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MODELING CONDUCTION PHENOMENA IN SOILS UNDER AN ELECTRIC CURRENT

MODELER LE PHENOMENE DE CONDUCTION DANS LE SOL SOUS L'INFLUENCE DU COURANT ELECTRIQUE

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SYNOPSIS : A theoretical treatise is provided for conduction phenomena in saturated soils under an electric current. A theoretical formalism is presented to model the transport of the hydrogen and hydroxyl ions generated at the electrodes and the flush of the acid front from the anode to the cathode across the soil mass to neutralize the base at the cathode. Predictions obtained through numerical modeling of the theoretical formulations for the acid breakthrough at the cathode are compared with the results of one-dimensional laboratory experiments. A methodology is presented to predict the time necessary for the acid breakthrough in one dimensional conditions. This time constitutes the minimum processing time necessary in electrokinetic remediation of contaminated soils.

INTRODUCTION

The challenging demand to develop new, innovative and cost effective in-situ remediation technologies in waste management stimulated the vision to employ conduction phenomena under electrical currents as a soil remediation technology (Acar and Gale 1992; Acar and Hamed 1992). This technology uses low level DC electrical potential differences (in the order of few volts per cm) or electrical currents (in the order of milliamps per cm^2 of cross sectional area) across a soil mass applied through inert electrodes placed in an open flow arrangement. The open flow arrangement constitutes the case when electrodes are manufactured or placed in a configuration which admits ingress and egress of water. Closed anode and open cathode arrangements have been conventionally used by geotechnical engineers in electro-osmotic consolidation and stabilization of soft, fine grained deposits (Esrig 1968; Casagrande 1983). The feasibility and cost-effectiveness of the electrokinetic remediation technology were recently demonstrated by bench-scale studies (Acar *et al.* 1989; Shapiro *et al.* 1989; Hamed *et al.* 1991; Bruel *et al.* 1992; Acar *et al.* 1992) and some pilot-scale studies (Lageman et al. 1989). Development of this technique requires a better understanding of the chemistry associated with conduction phenomena under electrical currents.

The pH at the anode will typically drop to below 2.0 and at the cathode it will increase to about 12.0, depending upon the applied current density (Acar *et al.* 1990). The acid front will advance across the specimen towards the cathode by advection of the pore fluid due to the prevailing electro-osmotic flow, or due to any externally applied or internally generated hydraulic potential differences, migration due to electrical gradients, and diffusion due to concentration gradients. As a result, the transport of the pore fluid and ions across the soil mass is accompanied by adsorption/desorption, precipitation/dissolution reactions and electrodeposition. The hydroxyl ion generated at the cathode will first advance towards the anode by back-diffusion and ionic migration; however, electro-osmosis induced advective flow will retard this back-diffusion and migration allowing the acid front to flush across the soil reaching the cathode and neutralizing the base.

The advance of the acid front and the activity of the H$^+$ ion results in its exchange with other exchangeable cations (including heavy metals) on the surfaces of the clay minerals. This exchange of ions will lead to release of the adsorbed cations into the pore fluid (Hamed *et al.* 1991). The migration, diffusion and advection will also result in transport of the exchangeable ions on the surface and the cations/anions in the pore fluid to respective electrodes in the porous medium (Hamed *et al.* 1991). The electrolysis reactions generated by the electrical current and transport of the hydrogen/hydroxyl ions constitute one of the fundamental driving mechanisms which facilitate desorption and transport of other ionic species. The efficiency of the process may be enhanced by controlling the chemistry at the electrodes. When this option is not used, breakthrough of the acid front at the cathode will be the basic criteria used in terminating the process. This breakthrough flags acidification of the soil mass across the electrodes and achievement of steady-state conditions where the hydrogen ion generated at the anode meets the hydroxyl ion generated at the cathode to form water. Appropriate modeling of the acid breakthrough is essential in estimating the time and energy requirements in electrokinetic remediation.

