

A mathematical model for the electrokinetic remediation of contaminated soil

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Abstract

We propose to develop a mathematical model for the electrokinetic remediation of contaminated soil. We assume that the contaminants are mostly heavy metals, water is in excess, the dissociation-association of water into hydrogen and hydroxyl ions is rapid, and that electroosmosis is insignificant when compared to electromigration as a transport mechanism. Steady-state solutions for the model are derived and results of the numerical simulations are given to show that heavy metals in the soil are removed by this method in the long run.

Keywords: Electrokinetic remediation; Contaminated soil

1. Introduction

Heavy metallic ions such as cadmium, chromium and lead are hazardous to humans' health. They can frequently be found in the groundwater of contaminated sites reacting with chemicals in the solutions, or, they can form chemical complexes with minerals such as iron and manganese oxides inside the soil and reside on the mineral surface [1]. It is important to have these ions removed.

The remediation of contaminated soil and groundwater in the subsurface have been and will continue to be the most costly and time consuming part of any site cleanup. In situ technologies for removing contaminants are preferred because they are more economical and also because of the declining number of land-fill sites which accept toxic material. In addition, such methods cause minimal environmental disruption.

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One way of treating the soil is to ‘wash’ out the contaminated groundwater and the metallic ion complexes adhered to the soil surface (flushing). Fine-grained soil has greater ability to adsorb contaminants and flushing is not an efficient method because the hydraulic gradient required to pump water through fine-grained soil is very high. Therefore, alternative methods have to be developed.

An alternative method is to insert electrodes into the soil and apply an electric potential across the electrodes. The electric field causes the metallic ions to migrate to the cathode, thus accelerating the decontamination process. This is known as electrokinetic soil remediation [2]. This process is found to be relatively insensitive to the pore size of the soil and hence suitable for treatment of fine-grained soil. Pilot experiments and large scale in situ trials have been conducted using this method [3–6]. A summary of the advances in the field until 1993 is presented in Ref. [7].

The principal mechanisms for the electrokinetic transport process are diffusion, electromigration, convection, electroosmosis and isoelectric focusing. Diffusion and electromigration will be explained later in the next section. As our focus here is on fine-grained soil remediation, the fluid flow is very slow and we shall assume that the convection velocity is zero. Electroosmosis is due to the drag interaction between the bulk of the liquid in the pore and a thin layer of charged fluid next to the pore wall [7, 8]. Depending on the circumstances, electroosmosis may or may not be important compared to electromigration. If the soil pH is low and the contaminants are charged, then very little electroosmosis transport occurs [8]. We shall assume this to be the case in our paper. Finally, isoelectric focusing is caused by a sharp jump in the soil pH moving from the anode to the cathode side. The metals near the cathode may become negatively charged, move towards the anode and eventually accumulate near the pH jump resulting in isoelectric focusing. One can prevent this from happening by rinsing the cathode frequently to wash away the hydroxyl ions generated by electrolysis [3].

Modeling electrokinetic soil remediation involves understanding the above transport mechanisms, interactions of the metallic ions with the minerals in the soil (sorption), and what happens at the electrodes. The electrodes are usually surrounded by a circulation system where fluids are passed through to wash out the contaminants. The contents of the fluid are adjusted so that the circulation system also acts as a pH control. We consider both cases in this paper, with or without a circulation system. The major difference between the two cases is the boundary conditions imposed at or near the electrodes which we discuss in Section 4. Section 5 contains the results of our numerical simulation and Section 6 contains a summary of the paper.

2. The mathematical model

Consider a mixture of charged particles, which we refer to as ions or species, inside the groundwater surrounding the contaminated soil. Two electrodes are placed inside the soil and an electric potential is maintained across them throughout the transport process.

Let the molar concentrations of the charged species be denoted by u_1, \dots, u_m and let the electric potential be denoted by ϕ . Each species has a characteristic mobility

constant μ_i such that its velocity under the influence of the electric field is given by $-\mu_i z_i \nabla \phi$ where z_i is its charge. The charge z_i must be integer valued and may be positive, negative or zero. The species also diffuse with diffusion constant $d_i > 0$. Assuming that the transport of ions are governed by the dilute aqueous solution theory [4, 8, 9], the flux of species i is given by $N_i = -d_i \nabla u_i - \mu_i z_i u_i \nabla \phi$. The two terms on the right-hand side of N_i model diffusion and electromigration, respectively. From the conservation of species, $u_i(x, t)$ satisfies the transport equation

$$\frac{\partial u_i}{\partial t} = -\operatorname{div} N_i + R_i, \quad i = 1, \dots, m, \quad (1)$$

in a bounded region Ω which contains the contaminated soil. The term R_i in (1) denotes the rate of production of species i due to reactions. In the definition of N_i , we shall assume that the Nernst–Einstein relation $\mu_i = \mu d_i$ holds for $i = 1, \dots, m$ where μ is a positive constant. By absorbing μ into ϕ , we may assume that $\mu = 1$.

