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## Analytical solutions for one-dimensional contaminant ion transport through electro-kinetic barriers

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## ABSTRACT

To prevent contaminant ions from spreading over the adjacent environment, it is of great interest to consider using electro-kinetic barriers to counteract contaminant transport through the combined effects of electro-osmosis and electro-migration. In this study, considering the bottom surface as a Cauchy boundary or a Dirichlet boundary condition, two analytical solutions are proposed to predict the contaminant ion transport in the electro-kinetic barrier. Analytical solutions are verified against experimental data and numerical solutions from the previous literature. Subsequently, the proposed analytical solutions are used to investigate the effects of average applied voltage gradient, barrier thickness, diffusion coefficient, retardation factor and electro-osmotic conductivity on the transport of contaminant through the electro-kinetic barrier. The results show that the steady state base contaminant concentration decreases with the increase in average voltage gradient and barrier thickness. Additionally, the logarithm of the final stable base contaminant concentration changes linearly with the average applied voltage gradient and barrier thickness. For the contaminants with a high diffusion coefficient, a larger average voltage gradient should be applied to improve the electro-kinetic effects. Clayey soils with high sorption capacity and relatively high electro-osmotic conductivity are the suggested material choice for constructing compacted soil liners within the electro-kinetic barrier, due to distinct advantages in contaminant migration prevention. Finally, a dimensionless factor is introduced to uniformly describe influences on the base relative concentration, and it can be used as an important parameter for the design of an electro-kinetic barrier.

### 1. Introduction

Improper disposal and accidental spillage of toxic and hazardous chemicals from domestic, agricultural and industrial activities have led to significant soil contamination, creating an urgent need to find feasible solutions to the problem. Containment barrier technology, such as slurry walls, sheet pile cut-off walls and grout curtains, is an effective method to protect the soil and ground water from potential contamination (Acar and Haider, 1990). However, these containment technologies are relatively expensive and time-consuming to construct and may require the use of specialized equipment. The availability of suitable access for machinery and large equipment to reach the contaminated site has become a major limitation for the application of these conventional techniques in some situations (Narasimhan and Ranjan, 2000). Moreover, the long-term behaviour of these conventional barriers under the interaction of compacted soil liners and contaminant ions is also an issue that should be addressed.

Electro-kinetic remediation is an emerging in situ method in which

contaminants are mobilized and eventually recovered by passing a low current intensity between a row of anode and cathode electrodes inserted in the ground (Acar and Alshwabkeh, 1993; Acar et al., 1995; Yeung et al., 1997; Mulligan et al., 2001; Page and Page, 2002). This application exploits the transport processes of ions in solution by electro-osmosis and electro-migration. Electro-osmosis is the movement of water that results from an applied electric gradient, while electro-migration is the movement of ions in solution in an electric field. By using electro-osmosis and electro-migration, the idea of creating an electro-kinetic barrier was conceived by Lageman et al. (1989) and successfully used to prevent the migration of heavy metal contaminants such as lead, copper, zinc and cadmium during the remediation of an abandoned paint factory (Godschalk and Lageman, 2005). As shown in Fig. 1, the idea underlying the use of an electro-kinetic barrier to prevent contaminant migration is simple. A counter-gradient opposite to the direction of the groundwater gradient is created by a continuous or periodic application of an electrical potential difference between the electrodes, which halts the movement of water within that region and

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effectively prevents the migration of contaminants (Yeung, 1990; Mitchell and Yeung, 1991; Lynch et al., 2007). Although the concept was proposed some time ago, little work on the calculation method of the electro-kinetic barrier has been carried out. It is now necessary to develop an effective calculation method to predict the transport of contaminant ions in the electro-kinetic barrier for design convenience and field applications of this method.

Considering four transport processes in the electro-kinetic system, namely, electro-migration, diffusion, electro-osmosis and advective flow under hydraulic gradients (Acar and Alshawabkeh, 1993; Shapiro and Probst, 1993; Acar et al., 1995; Yeung et al., 1997), several numerical models have been developed for the prediction of contaminant ion transport in electro-kinetic extraction and remediation (Choi and Lui, 1995; Alshawabkeh and Acar, 1996; Mattson et al., 2002; Kim et al., 2003, 2004; Amrate et al., 2005; Al-Hamdan and Reddy, 2008; Paz-García et al., 2011; Masi et al., 2017). Meanwhile, Yeung and Mitchell (1993) have developed a general coupled flow theory for the electro-kinetic barrier on the basis of the formalism of non-equilibrium thermodynamics for analysis of the physics involved in the transport processes. Narasimhan and Ranjan (2000) presented a numerical model that could predict the changes in pH, pore water pressure and the voltage gradient along the length of the electro-kinetic barrier. Numerical models play an important role in the prediction of contaminant transport in electro-kinetic remediation systems, but the level of numerical sophistication often greatly exceeds the sophistication of the available data (especially at the site selection and preliminary design stages), and the cost (in terms of man hours) of a detailed numerical analysis (with the necessary checks on discretization error) may not be justifiable under the circumstances (Rowe and Nadarajah, 1997). Thus, simplified analytical methods can provide an economic and efficient alternative to complex numerical models in many ways, although rigorous restricted conditions are required. In the field of conventional landfill barrier system, analytical methods have generally been used since they can readily analyse the sensitivity of each individual parameter in question. Chen et al. (2009) developed an analytical solution for 1D contaminant diffusion through a multi-layered landfill barrier system to investigate the effects of the half-life of contaminants on the solute flux of benzene diffused into the underlying aquifer considering arbitrary initial conditions. Subsequently, a series of analytical studies regarding the diffusion of contaminants in landfill barriers have been conducted by considering different combinations of fixed solute concentrations and zero-flux boundary conditions, degradation effects of the organic contaminants, sorption, convection and unsaturated soils beneath the barrier system (Li and Cleall, 2010; Xie et al., 2013; Zhao and Burns, 2013; Zhang et al., 2013; Chen et al., 2019). These analytical studies can provide the indications necessary to provide analytical solutions for the transport of contaminant ions in electro-kinetic barriers.

The objective of this paper is to present a 1D analytical model capable of predicting contaminant ion transport in electro-kinetic barriers considering the combined effect of concentration gradient,

hydraulic gradient, electro-osmosis and electro-migration. These analytical solutions are subjected to the Cauchy boundary and Dirichlet boundary conditions, respectively. The proposed analytical solutions were validated by comparison with experimental and numerical results presented in previous literature. Finally, using the proposed analytical solutions, a parametric study was performed to investigate the influences of an average applied voltage gradient, barrier thickness, diffusion coefficient, retardation factor and electro-osmotic conductivity on the contaminant ion migration in the electro-kinetic barrier.

## 2. Theoretical background

In this study, we considered diffusion, electro-osmosis, and electro-migration as the main transport mechanisms for contaminant ions in the electro-kinetic barrier. Since colloid migration is hindered by the immobile phase of the porous medium (Yu and Neretnieks, 1997), electrophoresis was neglected.

### 2.1. Electro-osmosis

Electro-osmosis is the movement of the pore water due to the viscous drag of the cations. The negative charge on the surface of most soil particles will cause an accumulation of positively charged cations near the surface. Thus, under an electrical potential gradient, the pore water will be dragged by the cations, and the net movement of the pore water will be towards the cathode.

The electro-osmotic flow rate can be expressed by the following formulation:

$$q_{eo} = -k_{eo} \nabla \phi \quad (1)$$

where  $q_{eo}$  is electro-osmotic flux ( $\text{m}\cdot\text{s}^{-1}$ ),  $\nabla \phi$  is electrical voltage gradient ( $\text{V}\cdot\text{m}^{-1}$ ), and  $k_{eo}$  is electro-osmotic conductivity ( $\text{m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ), which depends on several variables. According to the Helmholtz-Smoluchowski theory, it can be related to zeta potential  $\xi$  (V) and the dielectric constant  $\epsilon$  ( $8.854 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$ ) and the viscosity  $\eta$  ( $1 \times 10^{-3} \text{ N}\cdot\text{s}\cdot\text{m}^{-2}$ ) of the fluid (Eykholt and Daniel, 1994):

$$k_{eo} = -\frac{\epsilon \xi}{\eta} n \tau \quad (2)$$

where the negative sign indicates that negatively charged particles produce an electro-osmotic flow directed from anode to cathode. The tortuosity  $\tau$  and porosity  $n$  terms in Eq. (2) were introduced by Casagrande (1949) to include the porous matrix effects in the original Helmholtz-Smoluchowski formulation. In general, the values of electro-osmotic conductivity fall in the narrow range between  $1 \times 10^{-9}$  and  $1 \times 10^{-8} \text{ m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$  compared with the values of hydraulic conductivity between  $1 \times 10^{-13}$  and  $1 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$ , which is relatively independent of soil type (Mitchell, 1993). Therefore, an electrical gradient is more effective than a hydraulic gradient in moving liquid through fine-grained soils.

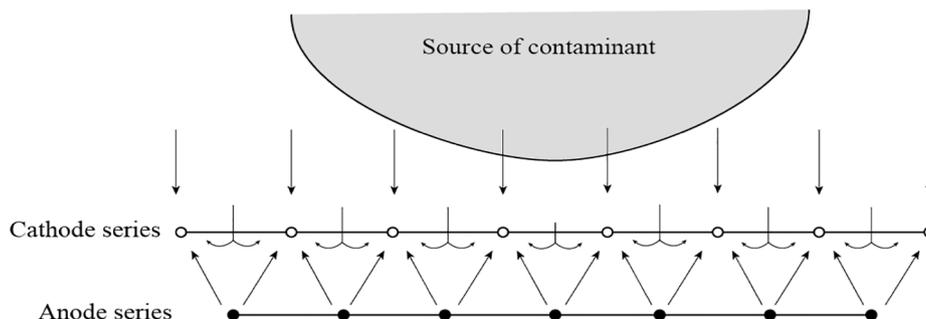


Fig. 1. Schematic field arrangement of electro-kinetic barrier.

