Modelling contaminant transport through clay membrane barriers

Un modèle pour le transport des contaminants par les barrières semi-perméables d'argile

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ABSTRACT

A model able to describe the macroscopic transport of an electrolyte solution through a semi-permeable clay membrane is proposed. Such a mechanical model may be derived imposing a dynamical equilibrium on the forces acting on the components of the solution. The partition of ions within the pores of the membrane is attributed to the presence of a fixed charge on the solid phase and is modelled as a Donnan partition mechanism. Such a model is able to explain the dependency, observed in laboratory experiments, of the chemico-osmotic efficiency coefficient, ω , on the solute concentration, C_s , and to explain the dependency of the other experimental parameters on ω .

RÉSUMÉ

Un modèle capable décrire le transport macroscopique d'une solution des électrolytes par une membrane semi-perméable d'argile est proposé. Le modèle mécanique peut être dérivé imposant un équilibre dynamique aux forces agissant sur les composants de la solution. La distribution des ions dans les pores de la membrane est attribuée à la présence d'une charge fixe sur la phase solide et est modelée comme un mécanisme de exclusion de Donnan. Ce modèle peut expliquer la dépendance expérimentale du coefficient d'efficacité chemico-osmotique, ω , de la concentration de l'électrolyte, C_s , et expliquer la dépendance des autres paramètres expérimentaux de ω .

1 INTRODUCTION

Clay soils are able to act as semipermeable membranes that restrict the passage of solutes. Restricted transport of charged solutes (anions and cations) through the pores of clay soils is due to electrostatic repulsion of the ions by the electric field generated by the surface charge of clay particles. The existence of membrane behavior also results in chemico-osmosis, or the movement of the solution in response to a solute concentration gradient. The existence of membrane behavior can affect significantly the transport of contaminants through clay barriers for subsoil pollutant control.

Semipermeable porous media are materials having an interconnected system of pores and a charged solid skeleton. Due to the charge of the solid phase (for clays, the charge is, generally, negative), the ionic species may be excluded or adsorbed, depending on the sign of their charge. As a result, the solution within the pores is not electrically neutral. In order to restore the electro-neutrality, the concentration of a fixed charge (moving with the solid skeleton), C_X, has to be introduced. As a consequence of the presence of the charge of the solid skeleton, the concentrations of the ions are discontinuous respect to the external bulk solutions in contact with the medium at the boundaries. The concentration of the counter-ions (charge opposite to that of the solid skeleton) is higher than that of the bulk solution, whereas the concentration of the co-ions is smaller. The discontinuity of the ion concentrations at the boundaries gives rise to a discontinuity also in the total pressure of the fluid phase. The pressure of the solution within the pores is different from that of the external bulk solution at the boundaries because the partial pressures of the ions, that are related to the concentrations, are discontinuous. Due to the fact that the accumulation of counter-ions is generally larger than the exclusion of co-ions, the total pressure of the solution within the pores is higher than that of the external solution (see Fig. 1).



Figure 1. Pressure (a) and concentration (b) profiles within a charged porous medium, having length $L_{\rm h}$ in contact with two external bulk solutions. P is the total pressure of the external bulk solutions and $\overline{P}_{\rm t}$ is the total pressure of the solution within the porous medium. $C_{\rm s}$ is the concentration of a (1:1) electrolyte in the external bulk solutions; $\overline{C}_1, \overline{C}_2$ are the concentration of the counter-ion and of the co-ion, respectively, within the porous medium.

2 MECHANICAL MODEL

The ionic molar fluxes, J_i, may be obtained from the momentum balance equations, neglecting inertial effects and assuming the solution "ideal" (i.e. very dilute):

$$J_{i} = \underbrace{q\overline{C}_{i}}_{Convection} \underbrace{-nD_{i}^{*} \frac{d\overline{C}_{i}}{dx}}_{Diffusion} \underbrace{-nz_{i}\overline{C}_{i}D_{i}^{*} \frac{F}{RT} \frac{d\Phi}{dx}}_{Migration}$$
(1)

where q = volumetric flux (or Darcy's velocity);

 \overline{C}_{i} = ion concentration of the i-th ion;

n = porosity;

 $D_i^* = \tau_m D_{i,0}^{}$ = effective diffusion coefficient, being

 τ_m the tortuosity factor that accounts for the tortuous nature of the actual diffusive pathways and $D_{i,0}$ the free solution diffusion coefficient;

- z_i = electro-chemical valence;
- F = Faraday constant;
- R = universal gas constant;
- T = absolute temperature;
- Φ = electric potential within the clay.

