Electric current and potential variations during electrokinetic removal of heavy metal from aquifer

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Abstract

The electrokinetic method for the remediation of contaminated aquifers is realized by applying a fixed low voltage direct current between anode and cathode which are set into the contaminated zone. The electric current and electric potential between anode and cathode is the important operational variables for the electrokinetic remediation. However, the variations of these variables have not been cleared, because this method is relatively new and is an innovative technique.

Depending on the time variation of the electric current, the removal process can be divided into the first stage and the second one. In the first stage the electric current increases with time, but in the second stage it is almost unchangeable. The distribution of electric potential between electrodes gradually becomes higher and higher (decrease in electric resistance) with time, although the applied voltage between the electrodes is maintained constant.

1 Introduction

Groundwater is utilized as one of the important water resources as well as surface water. However, groundwater in many aquifers has been seriously contaminated due to the migration of various hazardous organic and inorganic chemicals from the disposal of municipal and industrial wastes. The increase in need for water supply urges to clean up the contaminated groundwater and soil immediately.

Many new techniques for decontaminating groundwater and soil have been
presented. Among them, one of the most cost-effective technologies, as an in situ process, is electrokinetic decontamination. However, the study on the electrokinetic remediation is not only experimentally but also theoretically insufficient. This is because the technique is relatively new and innovative for soil remediation, although the electrokinetic method has been utilized in civil engineering for dewatering from soil. Only a few studies ([1], [2], [3], [6], [7], [8], [9] and [10]) can be utilized to construct the mathematical model of the electrokinetic remediation.

The electrokinetic method is realized by setting electrodes into the treatment zone of aquifer, which is saturated with groundwater, and by applying a fixed low voltage direct current between the electrodes (anode and cathode). Schematic representation of this method is given in Figure 1.

![Figure 1. Schematic Representation of Electrokinetic Remediation](image)

This study aims to develop a mathematical model based on physicochemical mass transport theory and to simulate the nonsteady characteristics of these operational variables especially the variations of the electric current and the distribution of electric potential in the treatment zone. The model developed here is composed of a kind of advective diffusion equation and its boundary conditions. The equation contains the electromigration of ionized heavy metal and the aqueous-phase reaction (dissociation in pore water) and interface reactions (sorption between soil and pore water). With use of the model, one-dimensional numerical simulations were carried out by the finite element method.

Heavy metals are ionized typically into cations in groundwater (e.g., Cu$^{2+}$, Pb$^{2+}$, and so on). Purge water is injected into the anode well and contaminant-concentrated water is drawn out from the cathode well. The injection of purge water causes a hydraulic flow in groundwater from the anode well to the cathode well. The electrokinetic driving force, which acts on the ionized heavy metal (cation), is superposed on the hydraulic flow so that the heavy metal can be accelerated to migrate to the cathode well and can be swept out of the contaminated aquifer.
2 Mathematical Model

2.1 Governing Equation

The application of a direct current across the soil between the anode and the cathode mobilizes charged species in pore water of soil. In pore water cations migrate to the cathode and anions migrate to the anode. Under steady uniform flow, the equation of mass conservation, which considers the advection, dispersion, and sorption for chemical species k in saturated homogeneous isotropic media, can be described as follows [8]:

$$\frac{\partial}{\partial t}(nR_d C_k) + \frac{\partial}{\partial z} \{ (u_S - u_{ezk})C_k \} = D_k^* \frac{\partial^2 C_k}{\partial z^2} + nR_{aq}^k$$  \hspace{1cm} (1)

where $C_k$ = concentration of species k (mol/L); $u_S$ = pore flow velocity (cm/s); n = porosity of soil (-); $R_d$ = retardation factor (-); $R_{aq}^k$ = molar rate due to liquid-phase chemical reactions (mol/L/s); and $D_k^*$ and $u_{ezk}$ = effective diffusion coefficient and effective electromigration velocity, respectively. They are given by:

$$D_k^* = \frac{n}{\tau^2} D_k$$ \hspace{1cm} (2)
$$u_{ezk} = \frac{n}{\tau^2} u_{ezk}$$ \hspace{1cm} (3)

where $\tau$ = tortuosity obtained experimentally (-); $D_k$ = diffusion coefficient of species k in pore water (cm²/s); and $u_{ezk}$ = electromigration velocity (cm/s).