## 2.2. Electro-migration

Electro-migration is the transport of charged ions in solution towards oppositely charged electrodes. Negatively charged anions will move towards the anode and positively charged cations will move towards the cathode. Electro-migration of ions is quantified by effective ionic mobility,  $U_j^*$ . Effective ionic mobility can be defined as the velocity of the ion in the soil under the influence of an electrical potential gradient. Because there is no established method to measure the effective ionic mobility of an ion in the soil, indirect methods are always adopted. The ionic mobility and the diffusion coefficient of an ion in dilute solution are related by the Nernst-Einstein equation (Koryta, 1982):

$$U_j^* = \frac{D_j z_j F}{RT} \tau n \quad (3)$$

where  $D_j$  is the diffusion coefficient of ion  $j$  in the dilute solution ( $\text{m}^2 \cdot \text{s}^{-1}$ ),  $z_j$  is the charge of the chemical species,  $F$  is Faraday's constant ( $96487 \text{C} \cdot \text{mol}^{-1}$ ),  $R$  is the universal gas constant ( $8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ), and  $T$  is the absolute temperature (K).

## 2.3. Interpretation of the electro-kinetic barrier

Fig. 1 shows the principle configuration of an electro-kinetic barrier. A series of electrodes (anodes and cathodes) are placed perpendicular to the contaminant migration direction. The electrodes are oriented in such a way that the electro-osmotic flow occurs in a direction opposite to the direction of contaminant ion migration under hydraulic gradient. Here, a simple example was used to illustrate the effectiveness of electro-osmosis over the flow caused by the hydraulic gradient. For instance, a clayey soil has a hydraulic conductivity  $k_h$  of  $1 \times 10^{-9} \text{m} \cdot \text{s}^{-1}$  and an electro-osmotic conductivity  $k_{eo}$  of  $5 \times 10^{-9} \text{m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . Assuming the volumes of pore water flow through the unit cross-sectional area, and the flow created by the electrical potential gradient and hydraulic gradient are equal to each other:

$$k_h \nabla h = k_{eo} \nabla \phi \quad (4)$$

An electrical potential gradient of  $25 \text{V} \cdot \text{m}^{-1}$  is applied, and the hydraulic gradient can be calculated as follows:

$$\nabla h = \frac{k_{eo}}{k_h} \nabla \phi = 125 \quad (5)$$

This indicates that the electro-osmotic flow created by an electrical potential gradient of  $25 \text{V} \cdot \text{m}^{-1}$  can oppose the water flow caused by a hydraulic gradient of 125, which is high compared to normal field conditions. A small electrical potential gradient is sufficient to stop the flow due to the high hydraulic gradient encountered in field applications. Thus, a sustained electro-osmotic potential could effectively control the transport of contaminants. Fig. 2 shows the relative migration of anions and cations under the action of an electric field. The presented system has a constant concentration boundary at the cathode end. The sample is assumed to be free of contaminant ions at the

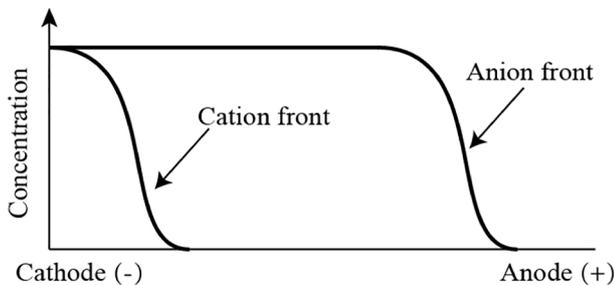


Fig. 2. Location of cation and anion fronts under combined action of electrical, hydraulic and chemical gradients.

beginning. With no electrical potential gradient applied, both anions and cations are migrating from the cathode towards the anode under the concentration gradient. After the voltage is applied, the electrical potential gradient can affect the movement of the anion front relative to the cation front. It can be seen that cation transport can be effectively controlled in the electro-kinetic barrier. However, to control the transport of anions, the polarity of the electrodes should be reversed. Doing so will create electro-osmotic flow in the same direction as ground water flow and increase the advective migration of the contaminant. Electro-migration of anions is from cathode to anode and is greater than the movement due to electro-osmotic flow in the opposite direction. Under such action, the transport of anions is prevented in the electro-kinetic barrier.

## 3. Theoretical analysis

### 3.1. Governing equation

A schematic diagram for 1D contaminant ion transport in the electro-kinetic barrier is shown in Fig. 3, with the anode placed at the bottom and the cathode at the top. A coordinate system ( $z$ ), with downward positive direction was adopted, and the top of the soil layer was chosen as the origin of  $z$ . Considering the minor changes of soil properties in the electro-kinetic barrier system (Mitchell and Yeung, 1991; Alshawabkeh and Acar, 1992, 1996; Acar and Alshawabkeh, 1996), the following assumptions were made to establish the analytical model for contaminant ion transport in the electro-kinetic barrier:

- (1) The soil is homogeneous and fully saturated, and the soil properties are constant over time.
- (2) The soil deformation induced by electro-osmosis is minor and can be neglected, the net electro-osmotic flow is always towards the cathode.
- (3) The applied voltage is useful in the transport of water and the chemical species.
- (4) Fluid flux and ionic flux due to electro-osmosis and electro-migration are linear functions of electrical potential gradient and can be linearly superimposed.
- (5) The flow caused by the thermal gradient and chemical concentration gradient is neglected, and the fluid flux induced by the hydraulic gradient and electrical potential gradient remains constant over time.
- (6) Both the electrophoresis of the fine-grained soil particles and the electro-chemical reaction are neglected.

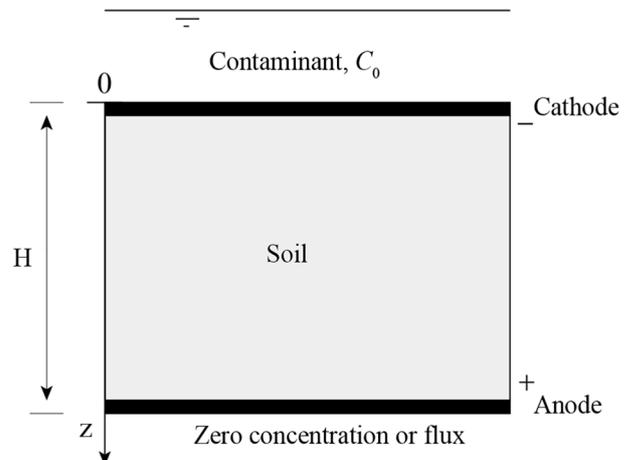


Fig. 3. Schematic diagram of 1D contaminant transport in electro-kinetic barrier.

Under these assumptions, the equations describing the coupled flow phenomena for total fluid flux, mass flux and charge flux have been given by Alshawabkeh and Acar (1992). The equation describing the total fluid flux can be expressed as:

$$J_w = -k_h \nabla h - k_{eo} \nabla \phi \quad (6)$$

where  $J_w$  is fluid flux per unit cross-sectional area of saturated clays ( $\text{m}\cdot\text{s}^{-1}$ ). Thereafter, the flux density per unit cross-sectional area of porous medium  $J_j$  ( $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) of a dissolved chemical species  $j$  can be expressed as (Alshawabkeh and Acar, 1992):

$$J_j = -D_j^* \nabla c_j + (J_w + U_j^* \nabla \phi) c_j \quad (7)$$

where  $D_j^*$  ( $\text{m}^2\cdot\text{s}^{-1}$ ) is the effective diffusion coefficient of the  $j$ -th specie;  $c_j$  is the concentration of the  $j$ -th specie ( $\text{mol}\cdot\text{m}^{-3}$ ). Due to the tortuous path of ions in the porous matrix, the effect of porosity  $n$  and tortuosity  $\tau$  (Shackelford and Daniel, 1991) was accounted for to give the effective diffusion coefficient as:

$$D_j^* = n\tau D_j \quad (8)$$

The tortuosity  $\tau$  may span in the range 0.01–0.84, which is dependent on the characteristics of the porous medium (Alshawabkeh and Acar, 1992). The effective ion mobility has been defined in Eq. (3) by the Nernst-Townsend-Einstein relation.

Applying the law of mass conservation to Eq. (7), the mass transport of the  $j$ -th contaminant ions in the electro-kinetic barrier is given by the Nernst-Planck equation:

$$D_j^* \frac{\partial^2 c_j(z, t)}{\partial z^2} - (J_w + U_j^* \nabla \phi) \frac{\partial c_j(z, t)}{\partial z} = nR_d^j \frac{\partial c_j(z, t)}{\partial t} \quad (9)$$

where  $t$  is time;  $R_d^j$  is the retardation factor of the soil for ion  $j$ , which is determined using following equation:

$$R_d^j = 1 + \rho K_j / n \quad (10)$$

where  $\rho$  represents the dry density of the soil; and  $K$  is the distribution coefficient for  $j$ -th specie.

