# CHEMICAL TRANSPORT MODELLING
## UNDER THE CONDITION OF AN ELECTRICAL POTENTIAL GRADIENT

By

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## SYNOPSIS

Among many of technologies for decontaminating soil and groundwater, electrokinetic remediation is gaining increasing attention. Before it can be implemented in the actual field, numerical simulations are indispensable to optimize running conditions. A few such numerical models have already been developed. However, the models which have been presented have not solved physical transport and chemical reaction, simultaneously. Therefore, the development of a new model which satisfies physical transport and chemical reaction is the goal of this study. In the first step of our study, we developed an ion diffusion-migration code to simulate the behaviour of dissolved ions under the condition of electrical potential gradient. A test for the case of instantaneously injected NaCl point source into the water solution revealed results comparable to the analytical solution. This code was employed for the simulation of electromigration-diffusion transport of chemical species under electrical potential gradient in the NaCl solution. The simulation shows a process in which the dissolved ions migrate toward oppositely charged electrode and accumulate with time. The formation process of a jump in pH is also shown in the numerical results.

## INTRODUCTION

Electrokinetic remediation is one of the methods for decontaminating soil and groundwater. In electrokinetic remediation, a pair of electrodes and a direct electric current are applied to the soils. This method is used not only to remove heavy metals but also to remove $NO_3^-$ and radio nuclides. Because it is in-situ and is cost effective, it has become of major interest. Since this technology is applied in fields, examinations of the planning of electrode distribution and applied voltage are required. Numerical modelling of the electrokinetic remediation is necessary, and this has been investigated very actively. Alshwabkeh and Acar [1] simulated one-dimensional chemical transport under constant direct current. Yu and Neretnieks [9] calculated chemical transport by a compartment model. Shaporo et al. [8] and Jacobs and Probstein [3] simulated chemical transport by a conserved quantities approach in one and two dimensions, respectively. Narasimhan and Ranjin [7] have also developed a one-dimensional numerical model for the performance of electrokinetic barriers. However these models neither solve the physical nor the chemical processes simultaneously. Therefore, the development of a new model which satisfies physical transport and chemical reaction is the focus of this study. In view of this, we developed a new one-dimensional model of electromigration and diffusion, as the first step of our investigation. This model was tested for the case of NaCl diffusion, which was injected instantaneously. Finally, we simulated chemical species transport under electric potential gradient.

## MATHEMATICAL MODEL

*Electromigration and electroosmosis*

Electrokinetic remediation uses mainly the phenomena of electroosmosis and electromigration. In general, the soil surface is negatively charged. Therefore, cations occupy the zone inside the diffusive double layer. They move toward the anode. Bulk water also flows toward the anode with these cations. This phenomenon is known as electroosmosis. Electromigration means that anions move toward the cathode and cations move toward the anode.

Electroosmosis, electromigration, convection, dispersion and diffusion are concerned with transport phenomena. In this investigation, we develop and verify a one-dimensional electromigration-diffusion model.

*Transport equation*

The driving forces in our model are electromigration and diffusion of each chemical species which are generated as a result of electrical potential gradient. Electromigration is defined as the result of the gradient of electrical potential. Electromigration velocity $u_{ei}$ (m s$^{-1}$) is

$$u_{ei} = -v_i z_i F \frac{\partial \phi}{\partial y}$$

(1)

where, $v_i$ is mobility (m mol N$^{-1}$S$^{-1}$), $z_i$ is charge, $F$ is Faraday's constant (C mol$^{-1}$) and $\Phi$ is the electrical potential (V). The subscript $i$ denotes the $i$ th chemical species. The flux $J_i$ depends on the electromigration velocity and diffusion, and is defined as

$$J_i = u_{ei} C_i - D_i \frac{\partial C_i}{\partial y}$$

(2)

Therefore, the one-dimensional transport equation is

$$\frac{\partial C_i}{\partial t} + \frac{\partial (u_{ei} C_i)}{\partial y} = \frac{\partial}{\partial y}\left( D_i \frac{\partial C_i}{\partial y} \right) + R_i$$

(3)

where , $C_i$ is concentration (mol m$^{-3}$), $D_i$ is the diffusion coefficient (m$^2$ s$^{-1}$), and $R_i$ is chemical reaction term (mol m$^{-3}$ s$^{-1}$). By solving transport equation (3), each species' concentration distribution can be found. Alshawabkeh and Acer [1] used the same type of equation, however, the chemical reaction is limited to linear isotherms. Jacobs and Probstein [3], Nakagawa *et al.* [5] and Nakagawa and Wada [6] solved the transport equation by a conserved quantities approach. This method is useful in that it can avoid H$^+$ and OH$^-$ transport. The reason for this is that the mobility of these ions is larger than other ions' due to the proton jump mechanism. However, if the purpose is to simulate real phenomena rationally, the physical transport process (in this case, electromigration and diffusion) and the chemical reaction process should both be satisfied. Therefore, we employed the physicochemical simultaneous approach [4].