Theoretical descriptions of conduction phenomena under electrical and hydraulic potentials have recently been proposed (Acar *et al.* 1989; Shapiro *et al.*, 1989; Acar *et al.* 1990; Mitchell 1991; Corapcioglu 1991; Eykholt 1992; Alshawabkeh and Acar 1992). This paper presents a treatise of the conduction phenomena under electrical currents with specific emphasis on the acid-base distribution and breakthrough of the acid front at the cathode compartment. An improved theoretical formalism is provided. Predictions obtained by numerical modeling of the introduced theoretical formalism are compared with the results of one-dimensional laboratory experiments.

THEORETICAL DEVELOPMENT

In the presence of hydraulic, electrical, and chemical gradients, the total mass flux of species j per unit area of the soil medium is described by (Alshawabkeh and Acar 1992),

$$J_j = -\,D_j^*\,\frac{\partial c_j}{\partial x} - c_j(u_j^* + k_e)\frac{\partial E}{\partial x} - c_j k_h \frac{\partial h}{\partial x} \tag{1}$$

where J_j is the total mass flux of species j, D_j^* is the effective diffusion coefficient of species j, c_j is the concentration of species j, u_j^* is the effective ionic mobility, E is the electric potential difference, k_e is the electro-osmotic coefficient of permeability, h is the hydraulic head, k_h is the hydraulic conductivity of the soil, and x is the linear distance. The effective diffusion coefficient and effective ionic mobility in the porous medium are related to the diffusion coefficient, D_j, and ionic mobility, u_j, in free solution at infinite dilution by (Alshawabkeh and Acar 1992),

$$D_j^* \;=\; D_j\,\tau\,n \tag{2}$$

$$u_j^* \;=\; u_j\,\tau\,n \;=\; \frac{D_j^*\,z_j\,F}{RT} \tag{3}$$

where z_j is the charge of species j, τ is a factor representing the effect of tortuosity of the medium, n is the porosity, F is Faraday's constant, R is the universal gas constant, and T is the absolute temperature.

The total mass flux of contaminants given in (1) is coupled with the following fluid flux, J_w, and charge flux, I,

$$J_w = k_h\,\nabla(-h) + k_e\,\nabla(-E) \tag{4}$$

$$I = F\sum_{j=1}^{N} z_j\,D_j^*\,\nabla\,(-C_j) \;+\; \sigma^*\,\nabla(-E) \tag{5}$$

where, J_w is the fluid flux per unit area of porous medium, I is the current density, N is the total number of species present, and σ^* is the effective electrical conductivity of the free fluid in the pores of soil evaluated as,

$$\sigma^* = F\sum_{j=1}^{N} z_j\,C_j\,u_j^* \tag{6}$$

Conservation of mass, charge, and energy in the continuum results in the following time–dependent equations, which model coupled reactive solute transport,

$$\frac{\partial n c_j}{\partial t} \;=\; -\,\nabla\cdot\mathbf{J}_j \;+\; nR_j \tag{7}$$

$$\frac{\partial \epsilon_v}{\partial t} \;=\; -\,\nabla\cdot\mathbf{J}_w \tag{8}$$

$$\frac{\partial T_e}{\partial t} \;=\; -\,\nabla\cdot\mathbf{I} \tag{9}$$

where ϵ_v is the volumetric strain of the soil medium, T_e is the volumetric charge density of the soil, t is time, and R_j is the production rate of the aqueous species j per unit fluid volume due to chemical reactions such as sorption/desorption, precipitation/dissolution, oxidization/reduction, and aqueous phase reactions.

MODELING ACID/BASE DISTRIBUTION

For the one–dimensional case and assuming constant hydraulic and electrical potential differences across the electrodes throughout the process, Equation 7 together with Equation 1 are used to model transport of chemical species; as follows,

$$\frac{\partial n c_j}{\partial t} \;=\; D_j^*\,\frac{\partial^2 c_j}{\partial x^2} \;+\; [\,(u_j^* \;+\; k_e)\frac{\partial E}{\partial x} \;+\; k_h\,\frac{\partial h}{\partial x}\,]\,\frac{\partial c_j}{\partial x} \;+\; nR_j \tag{10}$$

In most chemical systems the H^+ ion is a master variable since many chemical reactions including electrolysis, water ionization, and double layer ion exchange depends on its concentration. Other reactions involving H^+ depends on the type and concentration of other contaminants present.