As described in previous literature (Shackelford, 1990), a constant concentration of contaminant is often assumed, since this will lead to a conservative result in the barrier system. Thus, a constant concentration is also assumed at the top of the electro-kinetic barrier in this study, which can be described as:

$$c_j(0, t) = c_0 \quad (11)$$

where  $c_0$  is the concentration of contaminant ion  $j$  in the dilute solution. At the same time, in conventional landfill barriers, the horizontal flow velocity of groundwater is always assumed to be infinite and that once the contaminants drain out, the contaminant would be instantaneously flushed away via the groundwater movement (Chen et al., 2009). The contaminant concentration at the bottom of the electro-kinetic barrier can be set as zero (i.e., Dirichlet boundary condition):

$$c_j(H, t) = 0 \quad (12)$$

When the horizontal flow velocity of groundwater is not sufficient, the Cauchy boundary condition might be favoured as follows:

$$\lambda \frac{\partial c_j(H, t)}{\partial z} + \mu c_j(H, t) = 0 \quad (13)$$

where  $\lambda$  and  $\mu$  are two parameters to describe the Cauchy boundary condition. In general,  $\lambda$  is a parameter proportion to the diffusion coefficient, thus  $\lambda \neq 0$ . Under these circumstances, when parameter  $\mu$  is infinite, the Cauchy boundary condition can be degraded to the Dirichlet boundary condition. When parameter  $\mu$  is equal to zero, the Cauchy boundary condition can be degraded to the Neumann boundary

condition (zero mass flux boundary). In this study, both analytical solutions for the Dirichlet and Cauchy boundary conditions are presented.

Additionally, the system can be considered initially contaminant free with respect to the electro-kinetic barrier after construction. The initial condition can be assumed as:

$$c_j(z, 0) = 0 \quad (14)$$

Thus, the simplified governing equation, which could capture the main feature of the contaminant ion transport in the electro-kinetic barrier, and two corresponding boundary conditions and initial condition, are presented in the above section.

### 3.2. Analytical solutions

Since the horizontal flow velocity of groundwater at the lower boundary is insufficient, the Cauchy boundary condition is more suitable in reality. Thus, in the text, only the Cauchy boundary condition expressed in Eq. (13) is considered and discussed. With respect to the Dirichlet boundary condition Eq. (12), the main deviation process is shown in Appendix A and the solution is not discussed here.

Initially, we define two parameters as:

$$A = \tau D_j / R_d^j \quad (15)$$

$$B = (J_w + U_j^* \nabla \phi) / nR_d^j \quad (16)$$

Substituting Eqs. (15) and (16) into Eq. (9), we can obtain following equation:

$$A \frac{\partial^2 c_j(z, t)}{\partial z^2} - B \frac{\partial c_j(z, t)}{\partial z} = \frac{\partial c_j(z, t)}{\partial t} \quad (17)$$

According to Eq. (17), a new variable  $W(z, t)$  can be introduced as:

$$W(z, t) = c_j(z, t) e^{-\frac{Bz}{A} + \frac{B^2}{4A} t} \quad (18)$$

And Eq. (17) can be rewritten as:

$$A \frac{\partial^2 W(z, t)}{\partial z^2} = \frac{\partial W(z, t)}{\partial t} \quad (19)$$

To generalize the solution, two dimensionless variables are introduced as:

$$Z = \frac{z}{H} \quad (20)$$

$$T = \frac{At}{H^2} \quad (21)$$

From Eq. (15), we can see that the dimensionless time factor  $T$  in Eq. (21) is a function of time  $t$ , coefficients of diffusion, tortuosity, retardation factor, and the thickness of electro-kinetic barrier.

By using Eqs. (20) and (21), Eq. (19) can be further rearranged as:

$$\frac{\partial^2 W(Z, T)}{\partial Z^2} = \frac{\partial W(Z, T)}{\partial T} \quad (22)$$

Through corresponding transformations, the Cauchy boundary and initial conditions can be rewritten as follows:

$$\begin{cases} W(0, T) = c_0 e^{\frac{\mu^2 H^2}{4\lambda^2} T} \\ \frac{\partial W(1, T)}{\partial Z} - \bar{\lambda} W(1, T) = 0 \end{cases} \quad (23)$$

$$W(Z, 0) = 0 \quad (24)$$

where

$$\bar{\lambda} = -\left(\frac{B}{2A} + \frac{\mu}{\lambda}\right)H \quad (25)$$

To derive the analytical solution of Eq. (22),  $W(Z, T)$  can be separated into two parts such that:

$$W(Z, T) = S(Z, T) + f(Z, T) \quad (26)$$

To satisfy the boundary condition of Eq. (23), the auxiliary function  $f(Z, T)$  can be defined as:

$$f(Z, T) = c_0 \left( 1 + \frac{\bar{\lambda}Z}{1 - \bar{\lambda}} \right) e^{\frac{B^2 H^2}{4A^2} T} \quad (27)$$

Now, Eqs. (22), (23) and (24) can then be rewritten as:

$$\frac{\partial^2 S}{\partial Z^2} = \frac{\partial S}{\partial T} + \frac{\partial f}{\partial T} \quad (28)$$

$$\begin{cases} S(0, T) = 0 \\ \frac{\partial S(1, T)}{\partial Z} - \bar{\lambda}S(1, T) = 0 \end{cases} \quad (29)$$

$$S(Z, 0) = -c_0 \left( 1 + \frac{\bar{\lambda}Z}{1 - \bar{\lambda}} \right) \quad (30)$$

Referring to previous studies (Ozisik, 1968; van Genuchten and Alves, 1982; Chen and Liu, 2011), the solution to Eq. (28) can be supposed to have the following form:

$$S(Z, T) = \sum_{m=1}^{\infty} T_m(T) \sin(\beta_m Z) \quad (31)$$

where

$$\beta_m = \bar{\lambda} \tan \beta_m \quad (32)$$

By substituting Eq. (31) into Eq. (28), the following relation can be obtained:

$$-\sum_{m=1}^{\infty} T_m(T) \beta_m^2 \sin(\beta_m Z) = \sum_{m=1}^{\infty} T_m'(T) \sin(\beta_m Z) + \frac{\partial f}{\partial T} \quad (33)$$

Because of the orthogonality of the Fourier series, Eq. (33) can be simplified to:

$$T_m'(T) + \beta_m^2 T_m(T) = g(T) \quad (34)$$

where

$$g(T) = \frac{\beta_m (\cos \beta_m - 1) - \frac{\bar{\lambda}}{1 - \bar{\lambda}} (\cos \beta_m - \beta_m \cos \beta_m)}{2\beta_m^2 - \beta_m \sin(2\beta_m)} \frac{B^2 H^2 c_0}{A^2} e^{\frac{B^2 H^2}{4A^2} T} \quad (35)$$

Similarly, the following equation can be derived by substituting Eq. (31) into the initial condition Eq. (30) and using the orthogonality of the Fourier series:

$$T_m(0) = \frac{\beta_m (\cos \beta_m - 1) - \frac{\bar{\lambda}}{1 - \bar{\lambda}} (\cos \beta_m - \beta_m \cos \beta_m)}{2\beta_m^2 - \beta_m \sin(2\beta_m)} c_0 \quad (36)$$

Eqs. (34) and (36) are an ordinary differential equation and its corresponding initial condition. Thus, the expression for  $T_m(t)$  can be easily determined to be:

$$T_m(T) = e^{-\beta_m^2 T} \left[ \int_0^T e^{\beta_m^2 t} g(t) dt + T_m(0) \right] \quad (37)$$

Therefore, the concentration of  $j$ -th contaminant ion can be obtained by substituting Eq. (37) into Eq. (31) and combining Eqs. (18), (26) and (27):

$$c_j(Z, T) = \sum_{m=1}^{\infty} \left[ \int_0^T e^{-\beta_m^2 (T-t)} g(t) dt + T_m(0) e^{-\beta_m^2 T} \right] \sin(\beta_m Z) e^{\frac{B^2 H^2}{4A^2} T} + c_0 \left( 1 + \frac{\bar{\lambda}Z}{1 - \bar{\lambda}} \right) e^{\frac{B^2 H^2}{4A^2} T} \quad (38)$$

As the analytical solution for the contaminant concentration is obtained, the mass flux through the electro-kinetic barrier can then be obtained by substituting them into Eq. (7).

## 4. Verification

### 4.1. Experimental introduction

Yeung (1990) conducted an experiment to investigate the effectiveness of an electro-kinetic barrier to prevent the transport of contaminant ions. The results of his experiment are also presented in Yeung and Mitchell (1993). In their study, 1D column tests were carried out for different time periods. Sodium chloride was selected as a contaminant in their experiment for its stability and low attenuation in soils. The soil used in the experiment was a grey-brown silty clay of moderate plasticity from Livermore, California. Samples were compacted at an optimum moisture content of 21% and a dry bulk density of 1.6 g/cm<sup>3</sup>. Sodium chloride (0.022 M) was introduced to the top reservoirs of the permeameters to simulate the contaminant. A hydraulic gradient of 50 was applied continuously. An electrical potential gradient of 1 V·cm<sup>-1</sup> was applied across the samples for 1 h per day in a direction to create electro-osmotic flow opposite to the hydraulic flow. This was done by placing a cathode near the sample inlet and an anode near the sample outlet. In their study, one sample was sectioned for chemical analysis every 5 days. Sodium and chloride concentrations in each section of the soil sample were obtained by chemical analysis.

Table 1 presents the parameters used in the proposed analytical solution, which were also used in the numerical simulation by Narasimhan and Ranjan (2000). It should be pointed out, because the samples were collected for chemical analysis at different times, the data showing the ion distribution came from different samples. Hence, the hydraulic electro-osmotic conductivities, porosity and tortuosity used in the analytical solution were the average values from different samples. The diffusion coefficients for sodium and chloride ions were obtained from Mitchell (1993). The sample length and hydraulic gradient is presented by Yeung (1990).

