hexavalent chromium within the soil in the absence of any externally introduced reducing agents. The model predicted that hexavalent chromium in the region near the anode (i.e., low pH conditions) is adsorbed and there is no available aqueous chromium to be reduced.

Fig. 10 shows the spatial variation of aqueous, adsorbed, and precipitated fractions of chromium during electrokinetic treatment. It can be seen that, initially, most of the introduced Cr(VI) exists in aqueous form; however, the aqueous fraction decreases and the adsorbed fraction increases as Cr(VI) migrates toward the anode. The removal of Cr(VI) from the soil is retarded by the adsorption to soil surfaces in low pH regions close to the anode. Fig. 11 shows changes in the distribution of different chromium species as Cr(VI) migrates toward the anode at different electrokinetic treatment time periods. As shown, most of the chromium species are anionic complexes and the predominant aqueous species of chromium are HCrO$_4^-$, Cr$_2$O$_7^{2-}$, and CrO$_4^{2-}$. Electromigration of these species toward the anode resulted in the measured residual chromium distribution in the soil.

**Summary and Conclusion**

The developed EKGEOCHEM model incorporates transport processes such as electroosmosis, electromigration, and diffusion, as well as chemical reactions including complex formation, adsorption, and precipitation to predict transport of chromium, nickel, and cadmium in kaolin soil during electrokinetic remediation. The model also predicts spatial and temporal changes in the distribution of metal fractions (i.e., aqueous, adsorbed, and precipitated) and metal species within the soil during treatment.
The model predictions and their comparisons with the laboratory bench-scale electrokinetic experimental results demonstrate that very sharp changes in the pH, zeta potential, and species concentration profiles exist in kaolin. These changes, in the form of kinematic wave fronts, are observed with increasing treatment time. The contribution of electroosmosis may be insignificant for the removal of metal contaminants from low buffering soils such as kaolin. Results show that metal ions electromigrate toward the oppositely charged electrodes, but they accumulate in a narrow region in the soil near the anode or the cathode instead of migrating all the way to the cathode or anode. Such accumulation occurs due to a sharp jump in pH that develops relatively rapidly after applying the voltage gradient across the electrodes. The metals are typically in the form of cations deposited on the acid or anode side of the pH jump, and in the form of anionic complexes on the alkaline or cathode side. Consequently, the cationic metals such as nickel and cadmium species electromigrate toward the pH jump. Because the solubility of these metals is reduced at the intermediate pH values in this region, they accumulate as precipitates. The location of the pH jump advances toward the cathode as the treatment time increases, but only up to a certain distance, after which the pH profile and associated contaminant concentration profiles reach a steady condition (remain unchanged). Changes in the distribution of different fractions (aqueous, adsorbed, and precipitated) and the speciation of contaminants help to understand the major hindering mechanisms for the removal of heavy metals from soil during electrokinetic remediation. The model predictions may also be utilized to determine optimal conditions for enhanced electrokinetic remediation.

Overall, the model predictions and experimental results were in agreement for cationic metals (nickel and cadmium), but some variations are observed for chromium (an anionic metal). The difference in model predictions and experimental results is attributed to assumed constant voltage gradient across the soil, neglected temperature effects on reactions and zeta potential, neglected redox reactions with naturally occurring reducing agents, and neglected dissolution of soil constituents. In addition to addressing these assumptions and simplifications, overlapping of diffuse layers in the highly concentrated clay suspensions may also be required for accurate modeling of electrokinetic remediation systems.

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