In an aqueous solution water auto–ionization is an important reaction for hydrogen ions,

$$H_2O \;\longleftrightarrow\; H^+ \;+\; OH^- \tag{11}$$

Therefore, it is essential to incorporate this auto–ionization to model the coupled transport of H^+ and OH^-. When H^+ adsorption is accounted by the retardation factor R_d, the nondimensional mass balance equation for the hydrogen ion, H^+, transport becomes,

$$\frac{\partial c_{H^+}}{\partial T_{H^+}} \;=\; \frac{\partial^2 c_{H^+}}{\partial X^2} \;-\; P_{H^+}\,\frac{\partial c_{H^+}}{\partial X} \;+\; Da_{H^+} \tag{12}$$

and for the hydroxyl ion, OH^-,

$$\frac{\partial c_{OH^-}}{\partial T_{OH^-}} \;=\; \frac{\partial^2 c_{OH^-}}{\partial X^2} \;-\; P_{OH^-}\,\frac{\partial c_{OH^-}}{\partial X} \;+\; Da_{OH^-} \tag{13}$$

where,

$$Da_j \;=\; \frac{R_j\,L^2}{D_j^*} \tag{14}$$

$$P_j \;=\; \frac{\overline{v_j}\,L}{D_j^*} \tag{15}$$

$$T_j \;=\; \frac{D_j^*\,t}{n\,R_{dj}\,L^2} \tag{16}$$

$$X \;=\; \frac{x}{L} \tag{17}$$

$$\overline{v_j} \;=\; -(u_j^* \;+\; k_e)\,\frac{\partial E}{\partial x} \;-\; k_h\,\frac{\partial h}{\partial x} \tag{18}$$

P_j is known as Peclet number for species j and accounts for the ratio of advective mass transport to the diffusive mass transport, and Da_j is known as Damkohler number and represents the ratio of the chemical reaction rate to the diffusive mass transport of species j (Oran and Boris 1987). For water ionization reaction, the Damkohler number for the hydrogen ion is given as,

$$Da_{H^+} \;=\; -\,\frac{L^2}{D_{H^+}^*}\,\frac{\partial c_{H_2O}}{\partial t} \tag{19}$$

and for the hydroxyl ion as,

$$Da_{OH^-} \;=\; -\,\frac{L^2}{D_{OH^-}^*}\,\frac{\partial c_{H_2O}}{\partial t} \tag{20}$$

hence the Damkohler numbers for H^+ and OH^- relate to each other with,

$$Da_{H^+} \;=\; \frac{D_{OH^-}}{D_{H^+}}\,Da_{OH^-} \tag{21}$$

An additional relationship is obtained from mass equilibrium of water ionization,

$$c_{H^+}\,c_{OH^-} \;=\; K_w \tag{22}$$

where K_w is the water ionization constant (10^{-14}). Boundary conditions are developed from the chemistry of the primary reactions at the electrodes. Applying a constant current through the soil will generate H^+ at the anode and OH^- at the cathode by the following electrolysis reactions,

$$2H_2O\ -4e^- \longrightarrow O_2\uparrow + 4H^+ \qquad (anode) \qquad (23)$$

$$4H_2O\ +4e^- \longrightarrow 2H_2\uparrow + 4OH^- \qquad (cathode) \qquad (24)$$

According to Faraday's law the production rates of H^+ at the anode and OH^- at the cathode are equivalent to the current passing through the soil, therefore the following flux boundary conditions are specified at the electrodes,

$$c^a_{H^+}\ \frac{J_w\ L}{D^*_{H^+}} + \frac{I\ L}{F\ D^*_{H^+}\ n} = (-\ \frac{\partial c_{H^+}}{\partial X} + P_{H^+}\ c_{H^+})\ |_{X=0} \qquad (25)$$

$$c_{OH^-}\ \frac{J_w\ L}{D^*_{OH^-}} - \frac{I\ L}{F\ D^*_{OH^-} n} = (-\ \frac{\partial c_{OH^-}}{\partial X} + P_{OH^-}\ c_{OH^-})\ |_{X=1} \qquad (26)$$

where $c^a_{H^+}$ is the concentration of the hydrogen ion at the anode compartment.