Eq. (1) is the well-known Nernst-Planck that accounts for the presence of the electrochemical forces, analogous to that used for uncharged porous media (Malusis and Shackelford, 2002b). The momentum balance equation of the solvent (generally, water) provides for the volumetric flux of the solution (if the simplifying assumption that the flux of the solution is almost equal to that of the solvent is made):

$$q = -nd_{h} \left(\underbrace{\frac{d\overline{P}_{t}}{dx}}_{Pr \text{ essure-Force Electrochemical-Force}} - \varpi C_{x} F \frac{d\Phi}{dx} \right)$$
(2)

where d_h = mechanical permeability at zero electric potential gradient;

- $\overline{\mathbf{P}}_{t}$ = total pressure of the solution within the pores;
- ϖ = sign of the fixed charge (for clays, generally, $\varpi = -1$).

Eq. (2) accounts for the linear composition of two driving force (per unit volume): (i) the pressure force, that corresponds to the internal force associated to the thermal motion of the molecules composing the solution, and (ii) the electro-chemical force, representing the net drag exerted by the ions during their migration under the electric gradient. In the absence of a fixed charge (i.e. $C_x = 0$), Eq. (2) reduces to the Darcy's equation, commonly used in soil mechanics (Bear, 1972). In fact, in the absence of a fixed charge, the ion concentrations are not discontinuous and, at the boundaries, the total pressure of the solution within the pores is equal to the external one.

Eq. (1) and Eq. (2) may be considered as the generalization of the transport equations commonly used in environmental geotechnics practice (Bear, 1972; Shackelford and Daniel, 1991; Malusis and Shackelford, 2002b) to the case of soils having a charged solid skeleton. However, if the equations (1) and (2) are applied to the analysis of a contaminant propagation through a clay barrier, it is convenient to impose preliminarily the condition of absence of electric current (i.e. $I_e = F \sum_{i=1}^{N} z_i J_i = 0$, where I_e is the electric current density). The

ionic molar fluxes are given by:

$$J_{i} = q\overline{C}_{i} \left(1 + \frac{\overline{t}_{i}}{z_{i}} \frac{\varpi C_{x}}{\overline{C}_{i}} \right) - nD_{i}^{*} \frac{d\overline{C}_{i}}{dx} + n \frac{\overline{t}_{i}}{z_{i}} \sum_{j=1}^{N} z_{j} D_{j}^{*} \frac{d\overline{C}_{j}}{dx} .$$
(3)

where $\overline{t}_{i} = \frac{F^{2}}{RT} \frac{z_{i}^{2} \overline{C}_{i} D_{i}^{*}}{\overline{\kappa}} = \text{transfer number of the i-th ion,}$ being $\overline{\kappa} = \frac{F^{2}}{RT} \sum_{i=1}^{N} z_{i}^{2} \overline{C}_{i} D_{i}^{*}$ the equivalent electric

conductivity of the solution within the membrane.

The volumetric flux, in the absence of electric current, is given by:

$$q = -\frac{nd_{h}}{\underbrace{1+d_{h}C_{x}^{2}\frac{F^{2}}{\overline{\kappa}}}_{k_{h}/\gamma_{w}}} \left(\frac{d\overline{P}_{t}}{dx} + \varpi C_{x}\frac{F^{2}}{\overline{\kappa}}\sum_{i=1}^{N}z_{i}D_{i}^{*}\frac{d\overline{C}_{i}}{dx}\right).$$
(4)

Eqs. (3) and (4) are the appropriate equations for the contaminant migration analyses as only the pressure and the ion concentration gradients compare in them, whereas the electric potential gradient is eliminated by means of the condition of absence of electric current. In Eq. (4) the hydraulic conductivity at zero electric current, k_h, results to depend on the concentrations of the fixed charge and of the ions in solution. However, for physically plausible values of the parameters normally found in semipermeable porous media, such dependency results to be negligible and, as a first approximation, it may be assumed k_h \cong nd_h γ_w , where γ_w is the unit weight of the solvent.