Note that due to interface resistance between the cathodes and soils, the effective voltage applied on the soil sample is slightly less than 1 V·cm<sup>-1</sup>; it is closer to approximately 0.8 V·cm<sup>-1</sup>. In addition, the voltage gradient in the experiment was applied for 1 h per day, but the voltage gradient was assumed to be constant over time in the proposed analytical solutions. Considering the changes of effective voltage gradient and electro-osmotic flux are minor by using intermittent current (Micic et al., 2001), an average voltage is defined based on the principle of equal transport quantity for pore water and ions:

**Table 1**  
Parameters used in predicting ion transport with electro-kinetic barrier.

Parameter	Value
Hydraulic conductivity, $K_h$ , (m·s <sup>-1</sup> )	$1 \times 10^{-11}$
Electro-osmotic conductivity, $K_e$ (m <sup>2</sup> ·V <sup>-1</sup> ·s <sup>-1</sup> )	$3 \times 10^{-9}$
Diffusion coefficient of Na <sup>+</sup> ions, $D^{Na+}$ (m <sup>2</sup> ·s <sup>-1</sup> )	$13.3 \times 10^{-10}$ (Mitchell, 1993)
Diffusion coefficient of Cl <sup>-</sup> ions, $D^{Cl-}$ (m <sup>2</sup> ·s <sup>-1</sup> )	$20.3 \times 10^{-10}$ (Mitchell, 1993)
Porosity, $n$	0.38
Tortuosity, $\tau$	0.5
Average voltage gradient, $\nabla E_{avg}$ (V·m <sup>-1</sup> )	3.75
Hydraulic gradient, $\nabla h$	50
Length of sample, $H$ (m)	0.1

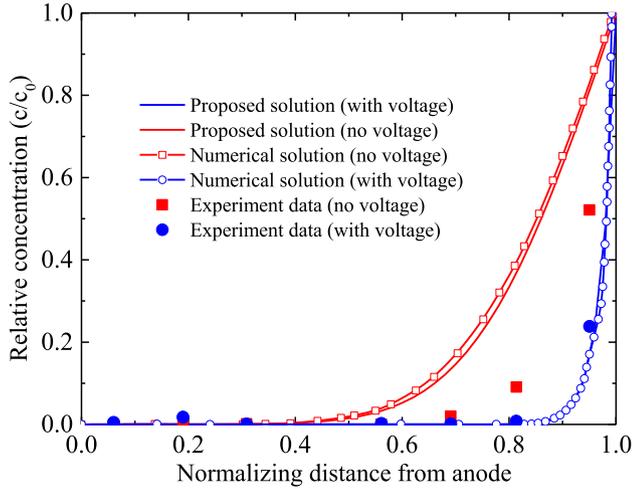
$$(k_{ev} + U_j^*) \frac{\phi_0 T_s}{H} = (k_{ev} + U_j^*) \frac{\phi_{avg} T_{int}}{H} \Rightarrow \phi_{avg} = \frac{T_s}{T_{int}} \phi_0 \quad (39)$$

where  $\phi_0$  is the effective voltage applied on the electro-kinetic barrier;  $\phi_{avg}$  is the average voltage;  $T_s$  is the time for sustained DC voltage applied each time; and  $T_{int}$  is the interval period. Therefore, the average voltage gradient is determined as 3.75 V/m in the calculation.

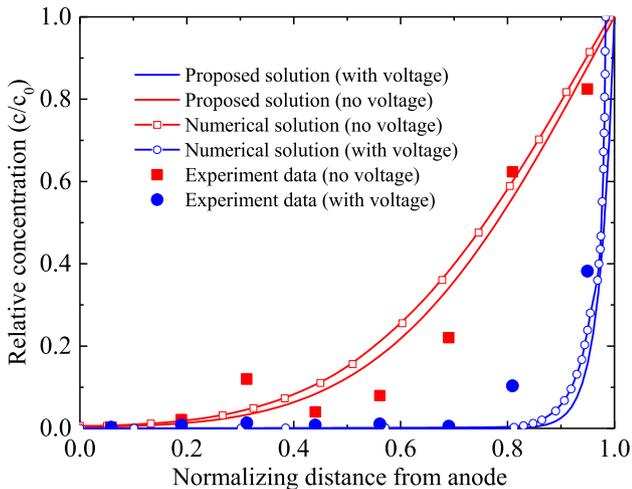
#### 4.2. Comparison between experimental and numerical results

In the experiments, sodium and chloride migrated from the anode end could not be flushed away completely, so the analytical solution considering the Cauchy boundary condition was used for comparison. The value of  $\mu/\lambda$  was chosen as 10.

Figs. 4 and 5 present the analytical predicted distributions of sodium and chloride with experimental and numerical results at different times. The figures show that the result of the proposed analytical solution agrees with the experimental and numerical results from previous studies (Yeung, 1990; Narasimhan and Ranjan, 2000), which indicates the validity and reasonability of the proposed analytical solution and the equivalent method to determine the average voltage gradient. Note that, the destructive chemical analyses of the samples lead to the loss of the sample at the end of each experimental period. Therefore, the data for

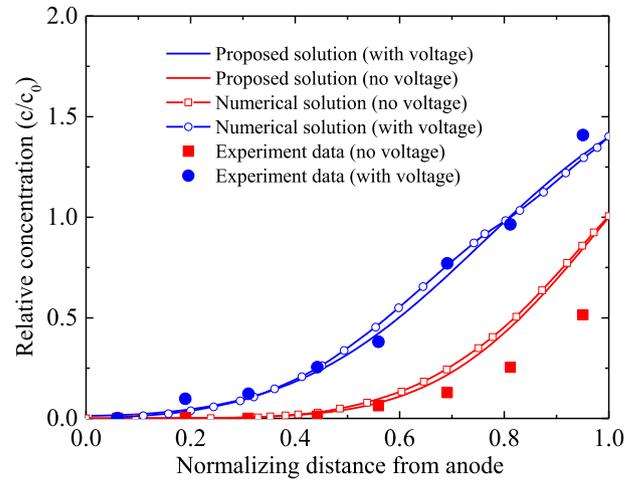


(a) after 10 days

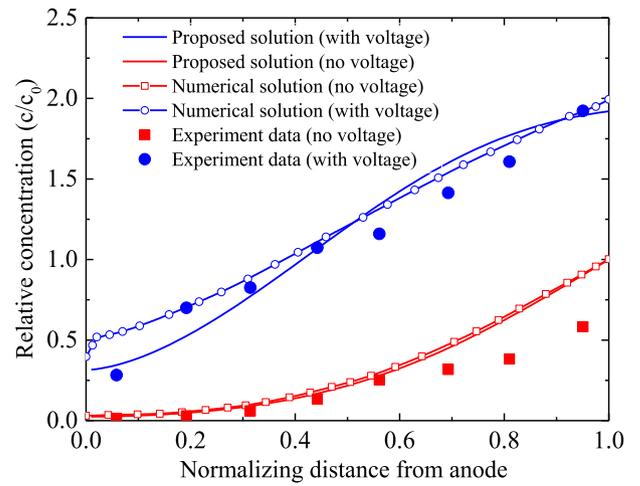


(b) after 25 days

Fig. 4. Comparisons of the distribution of sodium ions at different time.



(a) after 10 days



(b) after 25 days

Fig. 5. Comparisons of the distribution of chloride ions at different times.

10 days comes from a different sample than the data for 25 days. Since it is difficult to uniformly pack soil columns, it is inevitable that packing variations can result in the differences in initial concentrations. Thus, the soil parameters of all the samples were averaged before being used for simulations. It was found that there is a relatively large difference between the analytical solution and experimental data. However, the difference between the analytical solution and numerical solution is small, which may be caused by ignoring changes of soil parameters and soil deformation to derive the analytical solution. In general, the capability of the proposed analytical solution to predict the transport of the contaminant ions in the electro-kinetic barrier is confirmed according to the comparison results.

As shown in Fig. 4, when a hydraulic gradient of 50 was imposed from the cathode to the anode, the sodium ions moved towards the anode by advection and diffusion. Both the sodium and chloride ions have migrated considerably towards the anode under the action of hydraulic gradient merely. However, when the voltage gradient was applied to the electro-kinetic barrier, the migration of sodium ions from the cathode to the anode was significantly slowed, even after 25 days. Fig. 5 shows the distributions of the chloride ions at different times. It was found, except in the case of hydraulic gradient action, the prevailing electro-migration will tend to promote the transport of negatively charged chloride ions from the cathode towards the anode. Moreover, the electro-migration of chloride ions is dominant over the movement

due to the counter-flow created by electro-osmosis. In this case, the migration rate of chloride ions from the cathode towards the anode was enhanced by applying the voltage gradient. Therefore, if the contaminant of interest consists of negatively charged ions, the barrier cathodes arrangement in Fig. 1 should be reversed. Furthermore, if the contaminants include both negatively and positively charged ions, an additional row of cathodes should be installed below the anodes.

### 5. Parameter study

In this section, the parameter study was conducted using the proposed analytics to analyse the transport of lead ions (Pb(II)) in the electro-kinetic barriers. The diffusion coefficient and mobility of Pb(II) were taken from Kim et al. (2004). The constant concentration of Pb(II) at the top boundary,  $c_0$ , was assumed to be 2.0 g/L. The porosity and tortuosity of the soil were set as 0.48 and 0.4, respectively. The hydraulic and electro-osmotic conductivities were assumed to be  $1.0 \times 10^{-11} \text{ m}\cdot\text{s}^{-1}$  and  $3.0 \times 10^{-9} \text{ m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ , respectively. The retardation factor was set as 1.0. The basic calculation parameters required in the analytical solutions are given in Table 2. The influence of the average voltage gradient, barrier thickness, diffusion coefficient, retardation factor and electro-osmotic conductivity on the transport process of contaminant ions in the electro-kinetic barrier was studied.