Remark 2.1. The symbol div in Eq. (1) is the divergence operator. Suppose $\mathbf{f} = (f_1, f_2, \dots, f_n)$ is a vector field defined in R^n , then

$$\operatorname{div} \mathbf{f} = \frac{\partial f_1}{\partial x_1} + \frac{\partial f_2}{\partial x_2} + \dots + \frac{\partial f_n}{\partial x_n}.$$

Remark 2.2. Since the soil particles hinder the diffusion and migration of ions, both the diffusion coefficient d_i and ionic mobility μ_i as measured in pure aqueous phase have to be reduced to some effective values when applied to our situation. Such reduction factors are related to the porosity and tortuosity factors of the soil [8].

The electric potential $\phi(x, t)$ is an unknown function in Eq. (1). It satisfies the Poisson's equation,

$$\varepsilon \Delta \phi = -e \sum_{i=1}^m z_i u_i \quad (2)$$

where Δ is the Laplace operator, $e > 0$ is the molar charge and $\varepsilon > 0$ is the permittivity of the solvent. Since the permittivity is small upon non-dimensionalization of the Eq., (2) is usually replaced by the electroneutrality condition

$$\sum_{i=1}^m z_i u_i = 0. \quad (3)$$

We shall study Eqs. (1) and (3) in this paper.

The electric potential ϕ can be determined if all the u_i 's are known. To see this, multiply Eq. (1) by z_i and sum over i . Then the electroneutrality condition and $\sum z_i R_i = 0$ (charge conservation) imply that $-\operatorname{div} \sum z_i N_i = 0$. This is called the current equation which can be written as

$$a(x, t) \Delta \phi + \mathbf{b}(x, t) \cdot \nabla \phi + c(x, t) = 0$$

where $a = \sum z_i^2 d_i u_i$, $b = \sum z_i^2 d_i \nabla u_i$, and $c = \sum z_i d_i \Delta u_i$. If there is no circulation system, then the boundary conditions for the hydrogen and hydroxyl ions may be used as the boundary conditions for ϕ (see (11)). If there is a circulation system, then ϕ satisfies Dirichlet boundary conditions. Thus, ϕ can be determined for each $t > 0$ if we know all the u_i 's.

Remark 2.3. Eqs. (1)–(3) have also been used by the authors to study an electrochemistry model [10, 11] and by the first author to study electroplating [12].

We now explain the term R_i in Eq. (1) which models the formation of complexes due to interactions of the metallic ions and the minerals in the soil [1, 13]. For simplicity we restrict ourselves to a single reaction mechanism. Realistic chemistry can be incorporated in more sophisticated models. (In Ref. [1], a two-reaction mechanism was suggested. Usually such mechanism can explain the rapid retention and slow release of heavy metallic ions from the soil [14].)

Let SOH denote iron oxide or manganese oxide in the soil. A typical metallic ion like cadmium will react with them according to the reaction



In the above reaction, SOCd^+ represents precipitated complexes on the mineral surface. Assuming mass action kinetics, its reaction rate $r_1 = k_1[\text{SOH}][\text{Cd}^{2+}] - k_2[\text{SOCd}^+][\text{H}^+]$ where $k_1, k_2 > 0$. If the hydrogen ion concentration is increased, it will drive the above reaction to produce more soluble cadmium ions. This will allow easier extraction of metallic ions from the soil. In some laboratory experiments, this is achieved by purging acid solution around the cathode to increase hydrogen ion concentration [4].

Besides a possible external supply of hydrogen ions, there are two mechanisms that hydrogen ions can be generated or consumed in our model. One is through dissociation–association of water molecules in the bulk of the groundwater and the other is through electrolysis at the boundary electrodes. This second mechanism affects the boundary conditions and we will discuss it after the governing equations have been formulated.

The dissociation–association reaction of the water molecules is represented by



We shall denote the reaction rate by r_w . Assuming mass action kinetic, $r_w = K_f[\text{H}_2\text{O}] - K_r[\text{H}^+][\text{OH}^-]$ where K_f and K_r are positive constants.

