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MODELING OF CHEMICAL AND ELECTRICAL FLOWS IN LOW PERMEABILITY SOILS UNDER ELECTRICAL GRADIENT

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If an electrical gradient is imposed on wet fine-grained soil, contaminant transport occurs by a complex phenomenon called electrokinetics. Even though electrokinetics has been proven to be feasible in bench-scale experimental studies, there is still a lack of thorough understanding of its cleanup mechanisms. A theoretical model is derived for electrokinetic phenomena, a numerical formulation is presented, and a model is validated. Coupled flow theory is applied to derive the governing equations. The model is implemented by computer using finite element methods. Validation is based on one-dimensional experimental data from the literature. The model provides an effective tool to better understand the electrokinetic extraction processes and to optimize operation parameters.

INTRODUCTION

When an electric gradient is imposed to a wet soil, cations (positive ions) move toward the cathode (negative electrode) and anions (negative ions) move toward the anode (positive electrode). Fine-grained soils, such as clay, possess a negative charge due to isomorphous substitution and the presence of broken bonds in the soil structure. Therefore, excess mobile cations are required to balance the negative fixed charge on the soil solid particle surfaces. Mobile ions can drag water molecules when they are moved by an imposed electric field. As cations are in excess in the system, there is a net movement of pore water toward the cathode. These phenomena are called electrokinetics and can be analyzed as coupling effects between electrical gradient, contaminant concentration gradient, and hydraulic gradient.

Research on soil decontamination using electrokinetic phenomena has been actively carried out in many disciplines. Shapiro et al. (1993) developed a theoretical model for phenol and acetic acid extraction based on the advection-dispersion equation. Retardation of the contaminant was incorporated by using a linear sorption isotherm in their model. Even though they reported that the model satisfactorily predicts transport of contaminants and pH distribution, no attempt was made to model nonlinear voltage distribution and the coupling effect between gradients.

Eykholt and Daniel (1994) conducted a series of electrokinetic extraction tests to evaluate the capability of the process to remove heavy metals. They developed a theoretical formulation to predict concentration distribution, pH distribution, amount of flow, and voltage distribution along the length of the specimen. However, the assumption that the voltage distribution follows a bilinear distribution may not be always true. In addition, the model did not incorporate the buffer capacity of the soil for pH computations and surface complexation.

Alshawabkeh and Acar (1996) developed a theoretical model in an attempt to describe the transport of lead (Pb) and nitrate (NO_3) in a coupled system. The model can predict acid transport, lead transport, electric potential and pore pressure distribution across the electrodes in electrokinetic remediation. However, the model does not consider the surface conductance of clay particles and only a few dominant contaminant ions in the pore fluid are considered in their model. The concentration of NO_3^- is determined from the charge balance with Pb_2^+, H^+, and OH^-. This approach will lead to the misinterpretation of NO_3^- concentration.

The purpose of this research is to investigate the feasibility and practicability of electrokinetic treatment by numerical modeling, to find design parameters, and to provide appropriate values for field use.

MODEL DERIVATION

Many types of flows, such as hydraulic flow, heat transfer, electric current and chemical flow, exist in nature. These flows can be driven by a gradient of the same type. However, it is necessary to consider coupled flows under some circumstances. A coupled flow is a flow driven by another type of gradient, such as a water flow driven by an electrical potential.

If a wet contaminated soil mass is subjected to an electric gradient, coupled flows of contaminant and pore water occur. These flows may be time-dependent and non-linear because of soil heterogeneity and complex chemical-soil-water interactions.

In this research, a theoretical development of coupled flow is presented. Governing equations for describing contaminant movement and electric potential distribution are formulated. In addition, contaminant-soil-water interactions are mathematically modeled. The generalized coupled flow equation is as follows (Yeung, 1990):

$$J_{i}=\sum_{j=1}^{n} L_{ij} X_{j} \tag{1}$$

where

J_i = flux of type i

L_{ij} = coupling coefficient

X_j = gradient of type j

Under electrical gradient, cations dissolved in pore water migrate toward the cathode and anions migrate toward the anode. Hence, the movement of cations and anions are considered separately. Equation (1) can be expanded for cations and anions in the soil as follows (Yeung, 1990; Yeung 1994).

$$J_c = L_{CH}\nabla(-H) + L_{CE}\nabla(-E) + L_{CC}\nabla(-C_c) + L_{CA}\nabla(-C_a) \tag{2}$$

$$J_a = L_{AH}\nabla(-H) + L_{AE}\nabla(-E) + L_{AC}\nabla(-C_c) + L_{AA}\nabla(-C_a) \tag{3}$$