In order to solve Eqs. (3) and (4) (or, alternatively, Eqs. (1) and (2)), the following boundaries conditions have to be imposed:

$$\overline{C}_{i}' = C_{i}' \exp\left(-z_{i} \frac{F}{RT} \psi_{m}'\right) \quad i = 1, 2, \dots, N$$
(5a)

$$\overline{P}_{t}' = P' - RT \sum_{i=1}^{N} C_{i}' + RT \sum_{i=1}^{N} \overline{C}_{i}'$$
(5b)

where ψ_m' is the macroscopic electric potential of the charged porous medium, or Donnan's potential, and P' is the external hydraulic pressure. In Eqs. (5), all the variables (pressures and concentrations) are referred to the generic boundary ('). The Donnan's potential is given by the difference between the electric potential within the pores, Φ' , and the electric potential in the external bulk solution, ϕ' , i.e. $\psi_m' = \Phi' - \phi'$. The Donnan's potential may be evaluated with the help of the electroneutrality conditions in the external bulk solution and within the pores of the medium:

$$\sum_{i=1}^{N} z_i C_i' = 0$$
 (6a)
$$\sum_{i=1}^{N} z_i \overline{C}_i' + \overline{\omega} C_x = 0.$$
 (6b)

In a clay, the fixed charge concentration, C_X , may be assumed proportional to the Cation Exchange Capacity, CEC, and inversely proportional to the void ratio, e:

$$C_{x} = \phi_{x} CEC \rho_{s}^{T} \frac{1}{e}$$
⁽⁷⁾

where ϕ_X is the fixed charge coefficient and ρ_s^T is the true density of the solid phase. The fixed charge coefficient is generally smaller than one and accounts for a number of microscopic effects, as specific ion adsorption, and macroscopic effects, as non-homogeneity of charge distribution, that may reduce the

theoretical value of the fixed charge concentration, as estimated by the CEC.

Although the Eq. (1) and (2) represent a simple and physically consistent model, in many cases of practical interest they are transformed applying a change of variables. The motivation for such a change of variables is that a further simplification of the problem may be achieved, eliminating the discontinuities at the boundaries. If we look at the boundary conditions (5), it's evident that may be convenient to introduce a "virtual" solution, that, at any point x within the porous medium, is in thermodynamic equilibrium with the real solution, in analogy with the external bulk solutions. So we can pass from the real variables, \overline{P} .

and \overline{C}_i , to the virtual variables, P and C_i, that are the pressure and the ion concentrations of a fictive bulk solution that, at the generic distance x within the porous medium, is in thermodynamic equilibrium with the medium. In correspondence of the boundaries (x = 0 and x = L_h), the virtual solution coincides with the real external solution in contact with the porous medium. As a result, at the boundaries, the pressure of the virtual solution coincides with the pressure of the external bulk solution and, similarly, the ion concentrations of the virtual solution coincide with the ion concentrations of the external bulk solution. The relations that allow for the change of variables are similar to the boundary conditions (5), with the important difference that are valid not only at the boundaries, but at any point x within the porous medium:

$$\overline{C}_{i} = C_{i} \exp\left(-z_{i} \frac{F}{RT} \Psi_{m}\right) \qquad i = 1, 2, ..., N$$
(8a)

$$\overline{P}_{t} = P - RT \sum_{i=1}^{N} C_{i} + RT \sum_{i=1}^{N} \overline{C}_{i} .$$
(8b)

The ion concentrations of the virtual solution satisfy the electro-neutrality condition:

$$\sum_{i=1}^{N} z_i C_i = 0.$$
 (9)