We are now ready to propose our model for the electrokinetic remediation of contaminated soil. All the ions in the aqueous phase and solid phase will be accounted for in this model. Let u_1 be the concentration of water, u_2 be the concentration of hydrogen ion, u_3 be the concentration of hydroxyl ion, u_4 be the concentration of cadmium ion, and u_5 be the concentration of some other inert ion, say chloride. For simplicity, we shall assume that these are the only ions in the aqueous phase. Let u_6 be the concentration of SOH, and u_7 be the concentration of SOCd^+ . These are the only solid phase ions, which do not diffuse or migrate. Assuming the above, R_i in Eq. (1) can

be defined through r_i and r_w . The governing equations for our model are

$$\frac{\partial u_1}{\partial t} = -\operatorname{div} N_1 - r_w, \quad (6a)$$

$$\frac{\partial u_2}{\partial t} = -\operatorname{div} N_2 + r_1 + r_w, \quad (6b)$$

$$\frac{\partial u_3}{\partial t} = -\operatorname{div} N_3 + r_w, \quad (6c)$$

$$\frac{\partial u_4}{\partial t} = -\operatorname{div} N_4 - r_1, \quad (6d)$$

$$\frac{\partial u_5}{\partial t} = -\operatorname{div} N_5, \quad (6e)$$

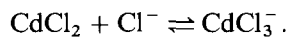
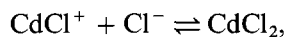
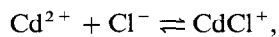
$$\frac{\partial u_6}{\partial t} = -r_1, \quad (6f)$$

$$\frac{\partial u_7}{\partial t} = r_1, \quad (6g)$$

$$\sum_{i=1}^7 z_i u_i = 0, \quad (6h)$$

where $z_1 = 0$, $z_2 = 1$, $z_3 = -1$, $z_4 = 2$, $z_5 = -1$, $z_6 = 0$, and $z_7 = 1$. It should be pointed out that ϕ is unknown in (6) so that there are eight equations and eight unknowns.

Remark 2.4. Besides (4), other reactions may occur in the groundwater in the soil and cadmium may occur in other forms besides cadmium ions (see Ref. [15, Chapter 6]). For example, cadmium may react with chloride ions according to the reactions



If we include the above reactions in our model, then we have to introduce new variables for the species CdCl^+ , CdCl_2 , CdCl_3^- , write down the reaction rates for the three reactions and include them in the calculations of R_4 and R_5 . The results will be three additional equations in (6) and equations (6d), (6e) and (6h) have to be modified. However, there is no conceptual difference between analyzing the new system and (6). With proper boundary conditions, Cd^{2+} , CdCl^+ , CdCl_2 and CdCl_3^- can all be shown to be removed in the long run.

3. Refined model

Eqs. (6) are derived using the dilute solution theory. Since water is present in excess and may be regularly replenished, dilute solution theory may not hold. However, it does allow us to assume that water concentration is constant. In addition, the reaction rate $r_w = K_f u_1 - K_r u_2 u_3$ is very rapid. Hence, equilibrium between water, hydrogen ion, and hydroxyl ion is attained instantaneously resulting in the equation

$$[H^+][OH^-] = K_w. \quad (7)$$

where K_w is a constant (at isothermal condition) that can be measured experimentally.

Let $\varepsilon > 0$ be a small parameter. (For example, we can take ε to be the ratio of the total initial concentration of cadmium ions to that of the water molecules.) Since water is in excess, we may assume that its expansion in ε is $u_1 = K_1/\varepsilon + O(1)$ where K_1 is a positive constant and $O(1)$ denotes a generic function bounded in x, t . If we substitute this expansion into (6a), we see that $r_w = O(1)$. Thus $r_w = 0$ to order $O(1/\varepsilon)$. From the definition of r_w , $u_2 u_3 = (K_f K_1)/(K_r \varepsilon) \equiv K_w$ which is Eq. (8a). The concentrations of hydrogen and hydroxyl ions are of the magnitude $O(1)$ so that Eqs. (6b) and (6c) are complicated by the fact that they involve the $O(1)$ term of r_w . To avoid this, we subtract the two equations to obtain Eq. (8b) below. Also, from (6),

$$\frac{\partial}{\partial t} (u_6 + u_7) = 0$$

so that $u_6(x, t) + u_7(x, t) = g(x)$ where g is determined by the initial data. This allows us to drop the equation for u_6 in (6). Putting everything together, the governing equations for our refined model are

$$u_2 u_3 = K_w \quad (8a)$$

$$\frac{\partial}{\partial t} (u_2 - u_3) = -\operatorname{div} N_2 + \operatorname{div} N_3 + r_1 \quad (8b)$$

$$\frac{\partial u_4}{\partial t} = -\operatorname{div} N_4 - r_1 \quad (8c)$$

$$\frac{\partial u_5}{\partial t} = -\operatorname{div} N_5 \quad (8d)$$

$$\frac{\partial u_7}{\partial t} = r_1 \quad (8e)$$

$$u_2 - u_3 + 2u_4 - u_5 + u_7 = 0 \quad (8f)$$

where $u_6 = g(x) - u_7$ and $r_1 = k_1 u_6 u_4 - k_2 u_7 u_2$. Note that ϕ is unknown in (8) so that there are six equations with six unknowns. We now turn to the boundary conditions.