*Electrical potential distribution*

In order to solve transport equation (3), electrical potential distribution should be given. The electrical potential is obtained from conservation of charge. The current density $I$ is defined as

$$I = F \sum_{i=1}^{N} z_i \left( u_{ei} C_i - D_i \frac{\partial C_i}{\partial y} \right)$$

(4)

where, $N$ is the total number of chemical species. The continuity equation of current density is expressed as

$$\frac{\partial I}{\partial y} = 0$$

(5)

Table 1 Mobilities and Diffusion Coefficients used in the simulation

| Species | Mobility (m mol $N^{-1}s^{-1}$) | Diffusion Coefficient ($m^2 s^{-1}$) |
|---|---|---|
| $H^+$ | $3.756 \times 10^{-12}$ | $9.311 \times 10^{-9}$ |
| $OH^-$ | $2.127 \times 10^{-12}$ | $5.273 \times 10^{-9}$ |
| $Na^+$ | $5.379 \times 10^{-13}$ | $1.334 \times 10^{-9}$ |
| $Cl^-$ | $8.197 \times 10^{-13}$ | $2.032 \times 10^{-9}$ |

The electrical potential distribution can be given as the solution of equation (5).

*Procedure to solve the transport equation*

At first, an initial condition of concentration distribution is assumed. Then, by solving eq. (5), the potential distribution can be found. By substituting potential gradient into eq. (1), the electromigration velocity can be obtained. After that, the transport equation (4) is solved by the method of characteristics (MOC). The chemical reaction term $R_i$ is solved by using the Levenberg-Marquardt method with appropriate criteria. In the case of the transport of chemical species under an applied electric field, dissociation reaction of water should be considered. Therefore, dissociation constant of water $K_W$ is used as the criteria in the Levenberg-Marquardt method.

$$[H^+][OH^-]=K_W, \quad K_W=1.0 \times 10^{-14}$$

where, $[H^+]$ and $[OH^-]$ are the concentrations of $H^+$ and $OH^-$, respectively. Initial conditions and boundary conditions for each numerical example are shown in the next chapter.

## DIFFUSION OF NaCl AND CHEMICAL SPECIES TRANSPORT UNDER AN APPLIED ELECTRIC FIELD

*Diffusion of NaCl*

In the next stage of this investigation, in order to verify our numerical code in the simplest system, the numerical results of NaCl diffusion are compared to an analytical solution. The domain length of one-dimensional simulation is $L=0.973$ m and the time interval is 1.0 s. This domain length was determined from conditions of the generation of the irregular finite deference mesh. Both of the side gradients of concentration are set to be zero. In this example, the transfer of hydrogen and hydroxide ions is not included because the electrode is not considered. To avoid the injection of Delta function, the analytical solution at time 3600 s was used as the initial condition of the concentration distribution. The applied analytical solution of concentration is expressed as

$$C(y,t) = \frac{Q}{2\sqrt{\pi D(t-t_0)}} \exp\left[-\frac{(y-y_0)^2}{4D(t-t_0)}\right]$$

(6)

where, $Q$ is input strength per unit area, $t_0$ is injected time, $y_0$ is injected position and $D$ is the diffusion coefficient. For the diffusion coefficient of the analytical solution, equation (7) was employed

$$D = D_{Na}\left(1 - \frac{D_{Na}-D_{Cl}}{D_{Na}+D_{Cl}}\right) = \frac{2D_{Na}D_{Cl}}{D_{Na}+D_{Cl}}$$

(7)

The analytical solution of the potential inside the diffusion area, that is, the area of inside the diffusion front (concentration is positive) can be written as Jacobs [2];

$$\phi(y,t) = \frac{RT(D_{Na}-D_{Cl})(y-y_0)}{4FD(D_{Na}+D_{Cl})(t-t_0)} + K$$

(8)

where, $K$ is an arbitrary constant. The mobilities and diffusion coefficients used here are summarized in