The chemical reaction in aquifers is composed of the homogeneous liquid-phase reaction, which generates the molar rate $R_{aq}^k$ in pore water, and heterogeneous adsorption-desorption reaction between pore water and soil, which generates the molar rate $R_{sp}^k$. Assuming adsorption is fast and reversible, the retardation factor $R_d$ is introduced to consider $R_{sp}^k$ (Inoue and Kaufman [4]). Retardation factor is defined as:

$$R_d = 1 + \frac{(1 - n)\rho}{n} K_d$$ \hspace{1cm} (4)
$$K_d = \frac{\partial s_k}{\partial C_k}$$ \hspace{1cm} (5)

where $\rho$ = density of soil solid (g/cm³); $K_d$ = distribution coefficient of species k (L/g); and $s_k$ = absorbed concentration of species k per unit mass of soil solid (mol/g). As typical absorption reaction attains the equilibrium rapidly, the adsorption isotherms between $s_k$ and $C_k$ are generally expressed by a linear function.

$R_{aq}^k$ by homogeneous liquid-phase reaction varies with the chemical species contained in the pore water. Because the homogeneous reactions in the pore water are usually fast dissociation-association reactions, the equilibrium states are assumed to be established among the dissolved species.

The electromigration velocity of species k, which plays an important role in the electrokinetic remediation, is given by:

$$u_{ezk} = \frac{F}{RT} z_k D_k \frac{\partial \phi}{\partial z}$$ \hspace{1cm} (6)
$$\frac{\partial \phi}{\partial z} = -\frac{RT}{F} f(t, z)$$ \hspace{1cm} (7)
where $F = \text{Faraday's constant} \ (\text{C/mol})$; $R = \text{universal gas constant} \ (\text{J/K/mol})$; $T = \text{liquid temperature} \ (\ ^\circ \text{K})$; $Z_k = \text{charge number of species} \ k \ (-)$; $\phi = \text{electric potential} \ (\text{V})$; and $i_S^* = \text{effective current density} \ (\text{A/cm}^2)$. Factor $10^3$ to $i_S^*$ is need for conversion of unit of concentration mol/L into mol/cm$^3$, when $C_k$ is measured in mol/L as usually. As $i_S(t) = I(t)/A$, $i_S^*(t)$ is given as follows:

$$i_S^*(t) = \frac{n}{\tau^2} \frac{i_S(t)}{A}$$

where $I(t) = \text{electric current supplied from power unit} \ (\text{A})$; and $A = \text{cross sectional area of column} \ (\text{cm}^2)$. If electroneutrality condition can be applied to pore water, the term $u_S \sum (z_k C_k)$ in the numerator of eqn (8) diminishes.

From eqn (7) electric potential $\phi(t,z)$ along the experimental column is estimated as follows:

$$\phi(t,z) = \phi(t,0) - \frac{RT}{F} \int_0^z f(t,z) \, dz$$

Therefore, the potential difference $E$ (Volt) applied between the anode ($z = 0$) and the cathode ($z = L$), which can be operated to be constant, is obtained as:

$$E(t) = \phi(t,0) - \phi(t,L)$$

The initial condition for the governing equation eqn (1) specifies the concentrations of chemical species in the pore water at $t = 0$ and is simply given by:

$$C_k = C_{k0} \quad \text{at} \quad t = 0$$

The anode ($z = 0$) and the cathode ($z = L$) are the two external boundaries of the one-dimensional domain where the governing equation is applied. At the anode, $\text{H}_2\text{O}$ gives electrons to the electrode. Then the principal reaction is the production of oxygen gas and $\text{H}^+$ as:

$$2\text{H}_2\text{O} - 4e^- \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+$$

Therefore, in the vicinity of the anode, $\text{H}^+$ concentration becomes high and pH decreases in its value. At the cathode, $\text{H}_2\text{O}$ takes electrons from the electrode and releases hydrogen gas and OH$^-$ as:

$$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$$

Therefore, the concentration of OH$^-$ is increased near the cathode. The production rate of $\text{H}^+$ at the anode and OH$^-$ at the cathode can be expressed in terms of their fluxes as follows:

$$J_{eH}^* = 10^3 \frac{i_S^*}{zHF}; \quad J_{eOH}^* = 10^3 \frac{i_S^*}{zOHF}$$
where $i^*_z$ is effective electric current density applied between the anode and the cathode. $J_{eH}^*$ and $J_{eOH}^*$ due to the electrode reactions must be superposed on the mass fluxes $J_H^*$ (for $H^+$) and $J_{OH}^*$ (for $OH^-$) due to the transportation by pore water, respectively. Therefore, the boundary conditions for the governing equation eqn (1) can be represented in terms of fluxes of chemical species as ($i^*_z = i^*_S/n$; $z_H = +1$; and $z_{OH} = -1$):

$$ \frac{\partial (D_k^*C_k)}{\partial z} + (u_S - u^{*}_{ezk})C_k = \begin{cases} u_SC_k^{IN} + 10^3 \frac{i^*_z}{F_n}, & \text{for } H^+, \\ u_SC_k^{IN}, & \text{for others} \end{cases} \quad \text{at } z = 0 \quad (17) $$

$$ \frac{\partial (D_k^*C_k)}{\partial z} + (u_S - u^{*}_{ezk})C_k = \begin{cases} u_SC_k - 10^3 \frac{i^*_z}{F_n}, & \text{for } OH^-, \\ u_SC_k, & \text{for others} \end{cases} \quad \text{at } z = L \quad (18) $$