4. The boundary conditions

Eqs. (8) have to be coupled with suitable initial and boundary conditions. Initial conditions must satisfy (8a) and the electroneutrality condition (8f). As for the boundary conditions, we assume that the contaminated region Ω is two-dimensional (see Fig. 1). If there is a circulation system, then there is an annulus surrounding the electrodes as shown in Fig. 1. Inside the annulus is the circulating fluid and Γ_1, Γ_2 correspond to the interface between the soil and the annulus. If there is no circulation system, then the annulus should be removed in Fig. 1 and Γ_1, Γ_2 correspond to the surface of the cathode and anode, respectively.

The following facts are true regardless of whether there is a circulation system around the electrodes. First, since the equations governing the solid phase ions u_6 and u_7 do not involve any spatial derivatives, no boundary condition is needed for them. However, u_6, u_7 can still depend on x . Second, at the outer boundary of Ω , we assume that all the aqueous ions satisfy zero-flux boundary conditions; i.e. $N_i \cdot \mathbf{n} = 0$ for $i = 2, 3, 4, 5$ and $x \in \Gamma_3$ where \mathbf{n} is the outward unit normal on Γ_3 .

We now consider the boundary conditions near the electrodes. We first assume that there is no circulation system. Then at the surface of the anode, all aqueous ions except hydrogen and hydroxyl ions satisfy zero-flux boundary conditions. At the surface of the cathode, the same is true except for cadmium ions. When the cadmium ions arrive at the cathode, we assume that they are removed by electroplating, ($\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd(s)}$), so that $u_4 = 0$ for $x \in \Gamma_1$.

The predominant reaction at the electrodes is electrolysis [8]. These reactions are represented by

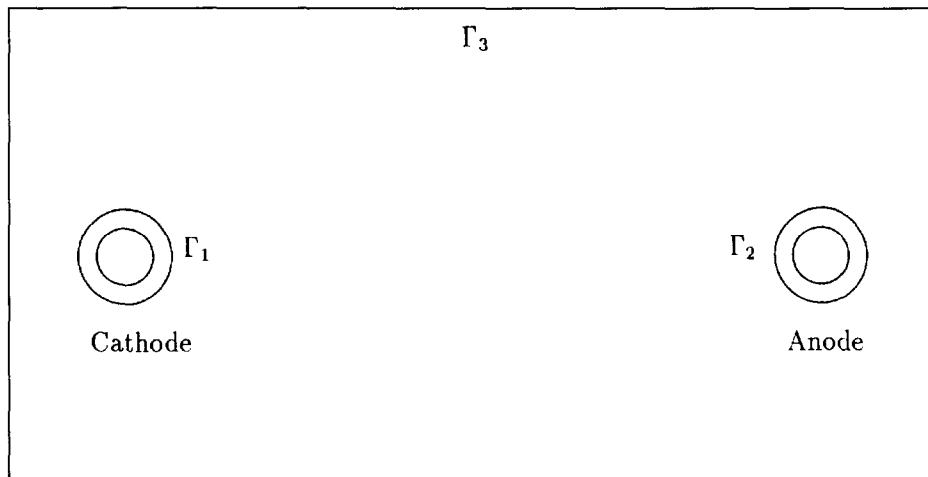


Fig. 1. Cross section of contaminated site Ω with a circulation system.

at the anode and



at the cathode. Since both oxygen and hydrogen gas escape once they are formed, the above reactions may be considered as irreversible. These reactions are modeled by the Butler-Volmer kinetics (see Case 1 below) which will provide the boundary conditions for water, hydrogen, and hydroxyl ions around the electrodes. We shall discuss Butler-Volmer kinetics in the appendix.

Next we consider the case when there is a circulation system. Cadmium ions are washed away by the circulation system and hence $u_4 = 0$ at the interface. In order to avoid introducing new species into our model, we assume that the circulating fluid contains hydrochloric acid which is completely ionized: $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$. Let the concentrations of the hydrogen, hydroxyl, and chloride ions in the circulating fluid be denoted by u_2^0 , u_3^0 , and u_5^0 , respectively. Since u_7 is governed by an ordinary differential equation which does not require any boundary condition, u_7 can be solved and the solution depends on the concentrations of the other species. Knowing the pH of the fluid will allow us to calculate u_2^0 which we can use to find u_3^0 , u_5^0 through the equations $u_2^0 u_3^0 = K_w$ and $u_2^0 - u_3^0 - u_5^0 + u_7^0 = 0$. As mentioned earlier, u_7^0 at the interface is known in terms of other species concentrations. Thus, hydrogen, hydroxyl, and chloride ions satisfy Dirichlet type boundary conditions. Finally, from experimental measurements, we may assume that ϕ is known at the interface. We now summarize the boundary conditions. Let E_1 and E_2 be the applied voltage on the electrodes at Γ_1 and Γ_2 , respectively, and let $E_2 > E_1$.