COMPARISON OF THE EXPERIMENTAL AND NUMERICAL RESULTS

Two kaolinite specimens were prepared to investigate the pH changes across the soil under electrical current. The specimens were compacted in a polyacrylite mold 10 *cm* in length and 10 *cm* inside diameter. A dry density of 11.7 kN/m^3 was achieved at 42% water content. The DC electric current was applied to the cell by a voltage regulator and a current density of 0.13 mA/cm^2 was selected for the test. Effluent pH was monitored during the process and at the end of the test the sample was subdivided into ten sections to measure the final in-situ soil pH.

The Finite Element Method was used to solve the differential equations describing the transport with a continuous iteration of the equilibrium water ionization equation at every time step.

Numerical solution of the effluent pH under a constant current at a density of 0.13 mA/cm^2 and no hydraulic gradients is compared with the experimental results. The average electro-osmotic coefficient of permeability, k_e, was measured as $1.0\text{x}10^{-5}\ cm^2/V-s$. All other phenomenological coefficients were taken from reported values. The diffusion coefficient of the hydrogen ion, D_{H^+}, and the ionic mobility, u_{H^+}, are $93.1\text{x}10^{-6} cm^2/s$ and $36.2\text{x}10^{-4}\ cm^2/V-s$, respectively. The hydroxyl ion the diffusion coefficient, D_{OH^-}, and the ionic mobility, u_{OH^-}, are $52.9\text{x}10^{-6} cm^2/s$ and $20.6\text{x}10^{-4} cm^2/V\cdot s$, respectively. A tortuosity factor, τ, of 0.35 and a retardation factor, $R_{d_{H^+}}$, of 21.5 were also used in the analysis. These model parameters render Peclet numbers, P_{H^+}, and P_{OH^-}, of 204.6 and -69.2 respectively. The Damkohler numbers depend upon the concentrations of the ions; therefore, they are calculated at every time step with continuous iteration between the differential equations governing ion transport and the mass equilibrium of water auto–ionization.

Figure 1 displays a comparison of experimental and theoretical model results for effluent pH. The increase in the effluent pH in the cathode compartment as a result of the electrolysis reaction described by Equation 24 and its subsequent decrease upon flushing of the acid compare quite well. Figure 2 demonstrates the evolution of pH distributions across the electrodes until steady–state conditions are reached as a result of the complete flush of the acid front. The steady–state pH distribution shows some differences in the pH values measured across the cell upon completion of the test, specifically in the vicinity of the anode.

DISCUSSION

The numerical solution of the described theoretical formalism demonstrates that the transport equations developed under electrical, chemical, and hydraulic gradients can be used successfully to model the flush and breakthrough of the acid from the anode to the cathode. Upon application of the current, the pH in the cathode compartment increases to a value of 10 to 11 due to the electrolysis reactions. The acid generated at the anode by electrolysis reaction sweeps progressively across the specimen and at the same time the base generated at the cathode moves towards the anode. When the acid meets the base, the advancing acid front will control the chemistry of the specimen since the electric mobility of the hydroxyl ion is about half the mobility of the hydrogen ion, and since the electro-osmotic flow enhances hydrogen ion transport and retards hydroxyl ion transport towards the cathode. Consequently, in the experiments the acid flushes across 10 *cm* of the specimen and breaks through the cathode compartment within 100 hours. Subsequently steady–state conditions are established.

The steady–state final pH values obtained through the model

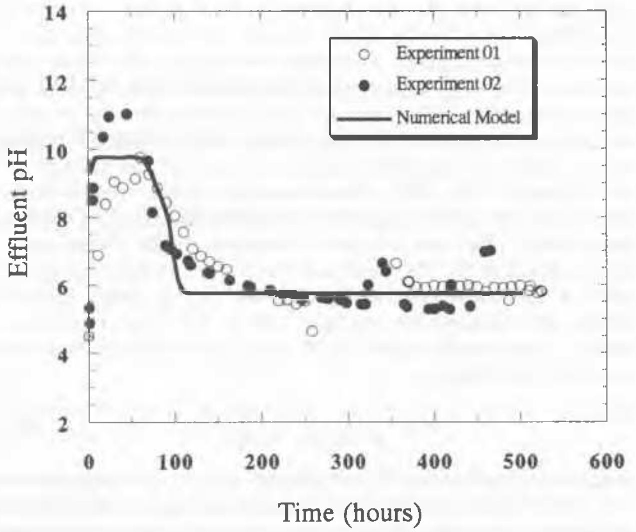

Fig. 1. A Comparison of Model Predictions of Effluent pH with Experimental Results