The locally defined Donnan's potential, ψ_m , may be evaluated at any point x by means of the condition of electroneutrality within the porous medium, accounting for the presence of the fixed charge:

$$\sum_{i=1}^{N} z_i \overline{C}_i + \varpi C_x = 0.$$
⁽¹⁰⁾

Using virtual variables, Eqs (3) and (4) are given by:

$$q = -\frac{nd_{h}}{1 + d_{h}C_{x}^{2}} \frac{F^{2}}{\overline{\kappa}} \left(\frac{dP}{dx} - RT \sum_{i=1}^{N} \frac{dC_{i}}{dx} + RT \sum_{i=1}^{N} \Gamma_{i} \frac{dC_{i}}{dx} + \varpi C_{x} \frac{F^{2}}{\overline{\kappa}} \sum_{i=1}^{N} z_{i} D_{i}^{*} \Gamma_{i} \frac{dC_{i}}{dx} \right)$$
(3bis)

$$J_{i} = qC_{i}\left(\Gamma_{i} + \frac{\overline{t}_{i}}{z_{i}}\frac{\varpi C_{x}}{C_{i}}\right) - nD_{i}^{*}\Gamma_{i}\frac{dC_{i}}{dx} + n\frac{\overline{t}_{i}}{z_{i}}\sum_{j=1}^{N} z_{j}D_{j}^{*}\Gamma_{j}\frac{dC_{j}}{dx}$$
(4bis)

where
$$\Gamma_i = \exp\left(-z_i \frac{F}{RT} \psi_m\right)$$
 = ion partition coefficient of the

i-th ion;

$\phi = \Phi - \psi_m$ = virtual electric potential.

It should be stressed that the equations written in terms of virtual variables are the only ones appropriated for the physical identification of the parameters of the phenomenological equations derived applying the formalism of the Classic Thermodynamics of Irreversible Processes by Staverman (1952), for discontinuous systems, and by Spiegler and Kedem (1966) and Yaroshchuk (1995), for continuous systems. As pointed out by Yaroshchuk (1995), adopting virtual variables is the only correct way of proceeding within the scope of the thermodynamic approach because, in this context, specifying any physical property of the membrane is not allowed, since the description of the transport is purely phenomenological. The evaluation of the ion concentrations, the electrostatic potential and the pressure in the porous medium requires the assumption of a physical model and, then, a restriction of the generality of the treatment. As a result, the phenomenological parameters are overall coefficients accounting for transport and partition mechanisms that have to be determined by means of macroscopic experiments. The phenomenological parameters that are measured experimentally may be specified in terms of material parameters using a mechanicistic approach (i.e. an approach where the transport and partition mechanisms are accounted for explicitly and separately).

A case of relevant interest for practical applications is that of a single electrolyte, completely dissociated, in solution. Dominijanni and Manassero (2005), based on the theoretical framework of Spiegler and Kedem (1966) and the experimental set of parameters measured by Malusis et al. (2001) and by Malusis and Shackelford (2002a,c) by means of a new testing apparatus, proposed the following phenomenological equations:

$$q = -\frac{k_{h}}{\gamma_{w}} \left[\frac{dP}{dx} - \omega \frac{d\Pi}{dx} \right]$$
(11)

$$J_{s} = (1 - \omega)qC_{s} - nD_{\omega}^{*}\frac{dC_{s}}{dx}$$
(12)

where $J_s = J_1/v_1 = J_2/v_2 = \text{molar salt flux, being } J_1$ the molar flux of the counter-ion (cation) and J_2 the molar flux of the co-ion (anion); $v_i = \text{stoichiometric coefficient of the i-th ion;}$ $\Pi = (v_1 + v_2) \text{RTC}_s = \text{osmotic pressure;}$

 $C_s = C_1/v_1 = C_2/v_2$ = salt concentration;

k_h = hydraulic conductivity at zero electric current;

 ω = chemico-osmotic efficiency coefficient;

 D^*_{ω} = osmotic effective diffusion coefficient.