Case 1. No circulation system

$$(N_2 - N_3) \cdot \mathbf{n} = 4g_1(\phi(x, t) - E_1) \quad \text{at } \Gamma_1, \quad (11a)$$

$$(N_2 - N_3) \cdot \mathbf{n} = -4g_2(E_2 - \phi(x, t)) \quad \text{at } \Gamma_2, \quad (11b)$$

$$N_4 \cdot \mathbf{n} = 0 \quad \text{at } \Gamma_2, \quad u_4 = 0 \quad \text{at } \Gamma_1, \quad (11c)$$

$$N_5 \cdot \mathbf{n} = 0 \quad \text{at } \Gamma_1, \Gamma_2, \quad (11d)$$

$$(N_2 - N_3) \cdot \mathbf{n} = 0, \quad N_4 \cdot \mathbf{n} = 0, \quad N_5 \cdot \mathbf{n} = 0 \quad \text{at } \Gamma_3, \quad (11e)$$

where $g_1(\phi) = \exp(\alpha_1 \phi) - \exp(-\alpha_2 \phi)$, $\alpha_1, \alpha_2 > 0$ and g_2 is similar function with different α_1, α_2 .

Case 2. With circulation system containing HCl:

$$u_2 = u_2^0, \quad u_3 = u_3^0, \quad u_4 = 0, \quad u_5 = u_5^0 \quad \text{at } \Gamma_1 \quad \text{and} \quad \Gamma_2, \quad (12a)$$

$$\phi = E_1 \quad \text{at } \Gamma_1, \quad \phi = E_2 \quad \text{at } \Gamma_2, \quad (12b)$$

$$(N_2 - N_3) \cdot \mathbf{n} = 0, \quad N_4 \cdot \mathbf{n} = 0, \quad N_5 \cdot \mathbf{n} = 0 \quad \text{at } \Gamma_3. \quad (12c)$$

Remark. Only three boundary conditions are needed for Eqs. (8) at each Γ_i , $i = 1, 2, 3$ because none is needed for u_7 and the two algebraic equations. In Case 2 above, the boundary conditions for u_2 , u_3 and u_5 constitute only one independent boundary condition since $u_2 u_3 = K_w$ and $u_2 - u_3 - u_5 + u_7 = 0$.

5. Steady-state solutions

The steady-state solutions for Eqs. (8) are functions $u_i(x)$, $i = 2, 3, 4, 5, 7$ and $\phi(x)$ which satisfy the equations

$$u_2 u_3 = K_w, \quad (13a)$$

$$-\operatorname{div} N_2 + \operatorname{div} N_3 + r_1 = 0, \quad (13b)$$

$$-\operatorname{div} N_4 - r_1 = 0, \quad (13c)$$

$$-\operatorname{div} N_5 = 0, \quad (13d)$$

$$r_1 = 0, \quad (13e)$$

$$u_2 - u_3 + 2u_4 - u_5 + u_7 = 0, \quad (13f)$$

and the boundary conditions described in section 4.

Case 1. No circulation system

Let $v = u_5 e^{-\phi}$. Then $\nabla v = -e^{-\phi} N_5$. Since u_5 satisfies zero-flux boundary conditions at $\Gamma_1, \Gamma_2, \Gamma_3$, v satisfies the condition $\nabla v \cdot \mathbf{n} = 0$ at the same boundaries. Furthermore, Eq. (13d) can be recast as $\operatorname{div}(e^{-\phi} \nabla v) = 0$. Multiplying this equation by v and integrating over Ω , we have, by the Green's identity,

$$\int_{\Omega} e^{\phi} |\nabla v|^2 \, dx = 0.$$

Therefore, $\nabla v = \mathbf{0}$ which implies that v is a constant and $u_5 = C e^{\phi}$. To determine C , integrate (8d) over Ω . From the divergence theorem and our boundary conditions, we have

$$\frac{\partial}{\partial t} \int_{\Omega} u_5 \, dx = - \int_{\Omega} \operatorname{div} N_5 \, dx = - \int_{\Gamma_1 \cup \Gamma_2 \cup \Gamma_3} N_5 \cdot \mathbf{n} \, dS = 0.$$

Therefore, $\int_{\Omega} u_5 \, dx$ is independent of time. Integrating $u_5 = C e^{\phi}$ over Ω , we have $C = \int_{\Omega} u_5(x, 0) \, dx / \int_{\Omega} e^{\phi(x)} \, dx$.

To continue, since $r_1 = 0$, Eq. (13c) reduces to $-\operatorname{div} N_4 = 0$. Let $v = u_4 e^{2\phi}$, then $v = 0$ at Γ_1 and $\nabla v \cdot \mathbf{n} = 0$ at Γ_2 and Γ_3 . Similar argument as above can be used to show that $v \equiv 0$. Hence, $u_4 \equiv 0$.