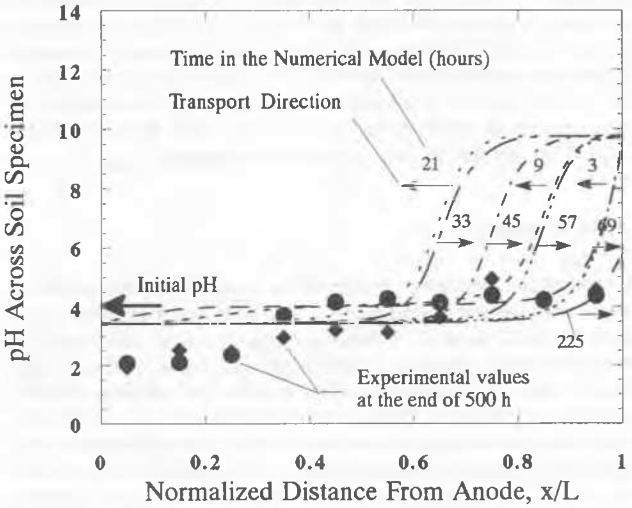

Fig. 2. Modeled and Experimental Values of pH Across the Specimen upon Completion of the Test

differ slightly from the experimental values depicted in Figure 2. This difference is fundamentally due to the simplification introduced by the assumption of constant electrical gradient across the specimen. The ionic concentration in the anode region will be orders of magnitude higher than the ionic concentration in the cathode region and therefore the ionic conductivity of the anode region will be orders of magnitude higher than that of the cathode region (Hamed *et al.* 1991). Since constant current conditions are maintained, the electrical gradients at the anode region will be less than those at the cathode region in response to the differences in ionic conductivities. This nonlinear distribution of electrical gradients has been measured and described by Hamed (1990), Eykholt (1992), and Alshawabkeh and Acar (1992). The final H^+ concentration at the anode region could simply be evaluated from the boundary condition as,

$$c_f^a = \frac{I}{F\, n\, \bar{v}_{H+}} + \frac{J_w}{\bar{v}_{H+}}\, c_i^a \tag{27}$$

It is clear that the final H^+ concentration, c_f^a, is inversely related to the electro–osmotic velocity which depends upon the electrical gradients at the anode. The measured electrical gradient of 4 V/cm was used in the model; this rendered a final pH value of about 3.5 in the anode region. Any decrease in the electrical gradient at the anode region will mean generation of lower pH values at this boundary. We have not yet incorporated a scheme to model the nonlinear changes in electrical gradients during the process; consequently, the pH values we get in the theoretical model is slightly higher than experimental values in the anode region and lower in the cathode region. It is essential to incorporate this nonlinearity in the electrical gradients in the model for more accurate predictions of the pH distribution across the electrodes.

CONCLUSIONS

A theoretical treatise is presented for conduction phenomena in soils under electrical gradients. The theoretical formalism developed for the transport of hydrogen and hydroxyl ions under an electrical current is used in modeling pH distributions. It is demonstrated that the theoretical model predicts the electrolysis reactions, the transport of hydrogen and hydroxyl ions across the electrodes and the prevailing rise and fall of pH in the cathode compartment. The higher pH values predicted by the model in the vicinity of the anode are due to the simplifying assumption of constant electrical potential gradient across the specimen. It is necessary to improve the theoretical formalism to include development of nonlinear electrical potential differences across the cell in an attempt to increase the accuracy in the predictions.