#### 5.1. Effect of average voltage gradient

Hydraulic conductivity and electro-osmotic conductivity (such that  $k_h \leq 1 \times 10^{-7} \text{ cm/s}$  and  $k_{eo} \approx 5 \times 10^{-5} \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ) for typical compacted clay liner materials, the required sustained DC voltage across a liner of typical thickness would be of the order of a few tenths of a volt (Mitchell and Yeung, 1991). Considering this, five different values of average voltage gradient  $\nabla\phi_{avg}$  (i.e., 0, 0.5, 1.0, 1.5 and 2.0 V/m) were considered to investigate the effect of varying voltages on Pb(II) transport within the electro-kinetic barrier, while the other parameters remained the same as those in Table 2. The value of  $\mu/\lambda$  was chosen as  $10 \text{ m}^{-1}$ . For the case of  $\nabla\phi_{avg} = 0$ , there is no DC voltage applied to impede diffusive migration of the contaminant. In this case, contaminant transport is only induced by diffusion and convection under the hydraulic gradient, and the base contaminant concentration reaches 90% of  $c_0$  at  $T = 0.28$  corresponding to approximately 94 years. Fig. 6 shows a series of contaminant breakthrough curves in terms of the base relative concentration  $c_b/c_0$  with respect to five different average voltage gradients. It can be found that the base contaminant concentration decreases significantly with the increase of average voltage gradient, and the time required to reach the steady state is shortened. It is seen that the final base relative concentration reduces to  $c_b^f/c_0 = 7.32 \times 10^{-3}$  when  $\nabla\phi_{avg} = 0.5 \text{ V/m}$ , which is much smaller than  $c_b^f/c_0 = 1.0$  without DC voltage applied. Furthermore, when voltage gradient increases to 2 V/m, the value of  $c_b^f/c_0$  decreases to  $2.0 \times 10^{-6}$ . Fig. 7 shows the relationship between the final base relative concentration and average voltage gradient. There is a linear relationship found between  $\log(c_b^f/c_0)$  and  $\nabla\phi_{avg}$  except when  $\nabla\phi_{avg} \leq 0.5 \text{ V/m}$ . Thus, by using this

Table 2

Parameters used in analytical solution for parametric studies.

Parameter	Value
Hydraulic conductivity, $K_h$ ( $\text{m}\cdot\text{s}^{-1}$ )	$1.0 \times 10^{-11}$
Electro-osmotic conductivity, $K_e$ ( $\text{m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ )	$3.0 \times 10^{-9}$
Diffusion coefficient of $\text{Pb}^{2+}$ ions, $D^{\text{Pb}^{2+}}$ ( $\text{m}^2\cdot\text{s}^{-1}$ )	$9.45 \times 10^{-10}$
Ionic mobility of $\text{Pb}^{2+}$ ions, $u^{\text{Pb}^{2+}}$ ( $\text{m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ )	$7.38 \times 10^{-8}$
Porosity, $n$	0.48
Tortuosity, $\tau$	0.4
Average voltage gradient, $\nabla E_{avg}$ ( $\text{V}\cdot\text{m}^{-1}$ )	1.0
Hydraulic gradient, $\nabla h$	5
Electro-kinetic barrier thickness, $H$ (m)	2.0
Retardation factor, $R_d$	1.0

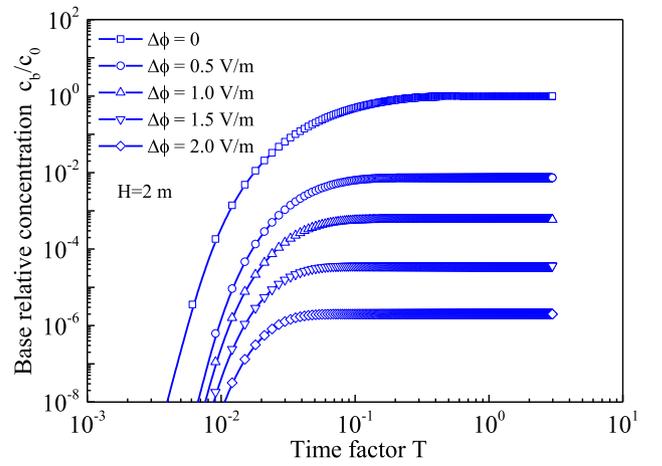


Fig. 6. Effect of average voltage gradient on the development of relative base concentration.

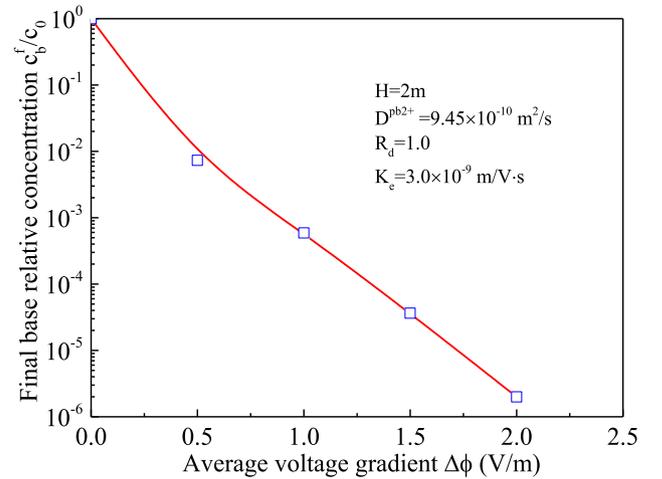


Fig. 7. Relationship of the final relative base concentration with the average voltage gradient.

relation, the value of the average voltage gradient can be determined as 0.9 V/m in this case when assuming the breakthrough criterion as  $c_b^f/c_0 = 1.0 \times 10^{-3}$ . If the DC voltage is intermittently applied in the field application with the applied voltage gradient 50 V/m and sustained for 1 h each time, the interval period can be determined as 56 h by using Eq. (39).

The influence of average voltage gradient on the mass flux at the bottom of the electro-kinetic barrier is shown in Fig. 8. Similar to changes in relative base concentration, the bottom mass flux decreases with increasing average voltage gradient, and the time to reach the steady state decreases with increasing average voltage gradient. For instance, when the average voltage gradient is 0.5 V/m, the 100-year ( $T = 0.298$ ) mass flux at the bottom of the electro-kinetic barrier decreases to 14% of that  $7.53 \times 10^7 \text{ mg/ha/year}$  without DC voltage applied. Furthermore, as the average voltage gradient increases from 0.5 V/m to 2.0 V/m, the bottom mass flux decreases by a factor of 3690. In general, the bottom mass flux for the conventional composite liners is usually within  $10^3$  and  $10^6 \text{ mg/ha/year}$  (Rowe et al., 2000). Thus, when the average voltage gradient is within the 1.0 to 2.0 V/m, the migration of Pb(II) in the electro-kinetic barrier can be effectively prevented.

#### 5.2. Effect of thickness of electro-kinetic barrier

To investigate the influence of the barrier thickness on the transport

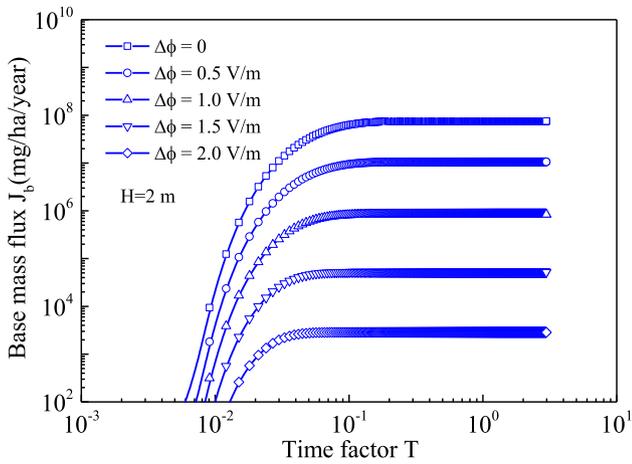


Fig. 8. Effect of the average voltage potential on the mass flux at the bottom.

process of Pb(II) in the electro-kinetic barrier, five thickness values  $H$  (i.e., 0.5 m, 1.0 m, 1.5 m, 2.0 m, and 2.5 m) were considered. In this analysis, the average voltage gradient was fixed as 1.0 V/m, while the other parameters were kept the same as values in Table 2. The value of  $\mu/\lambda$  was set as  $10 \text{ m}^{-1}$ . Fig. 9 shows the contaminant breakthrough curves in terms of base relative concentration with respect to different barrier thicknesses. As barrier thickness increases from 0.5 m to 2.5 m, a decreasing relative base contaminant concentration can be observed. Thicker compacted clayey soil layers showed greater contaminant retention, and smaller final relative base contaminant concentration. Additionally, it is apparent that the time required to achieve the same base contaminant concentration increases significantly with increasing thickness. Thus, the increase of the barrier thickness can not only decrease the final base contaminant concentration but also prolong the breakthrough time. Therefore, by using thicker electro-kinetic barrier, the average applied voltage gradient can be reduced, and the interval time for the intermittent current can also be prolonged.