Table 1. Figure 1(a) and (b) show numerical and analytical solutions of concentration and potential when $t=500$ s. The Numerical results of concentration and potential agree well with analytical ones. Figure 2 shows the numerical results of electromigration velocities of Na$^+$ and Cl$^-$ and total flux when $t=500$ s. The right direction is a positive direction on the coordinate in the figure. Therefore, the condition in which migration velocity and flux are positive shows chemical species migrate to the right. On the other hand, chemical species migrate to the left when these values are negative. Figure 1(a) gives evidence that the central in the calculating region is the diffusion area. Cl$^-$ migrates to the inside of the diffusion area, Na$^+$ migrates to the outside of the diffusion area, and the total flux diffuses from the center to both edges.
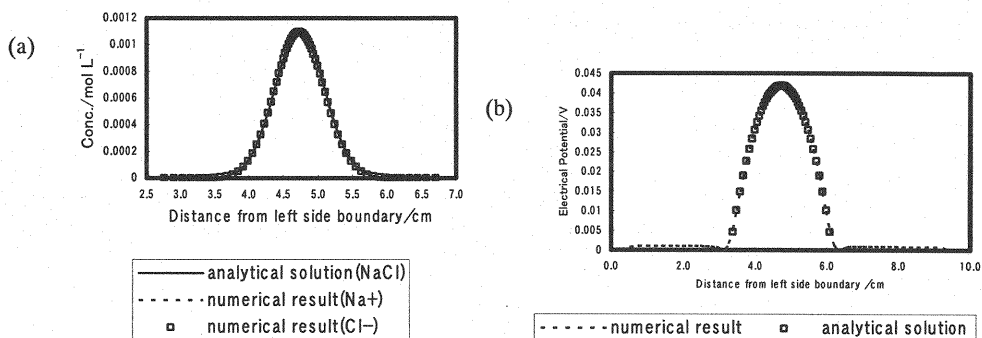


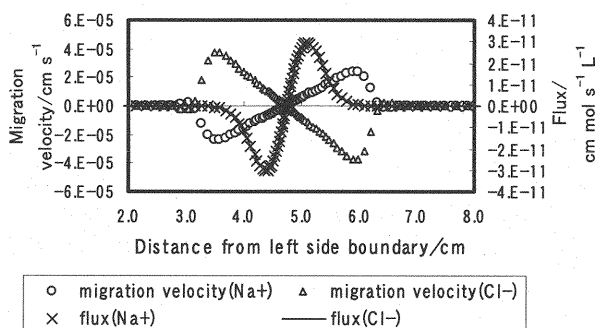Fig.1 Comparison of the numerical results with the analytical solutions (a) Concentration and (b) Potential



Fig.2 Migration velocity and total flux of numerical results

*Transport of chemical species under an applied electric field*

In this section, the numerical simulation of chemical species movement will be examined when a pair of electrodes is applied into a well-mixed NaCl solution. The chemical species Na$^+$, Cl$^-$, H$^+$, and OH$^-$ are considered. The numerical domain is defined from anode to cathode, over a length of 0.153 m. At the electrodes, electrolysis should be taken into account. As a result, for the boundary conditions of H$^+$ and OH$^-$ transport, the following relation should be used.

$$J_{OH^-}\Big|_{y=0} = \frac{I}{F}, \qquad J_{H^+}\Big|_{y=L} = \frac{I}{F} \qquad\qquad (9)$$

Applied voltages are assumed to be 10.0 V. The mobilities and diffusion coefficients which are given in Table 1 are used also in this case. Initial conditions for Na$^+$ and Cl$^-$, H$^+$ and OH$^-$ are 0.01 mol L$^{-1}$ and $1.0\times 10^{-7}$ mol L$^{-1}$, respectively. The finite difference grid interval is 0.0153 m and the time step is from 0.025 to