If the coupling coefficients L_{ij} for electric and chemicals (Kim, 1998) are substituted into Equation (2) and Equation (3), Equation (4) and Equation (5) can be obtained.

$$\left(D_c^{*} + \frac{D_c^{*} z_c C_c k_e F}{\sigma}\right)\nabla(-C_c) + \left(\frac{-D_a^{*} z_a C_c k_e F}{\sigma}\right)\nabla(C_a) + \left(u_c^{*} + \frac{k_e}{n}\right)\cdot C_c \cdot \nabla(-E) + r_f \cdot \frac{\partial C_c}{\partial t} = 0 \tag{4}$$

$$\left(\frac{D_c^{*} z_c C_a k_e F}{\sigma}\right)\nabla(-C_c) + \left(\frac{D_a^{*} z_a C_a k_e F}{\sigma}\right)\nabla(C_a) + \left(u_a^{*} + \frac{k_e}{n}\right)\cdot C_a \cdot \nabla(-E) + r_f \cdot \frac{\partial C_a}{\partial t} = 0 \tag{5}$$

Equation (4) is the governing equation for cation movement and Equation (5) is the governing equation for anion movement. When an electrical gradient is first imposed on soil, it is linearly distributed between electrodes. As the treatment time passes, however, the electrical gradient distribution becomes non-linear after a short time (Menon, 1996).

The governing equation of electrical gradient distribution is like the following:

$$\nabla\left((\sigma_o + n\cdot\sigma_e)\nabla(-E)\right) = 0 \tag{6}$$

When an electrical gradient is imposed on contaminated soil, complex chemical reactions occur in the soil-pore water-contaminant system. Important reactions are the acid-base reaction, adsorption-desorption, aqueous complexation and precipitation-dissolution. In this research, the models for chemical reactions are developed and numerical models are formulated. Electrolysis of water occurs at electrodes, with H^+ generated at the cathode migrating toward the anode by ionic migration. The OH^- generated at the anode migrates toward the cathode. While H^+ and OH^- migrate, they change soil pH. The magnitude of the pH change varies depending on the buffer capacity of the soil.

DEVELOPMENT OF THE NUMERICAL MODEL

A numerical model was formulated by the finite element method based on the theoretical model developed in this research. A finite element model based on the governing equations (Equations (4), (5) and (6)) is as follows:

$$\begin{bmatrix} K^{11} & K^{12} & K^{13} \\ K^{21} & K^{22} & K^{23} \\ K^{31} & K^{32} & K^{33} \end{bmatrix} \begin{Bmatrix} C_c \\ C_a \\ E \end{Bmatrix} + \begin{bmatrix} M^1 & 0 & 0 \\ 0 & M^2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} \dot{C_c} \\ \dot{C_a} \\ \dot{E} \end{Bmatrix} = \begin{Bmatrix} Q^1 \\ Q^2 \\ Q^3 \end{Bmatrix} \tag{7}$$

where

C_c = cation concentration at node

C_a = anion concentration at node

$\dot{C_c}$ = time derivative of cation concentration at node

$\dot{C_a}$ = time derivative of anion concentration at node

E = electrical potential at node

$\dot{E}$ = time derivative of electrical potential at node

K^{ij} = conductivity coefficient

M^{i} = mass element matrix

Q^{i} = flux matrix

The model developed in this research is composed of a contaminant transport model and a contaminant interaction model. A computer program was developed to predict the contaminant removal efficiency and contaminant characteristic change by electrokinetic extraction. Predictions made by the contaminant transport model were compared with the analytical solution of the advection-diffusion equations. The chemical interaction model was verified by comparing results obtained from the computer chemical speciation model, MINTEQA2.

RESULT AND DISCUSSION

The validity of the developed model is evaluated by comparing the contaminant concentration, pH, and electric gradient profiles predicted by the computer model with published experimental data. Menon (1996) performed electrokinetic tests with Georgia kaolinite uniformly contaminated with lead nitrate, $Pb(NO_3)_2$. The constant voltage gradient applied to the soil was 35 (V). The initial concentration of Pb^{2+} was 0.12065 (mole/liter) and NO_3^- was 0.2963 (mole/liter). The initial soil pH was 3.98.