The governing equation eqn (1) can be solved numerically using the initial condition eqn (12) and the boundary conditions eqns (17) and (18). For the convenience of numerical calculation, the dimensionless variables and constants are introduced as:

$$ \tilde{C}_k = \frac{C_k}{C_0}; \quad \tilde{t} = \frac{D_0 t}{nRd_0L^2}; \quad \tilde{z} = \frac{z}{L}; \quad \tilde{\phi} = \frac{F}{RT} \phi; $$

$$ \tilde{D}_k^* = \frac{D_k^*}{D_0}; \quad \tilde{u}_S = \frac{L}{D_0}u_S; \quad \tilde{u}^{*}_{ezk} = \frac{L}{D_0}u^{*}_{ezk}; $$

$$ \tilde{R}_{k}^{aq} = \frac{L^2}{D_0C_0} (nR_{k}^{aq}); \quad \tilde{R}_{k} = \frac{R_{k}}{R_{0}}; $$

$$ \tilde{i} = 10^3 \frac{L}{nFD_0C_0} i; $$

where $L = \text{distance between anode and cathode (cm)}$; and subscript $0$ denotes the standard quantity for normalization. The dimensionless form of the governing equation can be given as:

$$ \frac{\partial (\tilde{R}_{k} \tilde{C}_k)}{\partial \tilde{t}} + \frac{\partial}{\partial \tilde{z}} \left\{ (\tilde{u}_S + \tilde{u}^{*}_{ezk})\tilde{C}_k \right\} = \frac{\partial^2}{\partial \tilde{z}^2} (\tilde{D}_k^* \tilde{C}_k) + \tilde{R}_{k}^{aq} \quad (29) $$

where $L = \text{distance between anode and cathode (cm)}$; and subscript $0$ denotes the standard quantity for normalization. The dimensionless form of the governing equation can be given as:

The initial condition and the boundary conditions are also transformed into the dimensionless forms by using the dimensionless variables and constants.

### 2.2 Chemical Reactions

Aqueous phase chemical reaction given by $R_{k}^{aq}$ in the governing equation varies its formulation on the pollutant. In this study the remediation of the aquifer contaminated by copper sulfate (heavy metal) is simulated. Then, the chemical reactions in pore water may be represented as follows:

$$ \text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-} \quad (K_1); \quad \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^{+} + \text{HSO}_4^{-} \quad (K_2) \quad (30), (31) $$
HSO₄⁻ ⇌ H⁺ + SO₄²⁻ \ (K₄) ; \ H₂O ⇌ H⁺ + OH⁻ \ (K_w) \ (32), \ (33)

where K₁, K₂, K₄, and K_w are dissociation constants. The concentrations of chemical species treated here are defined as:

\[ (C₁, \ C₂, \ C₃, \ C₄, \ C₅, \ C₆) = ([\text{CuSO}_4], [\text{Cu}^{2+}], [\text{SO}_4^{2-}], [\text{HSO}_₄], [\text{H}^+], [\text{OH}^-]) \] \ (34)

As K₂ \gg 1 \text{ M}, from the dissociation reaction given by eqns (30)-(33) the reaction terms R_k^{aq} in eqn (1) are obtained as:

\[ R_1^{aq} = -(k_1^+ C_1 - k_1^- C_2 C_3) \] \ (35)
\[ R_2^{aq} = k_1^+ C_1 - k_1^- C_2 C_3 \] \ (36)
\[ R_3^{aq} = k_4^+ C_1 - k_4^- C_2 C_3 + k_4^+ C_4 - k_4^- C_3 C_5 \] \ (37)
\[ R_4^{aq} = k_4^+ C_4 - k_4^- C_3 C_5 \] \ (38)
\[ R_5^{aq} = k_4^+ C_1 - k_4^- C_3 C_5 + k_w^+ - k_w^- C_5 C_6 \] \ (39)
\[ R_6^{aq} = k_w^+ - k_w^- C_5 C_6 \] \ (40)

where k₁⁺, k₁⁻, k₄⁺, k₄⁻, kₜ+, and kₜ⁻ are reaction rate constants satisfying the next equations:

\[ K₁ = k_1^+/k_1^- ; \ K₄ = k_4^+/k_4^- ; \ K_w = k_w^+/k_w^- \] \ (41), \ (42), \ (43)

3 Numerical Simulation

The model simulations were carried out under the following conditions: column length (anode and cathode distance L) = 40 cm; cross-sectional area of column (A) = 100 cm²; porosity (n)= 0.4; tortuosity (τ) = 1.5; flow rate (Q) = 0.01 cc/s; and constant voltage applied between the anode and the cathode (E) = 5 V. Electric current efficiency is assumed to be 60%. The purge water is pure (pH = 7) and it is injected into the anode (z = 0) and drawn out from the cathode (z = L). Initial pH of pore water is assumed to be 6, which is a little acidic as natural water.