0.05 s, depending on the convergence in the numerical simulation. Simulation was continued until a jump in the pH distribution was formed. Figure 3(a) shows the distribution of Na$^+$ until 2900 s. In $y$=0.08-0.153 m, the concentration of Na$^+$ decreases gradually. By contrast the concentration of Na$^+$ increases toward the anode. In particular, concentration on the surface of the anode rapidly increases. This is due to an accumulation of Na$^+$, which is transported by electromigration and diffusion. Figure 3(b) shows the potential distribution. On both sides, the gradients are gentle and the mid point is sharp at 2900 s compared to 500 s, which shows a constant gradient over the whole area. The electromigration velocity increases more at the center than on the sides increasing with potential variation. Figure 3(c) shows the pH distribution. As predicted, alkaline front shifts from the anode and acid front shifts from the cathode with time, forming a pH-jump. The pH-jump is located about 0.06 m from the anode. This result is adequate, and was confirmed by another experimental study [10].
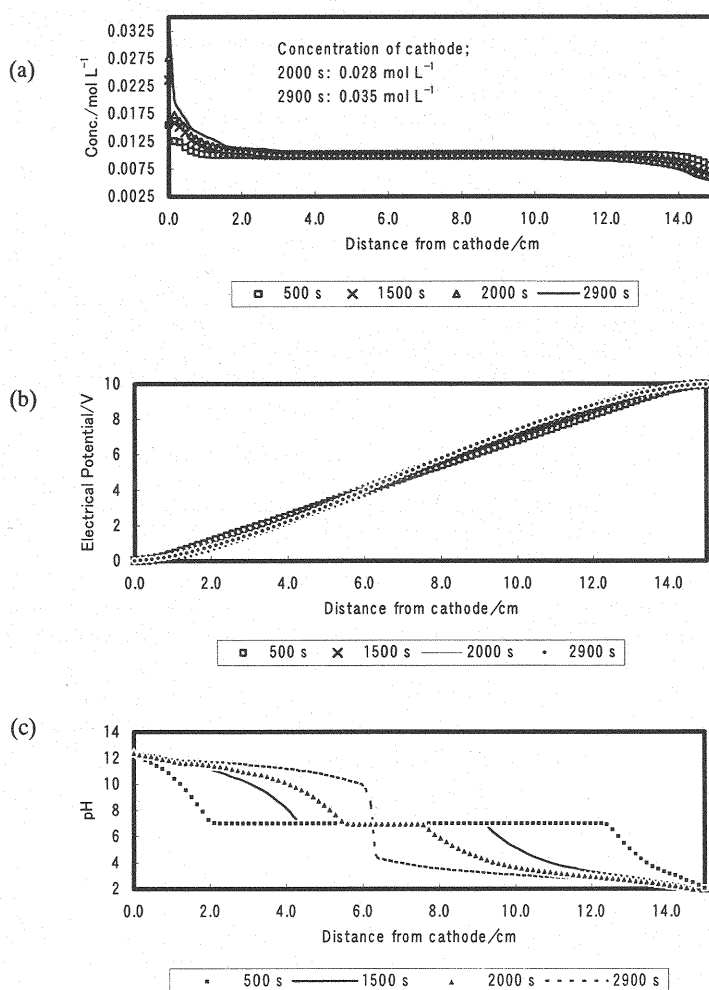
Fig.3 Numerical results for chemical species transport of Na$^+$ (a) Concentration, (b) Potential and (c) pH

## CONCLUSIONS

The purpose of our research was to develop a new model to examine applied voltage, location of electrodes, etc., when performing electrokinetic remediation. In the first stage of our investigation we present a basic model for chemical species transport under an electric field and study its applicability. In this model,

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the transport equation (4) is solved by MOC and the chemical reaction term is solved by the Levenberg-Marquardt method. This algorithm simultaneously complies with both the physical transport process and the chemical reaction process.

The findings of this study reveal the following:

1) From the application to NaCl diffusion, the results of numerical simulation for $Na^+$ and $Cl^-$ concentrations and potential agree well with the analytical results. It was confirmed that $Na^+$ migrates outside the diffusion, that $Cl^-$ migrates inside the diffusion, and that the total flux shifts toward both sides.

2) The simulation of chemical species movement under an applied electrical potential gradient showed that $Na^+$ migrates toward the anode where it accumulates. The potential gradient at the potential center has a tendency to steepen with time. Concerning the pH distribution, $H^+$ migrates from the cathode and $OH^-$ migrates from the anode, and a pH-jump is formed.

By subjoining adequate criteria, it is easy to expand the model to include chemical reactions for adsorption, desorption, and the formation of hydroxide. However, only basic cases were examined in this paper. A more advanced model, which includes electroosmosis and pressure driven flow, needs to be examined in another study.

## REFERENCES

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## APPENDIX-NOTATION

The following symbols are used in this paper:

| | | |
|---|---|---|
| $u_{ei}$ | = | electromigration velocity of $i$ species; |
| $v_i$ | = | mobility of $i$ species; |
| $F$ | = | Faraday's constant; |
| $\Phi$ | = | electrical potential; |
| $J_i$ | = | flux of electromigration and diffusion of $i$ species; |
| $C_i$ | = | concentration of $i$ species; |
| $D_i$ | = | diffusion coefficient of $i$ species; |
| $R_i$ | = | chemical reaction term of $i$ species; |
| $I$ | = | current density; *and* |
| $N$ | = | total number of chemical species. |