The phenomenological parameters ω and D^*_{ω} are depending on the porosity of the clay (i.e. on the stress-level) and on the salt concentration. For a fixed porosity, n, the following global parameters may be measured:

$$\omega_{\rm m} = \left(\frac{\Delta P}{\Delta \Pi}\right)_{q=0, {\rm I}_{\rm g}=0} = \frac{1}{\Delta C_{\rm s}} \int_{C_{\rm s}"}^{C_{\rm s}} \omega dC_{\rm s}$$
(13)

$$\mathbf{D}_{\omega,m}^{*} = \frac{\mathbf{L}_{h}}{n} \left(\frac{\mathbf{J}_{s}}{\Delta \mathbf{C}_{s}} \right)_{q=0,I_{s}=0} = \frac{1}{\Delta \mathbf{C}_{s}} \int_{\mathbf{C}_{s}^{*}}^{\mathbf{C}_{s}^{*}} \mathbf{D}_{\omega}^{*} d\mathbf{C}_{s} .$$
(14)

The testing apparatus developed by Malusis et al. (2001) allows for the determination of the parameters ω_m and $D^*_{\ \omega,m}$ on clay samples.

A physical identification of the phenomenological parameters may be obtained by comparing Eqs. (11) and (12) with the Eqs. (3bis) and (4bis) for the case of N = 2. The resulting relations between phenomenological and materials parameters are:

$$\omega = 1 - \frac{\nu_1 D_2^* + \nu_2 D_1^*}{\nu_1 \Gamma_2 D_2^* + \nu_2 \Gamma_1 D_1^*} \Gamma_1 \Gamma_2$$
(15)

$$D_{\omega}^{*} = (1 - \omega)D_{s}^{*}$$
⁽¹⁶⁾

where $D_s^* = \frac{(v_1 + v_2)D_1^*D_2^*}{v_1D_2^* + v_2D_1^*} = \text{effective salt diffusion coef-}$

An interesting result in closed-form may be obtained for the chemico-osmotic efficiency coefficient when there is a (1:1) electrolyte in solution:

$$\omega = 1 - \frac{2}{\sqrt{\xi^2 + 4} + (2t_1 - 1)\xi},$$
(17)

where $t_1 = D_{0,1}/(D_{0,1}+D_{0,2}) =$ transport number of the cation in the virtual solution;

 $\xi = C_X/C_s$ = relative fixed charge concentration. Using Eq. (17), the measured (or global) chemico-osmotic efficiency coefficient, ω_m , defined by Eq. (13), is given by:

$$\omega_{\rm m} = 1 + \frac{C_{\rm X}}{2\Delta C_{\rm s}} \left[Z_2 - Z_1 - (2t_1 - 1) \cdot \ln\left(\frac{Z_2 + 2t_1 - 1}{Z_1 + 2t_1 - 1}\right) \right]$$
(18)

where $Z_1 = \sqrt{1 + (2C_s'/C_x)^2}$ and $Z_2 = \sqrt{1 + (2C_s''/C_x)^2}$.

Eq. (18) has been applied for interpreting the experimental data of Malusis and Shackelford (2002a), finding a good correspondence between the theoretical model and the test results (see Fig.2).

From Eqs. (13), (14) and (16) the measured or global osmotic effective salt diffusion coefficient, $D^*_{\omega,m}$, results related linearly to the measured or global chemico-osmotic efficiency coefficient, ω_m :

$$\mathbf{D}_{\boldsymbol{\omega},\boldsymbol{m}}^* = (1 - \boldsymbol{\omega}_{\boldsymbol{m}})\mathbf{D}_{\boldsymbol{s}}^*. \tag{19}$$

The linear dependency of $D^*_{\omega,m}$ and $(1-\omega_m)$, deduced theoretically, is also in good agreement with the experimental data of Malusis and Shackelford (2002c), as shown in Fig. 3.



Figure 2. Interpretation of the experimental data of Malusis and Shackelford (2002a) with the mechanical model.



Figure 3. Linear regression of measured osmotic effective salt diffusion coefficients versus $(1-\omega_m)$ for a geosynthetic clay liner (data from Malusis and Shackelford, 2002c).

3 SUMMARY AND CONCLUSIONS

The dependency of the phenomenological coefficients on the porosity and the salt concentration may be investigated by means of a series of tests and modeled using a mechanical model, derived on the basis of the physical identification of the friction and partition mechanisms that governs the transport of the solution through the clay membrane. Although such a model implies some simplifying assumptions, it appears to be a useful tool for predicting plausible values of the phenomenological parameters when a direct experimental determination is not possible.

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