Fig. 10 presents the relation curves between the final base relative concentration and barrier thickness under four different average voltage gradients. The linear relationship is satisfied between  $\log(c_b^f/c_0)$  and  $H$ . Thus, it is possible either to select the barrier thickness or the average voltage gradient in the design of electro-kinetic barriers by using this chart, once the soil properties and breakthrough criterion is determined. If breakthrough criterion is selected as  $c_b^f/c_0 = 10^{-3}$ , the barrier thickness 1.0 m can be determined with an average voltage gradient of 2.0 V/m. Similarly, if electro-kinetic barrier thickness is designed to be 1.5 m,

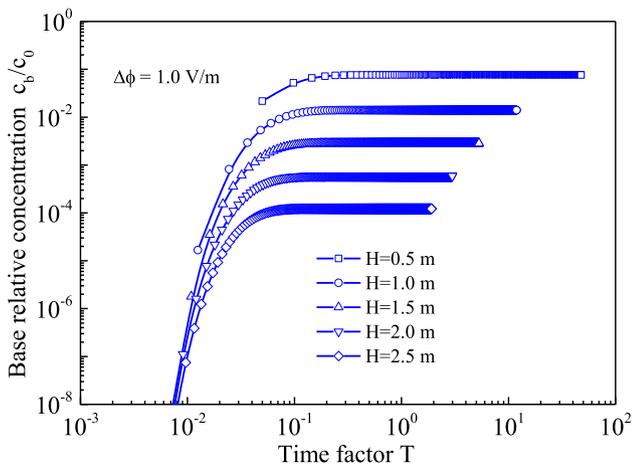


Fig. 9. Effect of the electro-kinetic barrier thickness on the development of base relative concentration.

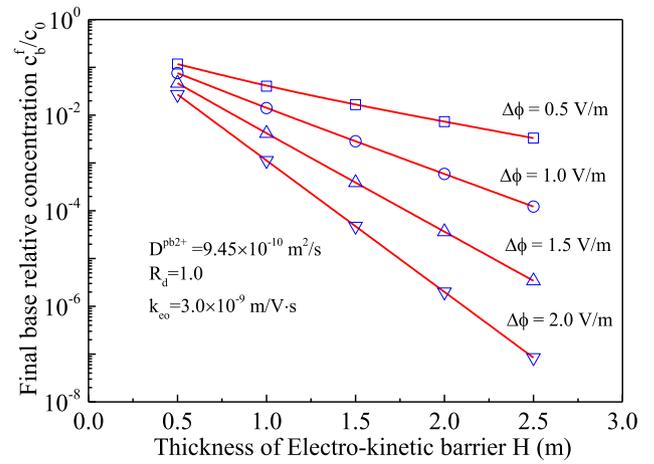


Fig. 10. Relationships of the final base relative concentration with the barrier thickness under different average voltage gradients.

the average voltage gradient can be determined as 1.25 V/m through Fig. 10. To give the deeper insights, a dimensionless factor will be defined in the next section.

### 5.3. Effect of diffusion coefficient

Fig. 11 presents the influence of a diffusion coefficient (i.e.,  $9.45 \times 10^{-10}$ ,  $18.9 \times 10^{-10}$ ,  $5.0 \times 10^{-9}$ , and  $9.45 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ ) on the changes of base concentration over time. In this analysis, the value of  $\mu/\lambda$  was set as  $10 \text{ m}^{-1}$ , the average voltage and barrier thickness was the same as the values in Table 2. It should be pointed out that the ionic mobility changes proportionally with the diffusion coefficient as Eq. (3). As shown in Fig. 11, a nonlinear increase of the relative base concentration can be found with the increase of diffusion coefficient. Using the diffusion coefficient  $D^{pb2+} = 9.45 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$  as the comparison, the final base concentration increases by a factor of approximately 43.1 when the diffusion coefficient increases by a factor of 5.29. Nevertheless, the final base concentration increases by a factor of 58.9 as the diffusion coefficient increases 10 times. In addition, the time to reach a steady state decreases with an increase in diffusion coefficient. Therefore, for the contaminant ions with high diffusion coefficients, a larger average voltage gradient is necessary to improve the electro-kinetic effect.

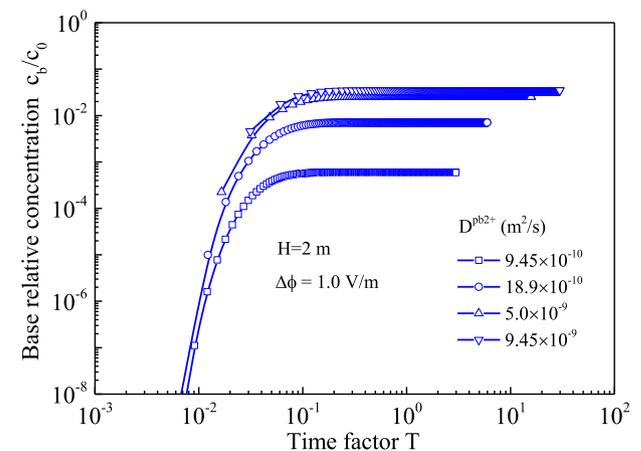


Fig. 11. Effect of the diffusion coefficient on the development of relative base concentration.

5.4. Effect of retardation factor

The sorption capacity of the soil barrier is represented by the value of the retardation factor ( $R_d$ ). A larger  $R_d$ , will yield a higher sorption capacity for the compacted soil layer of the electro-kinetic barrier. Fig. 12 shows the influence of the four different retardation factors (i.e., 1.0, 1.5, 2.0 and 3.0) on the development of the base concentration over time. The figure shows that the retardation factor has little influence on the curves between the relative base concentration and dimensionless time factor,  $T$ . The final base concentrations of different retardation factors approach a similar value. However, considering the time factor  $T$  defined in Eq. (21), the retardation factor has an obvious influence on the real time required to reach the steady state. For example, when taking the time for the base concentration arriving at 0.01% of  $C_0$  as the breakthrough time, the breakthrough time increases from 9 years to 26 years as retardation factor increases from 1.0 to 2.0. From this analysis, the time to break through the electro-kinetic barrier can be effectively prolonged by using clayey soils with a high sorption capacity.

5.5. Effect of electro-osmotic conductivity

To study the influence of electro-osmosis on the transport of Pb(II) in the electro-kinetic barrier, four ratios of electro-osmotic conductivity to diffusion coefficient  $k_{eo}/D^{Pb2+}$  (0.1, 1.0, 5.0, 10) with  $D^{Pb2+} = 9.45 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$  were set in this analysis, where the average voltage gradient was 1.0 V/m, and the barrier thickness was 2 m. The other parameters were held the same as those in Table 2. Fig. 13 presents the relationship between the final relative base concentration and value of  $k_{eo}/D^{Pb2+}$  in the double logarithmic coordinate system. The final relative base concentration decreases with the increase of electro-osmotic conductivity. Although the final base relative concentration decreases significantly as the value of  $k_{eo}/D^{Pb2+}$  increases from 0.1 to 1.0, it still changes within the order of  $10^{-2}$ , which is larger than the breakthrough criterion set at  $10^{-5}$ . However, as the value of  $k_{eo}/D^{Pb2+}$  increases to 1.0, the final relative base concentration decreases significantly with the increase of electro-osmotic conductivity. The final relative base concentration decreases from the order of  $10^{-2}$  to  $10^{-5}$  as the value of  $k_{eo}/D^{Pb2+}$  increases from 1.0 to 5.0, and further to  $10^{-9}$  as the value of  $k_{eo}/D^{Pb2+}$  reaches 10. Thus, we defined a concept of diffusion degree of contaminant migration  $U_c$  by dividing the base concentration by its final steady value. Fig. 14 gives the diffusion degree curves for contaminant migration with different electro-osmotic conductivities. Time to reach the steady state can be shortened with the increase of electro-osmotic conductivity. Nevertheless, when the value of  $k_{eo}/D^{Pb2+}$  is less than 1.0, the diffusion degrees of contaminant migration in the electro-kinetic barrier are almost equal. Therefore, with respect to the soil

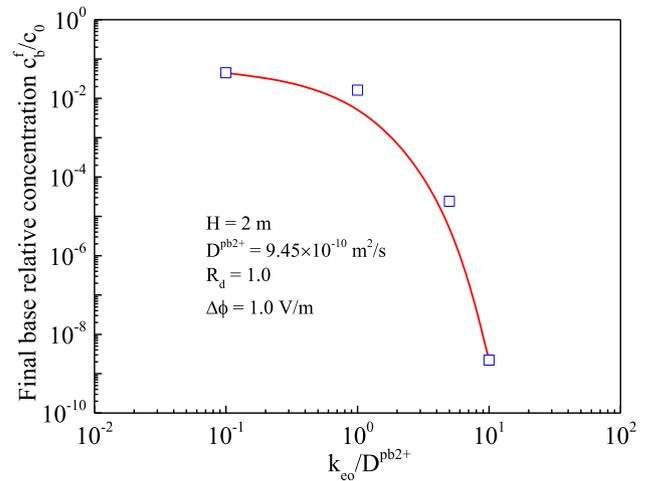


Fig. 13. Variation of final base relative concentration with electro-osmotic conductivity.

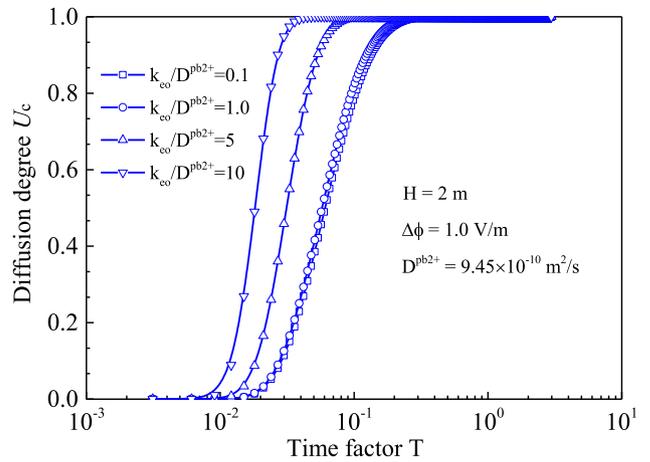


Fig. 14. Variation of diffusion degree with time.

with relatively large electro-osmotic conductivity, the influence of electro-osmosis on the transport of contaminant ions is considerable, which is an important consideration in the design.