From $r_1 = 0$ and its definition, $u_7 u_2 = 0$. Since $u_2 \neq 0$, we have $u_7 = 0$. Eqs. (13a) and (13f) now imply that

$$\begin{aligned} u_2 &= (C e^\phi + \sqrt{C^2 e^{2\phi} + 4K_w})/2, \\ u_3 &= (-C e^\phi + \sqrt{C^2 e^{2\phi} + 4K_w})/2. \end{aligned} \quad (14)$$

From (13b), ϕ satisfies the equation

$$(d_2 u_2 + d_3 u_3) \Delta \phi + \nabla(d_2 u_2 + d_3 u_3) \cdot \nabla \phi + (d_2 \Delta u_2 - d_3 \Delta u_3) = 0.$$

The boundary conditions for ϕ are given by (11a) and (11b) where

$$N_2 - N_3 = -\nabla(d_2 u_2 - d_3 u_3) - (d_2 u_2 + d_3 u_3) \nabla \phi.$$

One can express u_2, u_3 in terms of ϕ in the above two equations using (14) and obtain an integro-differential equation in ϕ because C contains $\int_{\Omega} e^\phi dx$.

Case 2. With circulation system containing HCl

The steady-state solutions are $u_2 = u_2^0, u_3 = u_3^0, u_4 = 0, u_5 = u_5^0$ in Ω and ϕ satisfies the equation $\Delta \phi = 0$ in $\Omega, \nabla \phi \cdot \mathbf{n} = 0$ at $\Gamma_3, \phi = E_1$ at Γ_1 , and $\phi = E_2$ at Γ_2 . Note that the boundary condition $\nabla \phi \cdot \mathbf{n} = 0$ at Γ_3 comes from $(N_2 - N_3) \cdot \mathbf{n} = 0$ at Γ_3 .

6. Numerical simulation of the refined model

In this section, we document the algorithm and results of our numerical simulation for Eqs. (8) under the two types of boundary conditions (11) and (12) in the one-dimensional case. We assume that Ω is the unit interval $[0, 1]$ with Γ_1 being $x = 0$ and Γ_2 being $x = 1$. The voltages at $x = 0$ and $x = 1$ are E_1 and E_2 , respectively, with $E_2 > E_1$.

Suppose $u_i, i = 2, 3, 4, 5, 7$ are known at time t . We would like to find ϕ at time t and use it to find $u_i, i = 2, 3, 4, 5, 7$ at time $t + \Delta t$.

Case 1. No circulation system

(i) From the current equation (see Section 2 after (3)), we have

$$\sum_{i=2}^5 d_i z_i \frac{\partial u_i}{\partial x} + \left(\sum_{i=2}^5 d_i z_i^2 u_i \right) \frac{\partial \phi}{\partial x} = I(t) \quad (15)$$

where $I(t)$ is the current at time t . Rearranging and integrating this equation from 0 to 1, we have

$$\phi(1, t) - \phi(0, t) = I(t) \int_0^1 \frac{1}{\sum_{i=2}^5 d_i z_i^2 u_i} dx - \int_0^1 \frac{\sum_{i=2}^5 d_i z_i \frac{\partial u_i}{\partial x}}{\sum_{i=2}^5 d_i z_i^2 u_i} dx. \quad (16)$$