Figure 2 discloses that the distributions of total copper concentration (C₁ + C₂) in the column are almost linear except for the very early stage \[ \hat{t} < 2 \times 10^{-4} \] (less than about 3 hours in real time) of the process and that the distributions remarkably vary in the slope and in the convergence point of lines, depending on the stage of process. The first stage is the duration \[ \hat{t} = 0 \sim 1.8 \times 10^{-2} \] and the second stage is the duration \[ \hat{t} = 2 \times 10^{-2} \sim 5 \times 10^{-2} \] (roughly speaking, 2 weeks ~ 34 days in real time). During the first stage the distributions have positive gradient (ascending) and at the cathode they converge to the point \( C₁ + C₂ = 0.8 \). Copper is removed from anode (upstream end) and it is transported and accumulated near cathode. These distributions accord qualitatively with the experimental results on heavy metals, which were executed with use of one-dimensional column by...
Figure 2. Time Variation of Dimensionless Total Copper Concentration ($\hat{C}_1 + \hat{C}_2$) in the Column.

Figure 3. Time Variation of Dimensionless Effective Current Density ($i_{S*}$) in A/cm².
Figure 4. Time Variation of pH Distribution between Anode and Cathode.

Figure 5. Time Variation of Electrical Potential $E$ (Voltage) Distribution between Anode and Cathode.
Nekrasova and Korolev [5]. At anode the copper concentration decreases rapidly to about 0.4, but at cathode it almost maintains constant value 0.8.

As is seen from the time variation of current density in Figure 3, during this stage the effective current density increases steadily with progress of the removal of copper. The high electric conductivity of pore water which causes increase of the current density is possibly brought about by the increase of the concentration of $\text{H}^+$ due to the electrode reaction and $\text{SO}_4^{2-}$ due to the desorption.

During the second stage the copper concentration at anode is nearly constant (Figure 2), but the ascending slope gradually decreases and ultimately becomes negative (descending). The decrease in the slope means the accumulated copper near the cathode is removed, although the concentration at anode stays almost constant to show the cease of the removal at anode. Effective current density is high and actually unchanged regardless of the reduction of $\text{Cu}^{2+}$ concentration due to the removal (Figure 3), because the high concentration of $\text{H}^+$ and $\text{SO}_4^{2-}$ increases the electric conductivity of the pore water.

Time variation of pH distribution between anode and cathode are shown in Figure 4. Since hydrogen ion is produced at anode and hydroxyl ion is at cathode, it is supposed that with lapse of time pH at anode decreases and pH at cathode increases, i.e., pH distribution curves are expected to have ascending gradient and the acid front (jump up of pH in the distribution). This anticipation is comes true except for the pH at cathode as seen from Figure 4. Against the anticipation pH at cathode remains constant at about 7.

Figure 5 demonstrates the time variation of electrical potential (voltage) distribution in the column. These potentials are measured as the difference from the anode potential, i.e., the base potential is set at anode. The initial distribution is linear. However, the distribution curve gradually expands upward, and it seems that ultimately it gets to the horizontal line $E = 0$ and to the vertical line $\tilde{z} = 1$. This means that with lapse of time the electric resistance is concentrated near cathode and in the most part of the column the resistance becomes small. Decrease in the resistance may be due to increase in the ion density of pore water. Increase in the high resistance near cathode seems not to be realistic.

4 Conclusions

From the numerical simulation of decontaminating the heavy metal (copper sulfate) by a 1-D mathematical model, it may be concluded that:

(1) The electrokinetic remediation is proved theoretically to be effective for removal of heavy metals;

(2) The removal process is composed of two stages, i.e., the first stage during which the upstream copper is removed and accumulated in downstream region, and the second stage during which the accumulated copper in downstream region is removed;

(3) For the operation of constant voltage, the density of effective electric current through the pore water increases with the progress of the removal process and ultimately it remains at some level.
(4) Time variation of pH distribution in the column is well simulated numerically by the mathematical model except for near cathode.
(5) With lapse of time the electric resistance of most part of column becomes small because of the increase in the ion density of pore water.

References