5.6. Normalized treatment and analysis

To achieve deeper insights into the previously mentioned influence factors, we introduce a dimensionless factor  $X$  as:

$$\chi = \frac{D_j^*}{(k_{eo}\Delta\phi + k_h\Delta h)H} \quad (40)$$

By using this equation, the dimensionless factors corresponding to the varying average voltage gradient, barrier thickness, diffusion coefficient, and electro-osmotic conductivity in the previous analysis can be calculated. Then, the relationship between the final relative base concentration and the dimensionless factor  $X$  can be plotted. Note that, the larger value of diffusion coefficient will lead to a larger  $\chi$ , while a larger value of electro-osmotic velocity and barrier thickness will lead to a decrease in  $\chi$ . Thus, the large value of  $\chi$  represents rapid contaminant migration, while a small value of  $\chi$  represents the slow contaminant migration. Fig. 15 presents the relationship curve between the final relative base concentration and dimensionless factor  $\chi$  in the double logarithmic coordinate system. As expected, the base concentration at the steady state increases with the increase of dimensionless factor  $\chi$  in the double logarithmic coordinate system. This means that a larger

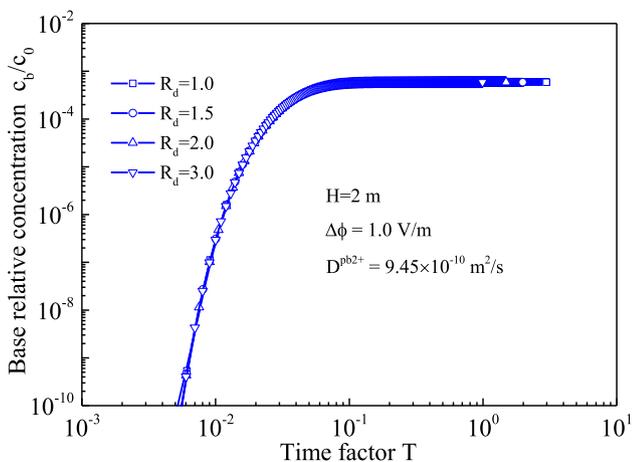


Fig. 12. Effect of the retardation factor on the development of relative base concentration.

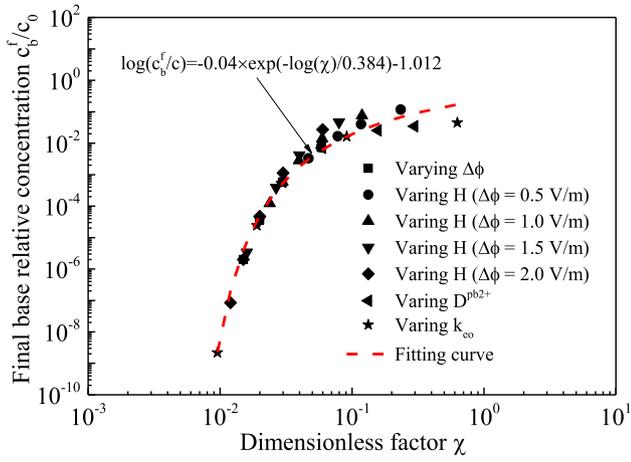


Fig. 15. Variation of final base relative concentration with dimensionless factor  $\chi$ .

quantity of contaminant will pass through the electro-kinetic barrier at the steady state with respect to the larger  $\chi$ . In addition, it can be seen that the predicted points with varying influence factors are slightly decreasing in a narrow strip with little discreteness. Through curve fitting, an exponential growth relationship can be used to describe the relationship between the final relative base concentration and the dimensionless factor  $\chi$  in the double logarithmic coordinate system. The function is given as:

$$\log\left(\frac{c_b^f}{c_0}\right) = a_1 \exp\left(\frac{\log\chi}{b_1}\right) + d_1 \quad (41)$$

where  $a_1$ ,  $b_1$  and  $d_1$  are fitting parameters.

Thus, by using this equation, the value of  $\chi$  can be calculated once the breakthrough criterion  $c_b^f/c_0$  is given in the design. Furthermore, if the diffusion coefficient and electro-osmotic conductivity of the clayey soil are given, the voltage gradient and barrier thickness can be determined.

## 6. Conclusions

The main conclusions obtained from the present study are as follows:

- (1) New closed-form analytical solutions for predicting transport of contaminant ions through electro-kinetic barrier are presented in this paper. Two different bottom boundary conditions, i.e., Cauchy boundary and a fixed zero-concentration boundary conditions, were considered. The results of the proposed analytical solution agree with experimental and numerical results.
- (2) The average applied voltage gradient and barrier thickness have a significant influence on the contaminant ion transport within the

electro-kinetic barriers. The final concentration and mass flux at the bottom boundary decrease with increases in the average voltage gradient and barrier thickness. The logarithm of final relative base concentration changes linearly with the changes of average voltage gradient and barrier thickness.

- (3) The diffusion coefficient of the contaminant ions and the sorption capacity of the clayey soil also have a distinct influence on the transport of contaminant ions in the electro-kinetic barriers. The final base concentration increases nonlinearly with the increase of ion's diffusion coefficient. The soil sorption capacity has little influence on the final base concentration, but the breakthrough time of the electro-kinetic barrier can be effectively prolonged by using clayey soils with a high sorption capacity.
- (4) The influence of electro-osmosis is important to be considered in the design of electro-kinetic barriers. With an increase in the electro-osmotic conductivity, the final base concentration and the time required to reach the steady state decrease, especially when the value of electro-osmotic conductivity excesses is larger than the value of diffusion coefficient.
- (5) A dimensionless factor  $\chi$  is proposed, which can be suggested as an important parameter for design, which can be used to determine the soil properties, average voltage gradient, and barrier thickness with the given breakthrough criterion. Exponential growth function can be used to fit the relation curve between the final base relative concentration and  $\chi$  in the double logarithmic coordinate system.

## CRediT authorship contribution statement

**L.J. Wang:** Conceptualization, Methodology, Software, Formal analysis. **P.H. Huang:** Software, Validation, Investigation. **S.H. Liu:** Methodology, Supervision. **C.M. Shen:** Visualization. **Y. Lu:** .

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A.: Derivation of the analytical solution considering Dirichlet boundary condition

Taking the Laplace transform of Eq. (22) and defining the transform by  $\overline{W}$ , one can obtain:

$$\overline{W}' - s\overline{W} = 0 \quad (A1)$$

where  $s$  is a complex variable.

The Laplace forms of boundary conditions Eqs. (11) and (12) are:

$$\begin{cases} \overline{W}(0, s) = D \\ \overline{W}(H, s) = 0 \end{cases} \quad (A2)$$

where

$$D = c_0/s - \frac{B^2 H^2}{4A^2} \quad (\text{A3})$$

By solving Eq. (A1) one can obtain:

$$\bar{W}(Z, s) = C_1 \cosh(\sqrt{s} Z) + C_2 \sinh(\sqrt{s} Z) \quad (\text{A4})$$

Substituting Eq. (A4) into Eq. (A2), one can get  $C_1$  and  $C_2$  as:

$$C_1 = D = c_0 / \left( s - \frac{B^2 H^2}{4A^2} \right) \quad (\text{A5})$$

$$C_2 = -\frac{C_1}{\tanh(\sqrt{s})} = -\frac{c_0}{s - \frac{B^2 H^2}{4A^2}} \frac{1}{\tanh(\sqrt{s})} \quad (\text{A6})$$

Substituting Eqs. (A5) and (A6) into Eq. (A4), a general solution can be obtained as:

$$\bar{W}(Z, s) = \frac{c_0}{s - \frac{B^2 H^2}{4A^2}} \frac{\sinh(\sqrt{s}) \cosh(\sqrt{s} Z) - \cosh(\sqrt{s}) \sinh(\sqrt{s} Z)}{\sinh(\sqrt{s})} \quad (\text{A7})$$

Eq. (A7) can be inverted using the residue theorem. It is obvious that Eq. (A7) has poles such that:

$$s = s_0 = \frac{B^2 H^2}{4A^2} \quad (\text{A8})$$

$$s = s_n = -n^2 \pi^2, \quad n = 1, 2, 3, \dots \quad (\text{A9})$$

For pole  $s = s_0$ , the residue of Eq. (A7) can be obtained as:

$$\text{Re } s \left( e^{sT} \bar{W}(Z, s), s_0 \right) = \lim_{s \rightarrow s_0} (s - s_0) e^{sT} \bar{W}(Z, s) = c_0 \frac{\sinh\left(\frac{BH}{2A}(1-Z)\right)}{\sinh\left(\frac{BH}{2A}\right)} e^{\frac{B^2 H^2}{4A^2} T} \quad (\text{A10})$$

Meanwhile, for pole  $s = s_n$ , the residue of Eq. (A7) can be obtained as:

$$\text{Re } s \left( e^{sT} \bar{W}(Z, s), s_n \right) = \lim_{s \rightarrow s_n} (s - s_n) e^{sT} \bar{W}(Z, s) = (-1)^n \frac{2n\pi c_0 \sin(n\pi(1-Z))}{n^2 \pi^2 + \frac{B^2 H^2}{4A^2}} e^{-n^2 \pi^2 T} \quad (\text{A11})$$