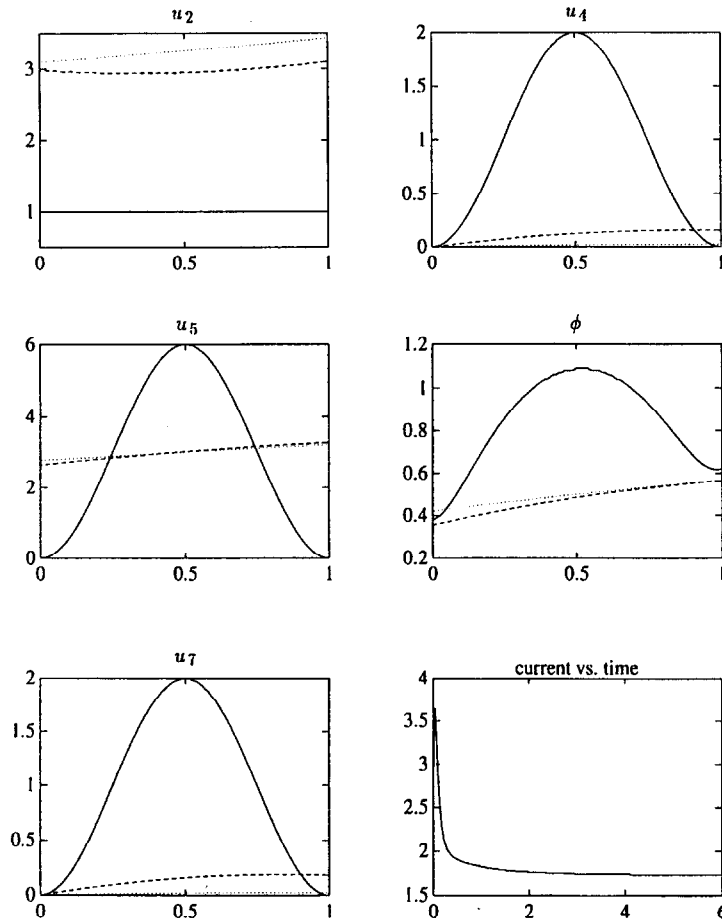


Fig. 2. Case 1: No circulation system. The solid, dash and dot curves in each but the last plot represent the solutions on the domain $[0, 1]$ at $t = 0, 3, 6$, respectively.

The terms inside the integrals are known since all the u_i 's are known. This together with Eqs. (11a) and (11b) constitute 3 equations for the 3 unknowns $\phi(0, t)$, $\phi(1, t)$ and $I(t)$. After solving for these unknowns, $\phi(x, t)$ can be completely determined at time t .

(ii) $u_7(x, t + \Delta t)$ is found by advancing the ordinary differential Eq. (8c) for a time Δt with known initial condition $u_7(x, t)$.

(iii) We can advance Eq. (8c) for time Δt from initial condition $u_4(x, t)$ and boundary conditions (11) to obtain $u_4(x, t + \Delta t)$. Throughout this process, we let ϕ to be the $\phi(x, t)$ found in step (i). To avoid numerical instability, fully implicit scheme should be implemented on the diffusion term.

(iv) A similar treatment as in (iii) gives $u_5(x, t + \Delta t)$.

(v) With u_4 , u_5 and u_7 known at time $t + \Delta t$, then $u_2(x, t + \Delta t)$ and $u_3(x, t + \Delta t)$ can be found from algebraic Eqs. (8a) and (8f).

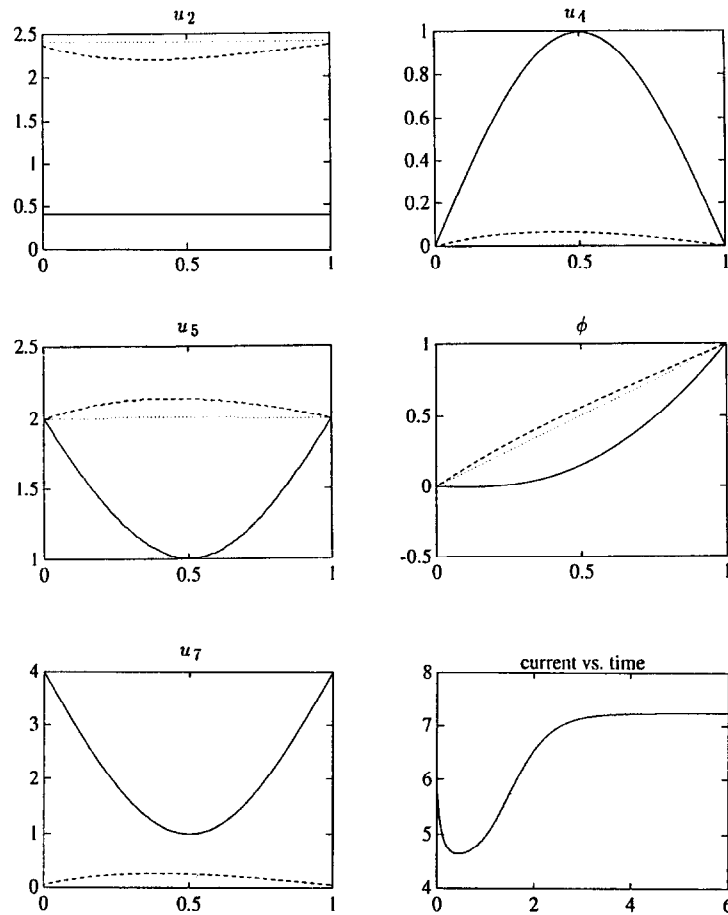


Fig. 3. Case 2: With circulation system containing HCl. The solid, dash and dot curves in each but the last plot represent the solutions on the domain $[0, 1]$ at $t = 0, 3, 6$, respectively.

Case 2. with circulation system containing HCl

Since $\phi(0, t) = E_1$ and $\phi(1, t) = E_2$, $I(t)$ can be calculated from Eq. (16). Then $\phi(x, t)$ can be completely determined. Steps (ii)–(v) are similar to the algorithm with No Circulation System with obvious changes of boundary conditions for u_4 and u_5 .