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REFERENCES

Acar, Y. B., and Gale, R. J. (1992) "Electrochemical Decontamination of Soils and Slurries," US Patent No. 5,137,608, August 11, 1992, Commissioner of Patent and Trademarks, Washington, D.C., USA.

Acar, Y. B. and Hamed, J. (1992), "Electrokinetic Soil Processing in Remediation/Treatment; Synthesis of Available Data," Bulletin of the Transportation Research, Record No. 1312, Soils Geology and Foundations, Geotechnical Engineering 1991, pp. 152–161.

Acar Y. B., Li, H. and Gale, R. J. (1992) " Phenol Removal from Kaolinite by Electrokinetics," Journal of Geotechnical Engineering, ASCE, 118(11), pp. 1837–1852.

Acar, Y. B., Hamed, J., Gale, R. J. and Putnam, G. (1991), "Acid/Base Distributions in Electro–osmosis," Bulletin of the Transportation Research, Record No. 1288, Soils Geology and Foundations, Geotechnical Engineering 1990, pp. 23–34.

Acar, Y. B., Gale, R. J., and Putnam, G. (1990) " Electrochemical Processing of Soils: Theory of pH Gradient Development by diffusion and Linear convection," Journal of Environmental Science and Health, Part (a), 25(6), pp. 687–714.

Acar, Y. B., Gale, R. J., Putnam, G. and Hamed, J. (1989), "Electrochemical Processing of Soils: Its Potential Use in Environmental Geotechnology and Significance of pH Gradients," 2nd Int. Symp. on Environmental Geotechnology, Shanghai, China, May 14–17, Envo Publishing, Bethlehem, PA, Vol. 1, pp. 25–38.

Alshawabkeh, A. N., and Acar, Y. B. (1992) "Removal of Contaminants from Soils by Electrokinetics: A Theoretical Treatise," Journal of Environmental Science and Health, Part (a), A27(7), pp. 1835–1861.

Bruell, C. J., Segall, B. A., and Walsh, H. T. (1992), "Electro–Osmotic Removal of Gasoline Hydrocarbons and TCE from Clay," ASCE, Journal of Environmental Engineering, 118(1), pp. 84–100.

Casagrande, L. (1983), "Stabilization of Soils by Means of Electro–Osmosis: State of the Art," J. of Boston Society of Civil Engineering, ASCE, 69(2), pp. 255–302.

Corapcioglu, M. Y. (1991) "Formulation of Electro–Chemico–Osmotic Processes in Soils," Transport in Porous Media, No. 6, Klower Academic Publisher, pp. 435–444.

Esrig, M. I. (1968), "Pore Pressures, Consolidation, and Electrokinetics," Journal of Soil Mechanics and Foundation Division, ASCE, 94(4), pp. 899–921.

Eykholt, G. R. (1992) "Driving and Complicating Features of the Electrokinetic Treatment of Contaminated Soils," A Dissertation submitted to the Graduate School of The University of Texas at Austin in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy, 269p.

Hamed, J. (1990) "Decontamination of Soil Using Electro–osmosis," A Dissertation submitted to the Graduate School of Louisiana State University in Partial Fulfillement of the Requirements for Degree of Doctor of Philosophy, 229p.

Hamed, J., Acar, Y. B. and Gale, R. J. (1991), "Pb(II) Removal from Kaolinite by Electro–kinetics," ASCE, Journal of Geotechnical Engineering, 117(2), February 1991, pp. 241–271.

Lageman, R., Pool, W., and Seffinga, G. (1989), "Electro–Reclamation Theory and Practice," Chemistry and Industry, Society of Chemical Industry, London, September 1991, pp. 585–590.

Mitchell, J. K. (1991) "Conduction Phenomena: From Theory to Geotechnical Practice," Geotechnique, 41(3), pp. 299–340.

Oran, E. S. and Boris, J. P. (1987) *Numerical Simulation of Reactive Flow*, Elsevier Science Publishing Co., Inc., New York, 601 p.

Shapiro, A. P., Renauld, P. and Probstein, R. (1989), "Preliminary Studies on the Removal of Chemical Species from Saturated Porous Media by Electro–osmosis," Physicochemical Hydrodynamics, 11(5/6), pp. 785–802.