The model predictions and the experimental data for lead nitrate extraction from Georgia kaolinite are compared in Figures 1, 2 and 3. The comparison of total lead(II) concentration profile predicted by the model and that obtained from experiment is shown in Figure 1. The experimental and

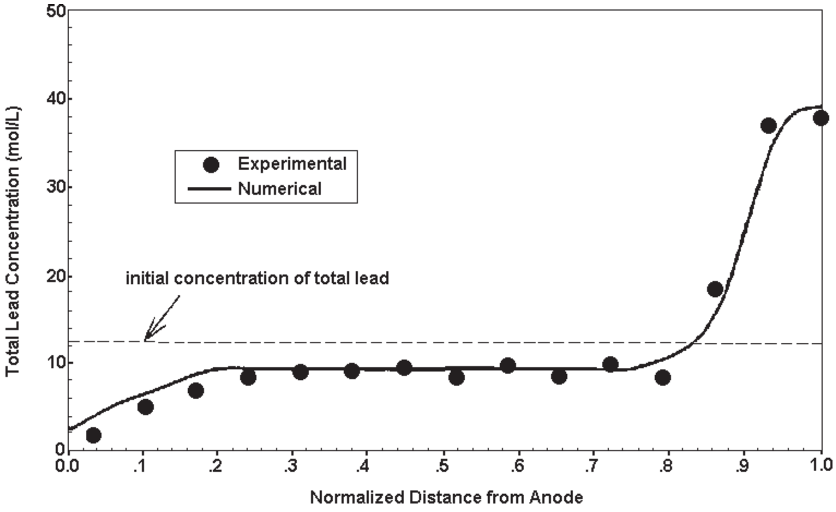

Figure 1. Comparison of numerical and experimental profiles of total lead concentration (soil = Georgia kaolinite, time = 25 hrs, voltage = 35V).

numerical results show good agreement. Transported lead is accumulated at the cathode side because high pH is developed in the vicinity of the cathode.

The comparison between the model prediction and experimental results for pH distribution along the length of the specimen is shown in Figure 2. Experimental results and simulation results show good agreement to each other. Due to the steep increase of pH at the cathode side, lead is accumulated.

The comparison of final voltage distribution between the model prediction and experimental results is shown in Figure 3. The electrical conductivity of soil was estimated by the hydrogen concentration of the soil versus electrical conductivity relationship. The experimental and simulation results show the same trends and are in good agreement. From this figure, it can be inferred that pH is the possible indicator to estimate the electrical conductivity.

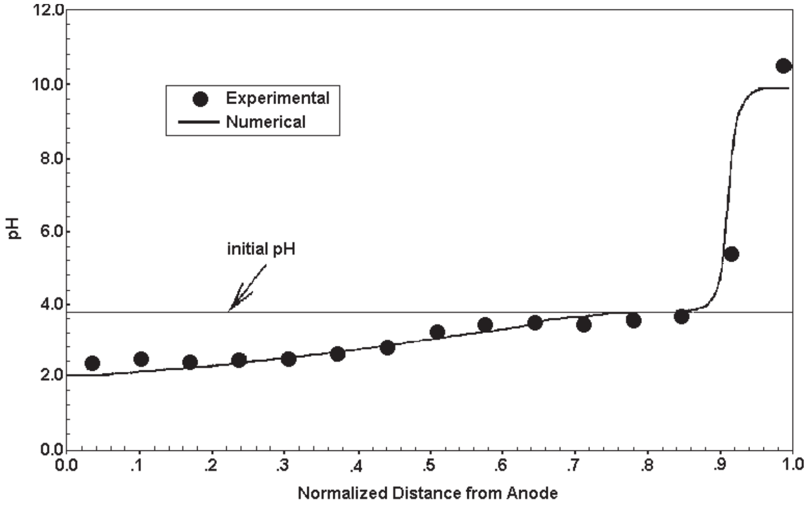

Figure 2. Comparison of numerical and experimental profiles of pH (soil = Georgia kaolinite, time = 25 hrs, voltage = 35V).