We now document the numerical results for Cases 1 and 2 in Figs. 2 and 3, respectively. Since our purpose is to illustrate how the algorithm works rather than compare the results with actual data, we let, for simplicity, $g_1(\phi) = g_2(\phi) = \phi$, $k_1 = k_2 = 1$, $K_w = 1$, $E_1 = 0$, $E_2 = 1$, $d_2 = 2$, $d_3 = 1$, $d_4 = 0.5$ and $d_5 = 1$. We take the spatial mesh size $\Delta x = 0.01$ and the time step $\Delta t = 0.001$. In all numerical results we tested, the unsteady-state solutions will tend to the steady-state solutions given in Section 5 as time becomes large. Our numerical results also show that the cadmium ions are ultimately removed from the soil.

7. Summary

In this paper, we developed a mathematical model for the electrokinetic remediation of soil contaminated with heavy metals. We assumed that diffusion and electromigration are the dominant transport forces for the aqueous ions in the soil, wrote down equations for both the aqueous and solid ions and arrived at a system of partial and ordinary differential equations coupled with an algebraic Eq. (6h). The electric potential ϕ is an unknown function in this system. We then assumed that water is in excess and that the hydrogen and hydroxyl ions satisfy (7) in the soil resulting in an overdetermined system. Perturbation technique was employed to resolve this issue, resulting in Eqs. (8).

One of the main contributions of this paper is to make clear the boundary conditions for the model. We consider both cases, with and without a circulation system around the electrodes. We state the boundary conditions for each case in Section 4 and derived the steady-state solutions in Section 5. Numerical simulations were carried out to show that solutions of (8) actually converge to their steady states as time goes to infinity. According to our model, cadmium ions are ultimately removed from the soil. This is because of our assumption that cadmium ions are removed at the cathode. Isoelectric focusing effect is therefore not observed in our model. However, in practice, the electroplating reaction may be slow due to high concentration of hydroxyl ions near the cathode. Then isoelectric focusing of cadmium ions may be observed for a long time before they are ultimately removed.

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Appendix

We now explain the boundary conditions (11a) and (11b). To do that, we have to consider electrical double layer which is a thin layer immediately adjacent to the electrode surface. In electrode kinetics [16], one often assumes that the following Butler-Volmer kinetics holds in the double layer

$$i = i_0[\exp(\alpha_a \eta_s) - \exp(-\alpha_c \eta_s)]. \quad (\text{A.1})$$

Here, i_0 is the exchange current density, η_s is the surface overpotential and α_a, α_c are known constants. Let us consider what happens at the anode (Γ_2) in our model. According to (9), water undergoes irreversible electrolysis reaction. Let E_1, E_2 be the externally prescribed electrode potentials at Γ_1 and Γ_2 , respectively. Then the surface overpotentials at the cathode and anode are given by $\phi(x, t) - E_1$ at Γ_1 and

$E_2 - \phi(x, t)$ at Γ_2 , respectively. At the anode, the exchange current density i_0 is proportional to the density of the reactive species which is water. Since water is in excess, we may assume that i_0 is a constant. The hydroxyl ion is non-reactive at the anode. Therefore, the boundary conditions at the anode are

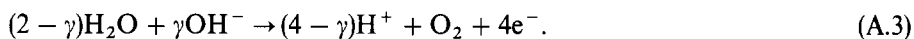
$$\begin{aligned} N_2 &= -4g_2(E_2 - \phi(x, t)) \quad \text{at } \Gamma_2, \\ N_3 &= 0 \quad \text{at } \Gamma_2, \end{aligned} \tag{A.2}$$

where g_2 is the function defined on the right-hand side of (A.1).

In our refined model, we have to modify condition (A.2) in order to adopt the additional constraint (7). Physically (7) holds because the reaction rate r_w of (5) is very fast. Hence, upon production of hydrogen ions at the anode, some of the excess hydrogen ions will combine with the hydroxyl ions almost immediately inside the double layer. This association reaction in the double layer stops only when there is equilibrium between water, hydrogen and hydroxyl ions. Hence, constraint (7) will be enforced. We can therefore superimpose reaction (9) with



to obtain



From (A.3), the boundary conditions at the anode are

$$\begin{aligned} N_2 &= -(4 - \gamma)g_2(E_2 - \phi(x, t)) \quad \text{at } \Gamma_2, \\ N_3 &= \gamma g_2(E_2 - \phi(x, t)) \quad \text{at } \Gamma_2. \end{aligned} \tag{A.4}$$

In the above reactions, γ is a function of time and is chosen so that Eq. (7) is satisfied. Subtracting the second equation from the first in (A.4) yields Eq. (11b). Eq. (11a) can be derived in a similar manner.

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