After calculating the sum of residues, one can get the solution of contaminant ion  $j$  for Dirichlet boundary condition as:

$$c_j(Z, T) = c_0 \frac{\sinh\left(\frac{BH}{2A}(1-Z)\right)}{\sinh\left(\frac{BH}{2A}\right)} e^{\frac{BH}{2A} Z} + \sum_{n=1}^{\infty} (-1)^n \frac{2n\pi c_0 \sin(n\pi(1-Z))}{n^2 \pi^2 + \frac{B^2 H^2}{4A^2}} e^{\frac{BH}{2A} Z - \left(n^2 \pi^2 + \frac{B^2 H^2}{4A^2}\right) T} \quad (\text{A12})$$

## References

- Acar, Y.B., Alshawabkeh, A.N., 1993. Principles of electrokinetic remediation. *Environ. Sci. Technol.* 27 (13), 2638–2647.
- Acar, Y.B., Alshawabkeh, A.N., 1996. Electrokinetic remediation: I. Pilot-scale test with lead-spiked kaolinite. *J. Geotech. Eng.* 122 (3), 173–185.
- Acar, Y.B., Gale, R.J., Alshawabkeh, A.N., Marks, R.E., Puppala, S., Bricka, M., Parker, R., 1995. Electrokinetic remediation: basics and technology status. *J. Hazard. Mater.* 40, 117–137.
- Acar, Y.B., Haider, L., 1990. Transport of low concentration contaminants in saturated earthen barriers. *J. Geotech. Eng., ASCE* 116 (7), 1031–1052.
- Al-Hamdan, A., Reddy, K., 2008. Electrokinetic remediation modeling incorporating geochemical effects. *J. Geotech. Geoenviron. Eng.* 134, 91–105.
- Alshawabkeh, A.N., Acar, Y.B., 1992. Removal of contaminants from soils by electrokinetics: a theoretical treatise. *J. Environ. Sci. Health. Part A Environ. Sci. Eng.* 27 (7), 1835–1861.
- Alshawabkeh, A.N., Acar, Y.B., 1996. Electrokinetic remediation. 2. Theoretical model. *J. Geotech. Eng.* 122 (3), 186–196.
- Amrate, S., Akretche, D.E., Innocent, C., Seta, P., 2005. Removal of Pb from a calcareous soil during EDTA-enhanced electrokinetic extraction. *Sci. Total Environ.* 349 (1–3), 56–66.
- Casagrande, L., 1949. Electroosmosis in soils. *Geotechnique* 1 (3), 159–177.
- Chen, R., Ge, Y.H., Chen, Z.K., Liu, J., Zhao, Y.R., Li, Z.H., 2019. Analytical solution for one-dimensional contaminant diffusion through unsaturated soils beneath geomembrane. *J. Hydrol.* 568, 260–274.
- Chen, J.-S., Liu, C.-W., 2011. Generalized analytical solution for advection-dispersion equation in finite spatial domain with arbitrary time-dependent inlet boundary condition. *Hydrol. Earth Syst. Sci.* 15 (8), 2471–2479. <https://doi.org/10.5194/hess-15-2471-2011>.

- Chen, Y., Xie, H., Ke, H., Chen, R., 2009. An analytical solution for one-dimensional contaminant diffusion through multi-layered system and its applications. *Environ. Geol.* 58, 1083–1094.
- Choi, Y.S., Lui, R., 1995. Multi-dimensional electrochemistry model. *Arch. Ration. Mech. Anal.* 130 (4), 315–342.
- Godschalk, B., Lageman, R., 2005. Electrokinetic Biofence, remediation of VOCs with solar energy and bacteria. *Eng. Geol.* 77 (3), 225–231.
- Kim, S.O., Kim, J.J., Kim, K.W., Yun, S.T., 2004. Models and experiments on electrokinetic removal of Pb(II) from kaolinite clay. *Sep. Sci. Technol.* 39 (8), 1927–1951.
- Kim, S.O., Kim, J.J., Yun, S.T., Kim, K.W., 2003. Numerical and experimental studies on cadmium (II) transport in kaolinite clay under electrical fields. *Water Air Soil Pollut.* 150, 135–162.
- Koryta, J., 1982. *Ions, Electrodes, and Membranes*. Wiley, New York.
- Li, Y., Cleall, P., 2010. Analytical solutions for contaminant diffusion in double-layered porous media. *J. Geotech. Geoenviron. Eng.* 136 (11), 1542–1554.
- Lynch, R.J., Muntoni, A., Ruggeri, R., Winfield, K.C., 2007. Preliminary tests of an electrokinetic barrier to prevent heavy metal pollution of soils. *Electrochim. Acta* 52, 3432–3440.
- Mattson, E.D., Bowman, R.S., Lindgren, E.R., 2002. Electrokinetic ion transport through unsaturated soil: 1. Theory, model development, and testing. *J. Contam. Hydrol.* 54, 99–120.
- Masi, M., Ceccarini, A., Iannelli, R., 2017. Multispecies reactive transport modelling of electrokinetic remediation of harbour sediments. *J. Hazard. Mater.* 326, 187–196.
- Micic, S., Shang, J.Q., Lo, K.Y., Lee, Y.N., Lee, S.W., 2001. Electrokinetic strengthening of a marine sediment using intermittent current. *Can. Geotech. J.* 38 (22), 287–302.
- Mitchell, J.K., Yeung, A.T., 1991. Electro-kinetic flow barriers in compacted clay. *Transp. Res. Rec.* 1288, 1–9.
- Mitchell, J.K., 1993. *Fundamentals of soil behaviour*. In: *Series in Soils Engineering*. Wiley, New York, NY, p. 437.
- Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Eng. Geol.* 60, 193–207.

- Narasimhan, B., Ranjan, R.S., 2000. Electrokinetic barrier to prevent subsurface contaminant migration: theoretical model development and validation. *J. Contam. Hydrol.* 42, 1–17.
- Page, M.M., Page, C.L., 2002. Electroremediation of contaminated soils. *J. Environ. Eng.* 128 (3), 208–219.
- Lageman, R., Pool, W., Seffinga, G., 1989. Electro-reclamation: theory and practice. *Chem. Ind. (London)* 585–590.
- Paz-García, J.M., Johannesson, B., Ottosen, L.M., Ribeiro, A.B., Rodríguez-Maroto, J.M., 2011. Modeling of electrokinetic processes by finite element integration of the Nernst–Planck–Poisson system of equations. *Sep. Purif. Technol.* 79, 183–192.
- Rowe, R.K., Nadarajah, P., 1997. An analytical method for predicting the velocity field beneath landfills. *Can. Geotech. J.* 34 (2), 264–282.
- Rowe, R.K., Lake, C.B., Petrov, R.J., 2000. Apparatus and procedures for assessing inorganic diffusion coefficients for geosynthetic clay Liners. *Geotech. Test. J., GTJODJ* 23 (2), 206–214.
- van Genuchten, M.Th., Alves, W.J., 1982. Analytical solutions of the one-dimensional convective-dispersive solute transport equation, US Department of Agriculture Technical Bulletin No. 1661, 151 pp.
- Ozsisik, M.N., 1968. *Boundary Value Problems of Heat Conduction*. Dover Publications Inc., New York.
- Shackelford, C., 1990. Transit-time design of earthen barriers. *Eng. Geol.* 29 (1), 79–94.
- Shackelford, C., Daniel, D., 1991. Diffusion in saturated soil. I: background. *J. Geotech. Eng.* 117, 467–484.
- Shapiro, A.P., Probstein, R.F., 1993. Removal of contaminants from saturated clay by electroosmosis. *Environ. Sci. Technol.* 27 (2), 283–291.
- Xie, H., Lou, Z., Chen, Y., 2013. An analytical solution to organic contaminant diffusion through composite liners considering the effect of degradation. *Geotext. Geomembr.* 36, 10–18.
- Yeung, A.T., Mitchell, J.K., 1993. Coupled fluid, electrical and chemical flows in soil. *Geotechnique* 43 (1), 121–134.
- Yeung, A.T., 1990. Coupled flow equations for water, electricity and ionic contaminants through clayey soils under hydraulic, electrical and chemical gradients. *J. Non-Equil. Thermodyn.* 15 (3), 247–267.
- Yeung, A.T., Scott, T.B., Gopinath, S., Menon, R.M., Hsu, C., 1997. Design, fabrication, and assembly of an apparatus for electrokinetic remediation studies. *Geotech. Test. J.* 20 (2), 199–210.
- Zhang, W.J., Huang, Y.Y., Zhang, G.G., 2013. Analytical solution for 1D advection-diffusion-adsorption transport of landfill contaminants through a soil layer with finite thickness. *Chin. J. Geotech. Eng.* 35 (7), 1197–1201 (in Chinese).
- Zhao, Q., Burns, S.E., 2013. Modeling sorption and diffusion of organic sorbate in hexadecyltrimethylammonium-modified clay nanopores—a molecular dynamics simulation study. *Environ. Sci. Technol.* 47 (6), 2769–2776.
- Yu, J.W., Neretnieks, I., 1997. Theoretical evaluation of a technique for electrokinetic decontamination of soils. *J. Contam. Hydrol.* 26, 291–299.
- Eykholt, G.R., Daniel, D.E., 1994. Impact of system chemistry on electroosmosis in contaminated soil. *J. Geotech. Eng.* 120, 797–815.