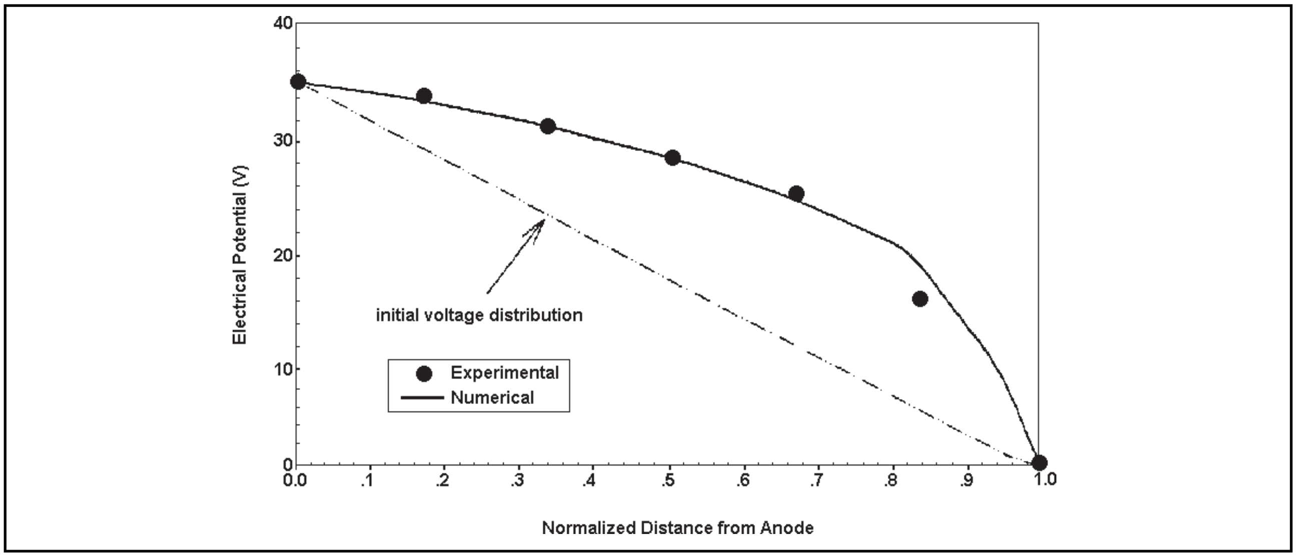

Figure 3. Comparison of numerical and experimental profiles of voltage distribution (soil = Georgia kaolinite, time = 25 hrs, voltage = 35V).

CONCLUSIONS

This research is a modeling study on electrokinetic extraction of reactive contaminants from fine-grained soils. An approach was to model the non-linear electrical gradient distribution during imposition of an electrical gradient. Models for a detailed description of contaminant-contaminant and contaminant-clay interactions are developed. The model can predict pH variation during treatment. Governing equations for contaminant transport under electrical gradient using coupled theory were also formulated. The validity of the developed model was established by its successful simulation of one-dimensional electrokinetic extraction experiments. We conclude that the model developed by this research provides a better understanding of contaminant transport by electrical gradients.

REFERENCES

Alshwabkeh, A. N., and Y. B. Acar; Electro-kinetic remediation. II: Theoretical model, *J. Geotech. Engrg.*, ASCE, Vol.122, No.3, pp.186-196, 1996.

Dean, A. J.; *Lange's handbook of chemistry*, 14th Ed., McGraw-Hill, New York, New York, 1992.

Kim, G.; Two-dimensional numerical modeling of electrokinetic extraction of contaminants from fine-grained soils, Ph.D. dissertation, Dept. of Civil Engrg., Texas A&M Univ., College Station, Texas, 1998.

Menon, R. M.; Numerical modeling and experimental studies on electro-kinetic extraction, Ph.D. dissertation, Texas A&M Univ., College Station, Texas, 1996.

Shapiro, A. P., and R. F. Probstein; Removal of contaminants from saturated clay by electroosmosis, *Environmental Sci. Technol.*, Vol.27, No.2, pp. 283-291, 1993.

Yeung, A. T.; Coupled flow equations for water, electricity and ionic contaminants through clayey soils under hydraulic, electrical and chemical gradients, *J. Non-Equilibrium Thermodynamics*, Vol.15, No.3, pp. 247-267, 1990.

Yeung, A. T.; Electro-kinetic flow processes in porous media and their applications, *Advances in porous media*, Elsevier, Amsterdam, The Netherlands, Vol. 2, 309-395, 1994.

NOMENCLATURE

$\nabla(-C_a)$: anion concentration gradient (mol/Lm)

$\nabla(-C_c)$: cation concentration gradient (mol/Lm)

$\nabla(-E)$: electric gradient (V/m)

$\nabla(-P)$: hydraulic gradient (m/m)

σ_o : bulk electrical conductivity of soil (S/m)

σ_e : conductivity of electrolyte (S/m)

γ_f : unit weight of pore water (N/m^3).

u_a^* : effective ion mobility of anion $= \left(D_a^* z_a F\right) / (RT) \left(\mathrm{m}^2 / \mathrm{Vs}\right)$

u_c^* : effective ion mobility of cation $= \left(D_c^* z_c F\right) / (RT) \left(\mathrm{m}^2 / \mathrm{Vs}\right)$

D_a^* : effective diffusion coefficient of anion (m^2/s)

D_c^* : effective diffusion coefficient of cation (m^2/s)

J_a : flux of anion (mol/Lm^3)

J_c : flux of cation (mol/Lm^3)

Q : quantity of flow (m^3/s)

V : applied voltage (V)

i_e : V/L= electrical gradient (V/m)

k_e : electroosmotic conductivity coefficient (m^2/V$s)

k_h : hydraulic conductivity of the soil (m/s)

n : soil porosity (dimensionless)

z_a : valence of anion (dimensionless)

z_c : valence of cation (dimensionless)

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