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Relevance of chemico-osmotic and electro-osmotic phenomena in bentonite-based barriers

Nicolò Guarena[1,*], Andrea Dominijanni[1] and Mario Manassero[1]

[1] Department of Structural, Geotechnical and Building Engineering (DISEG), Politecnico di Torino
Corso Duca degli Abruzzi 24, 10129, Torino (Italy)
nicolo.guarena@polito.it

Abstract Osmosis is known to play a key role in reducing the transport rate of contaminants through the natural and engineered clay barriers that are used for a number of geoenvironmental applications, such as the lining of landfills and the deep geological disposal of radioactive wastes. Although a significant body of experimental research has focused on the quantification of osmotic phenomena in smectite clays permeated with single-electrolyte solutions, no evidence has been provided about the membrane behaviour of clays in solute mixtures and, specifically, about the so-called osmotic anomalies (i.e. membrane efficiency coefficient outside the 0 to 1 range) that have been documented in the biological and chemical literature for fine-porous charged diaphragms in the presence of two or more electrolytes. In view of the similarities between such fine-porous media and smectite clays, the aim of the paper is to discuss the conditions under which bentonite-based barriers are expected to exhibit the aforementioned osmotic anomalies, which are shown to be caused by the different diffusivities and electrochemical valences of the migrating cations.

Keywords: Anomalous osmosis, bentonite, coupled flows, geosynthetic clay liners, membrane behaviour, waste disposal.

1 Introduction

Smectite clays (e.g. bentonites), in addition to extremely low hydraulic conductivity values ($< 10^{-10}$ m/s) when permeated with diluted solutions and self-healing properties due to the high swelling potential, are also able to exhibit semipermeable membrane behaviour, as the transport of solvent is permitted while the migration of ion species is partially restricted. Clay membranes have large enough pore sizes to accommodate hydrated ions and, therefore, the selective restriction of charged solutes cannot be attributed to the steric hindrance, which arises when the molecules have a larger size than the membrane pores, but should instead be attributed to the electrical interactions that occur between the ions in solution and the clay particles (Shackelford et al., 2016), which carry a net negative charge as a consequence of the isomorphic substitution of lower-valence cations for higher-valence cations within the crystal lattice.

Although a conservative assessment of the performance of geoenvironmental containment barriers that wholly or partly consist of smectite clays can be obtained by modelling pollutant migration according to the classical advective-diffusive transport theory, natural and engineered clay barriers are generally able to restrict contaminant migration more effectively as a result of their semipermeable properties, which lead to the chemico-osmotic counter-advection and a decrease in the pore volume that is accessible to solute transport (Guarena et al., 2020). Thus, in view of the advantages that arise from the ability to model coupled flow phenomena in clay soils, extensive research has been conducted over the past few decades in order to gain a better understanding of the fundamental mechanisms that govern membrane behaviour, which is usually quantified through the laboratory measurement of the reflection coefficient, ω, also known as the chemico-osmotic or membrane efficiency coefficient (Manassero et al., 2018). The reflection coefficient of natural clays is generally considered to vary from zero ($\omega = 0$), in the case of the absence of membrane behaviour, to unity ($\omega = 1$), in the case of ideal or perfect clay membranes that are able to completely prevent anions from entering the pores, even though the range of variation of such a phenomenological parameter is not restricted to 0 and 1 on a thermodynamic ground. Accordingly, lower values of ω than zero ($\omega < 0$) are classified as manifestations of "negative anomalous osmosis", whereby the volumetric flux of water is directed against the osmotic pressure gradient under isobaric conditions (Röttger and Woermann, 1993), and larger values of ω than unity ($\omega > 1$) are regarded as manifestations of "positive anomalous osmosis", which results in the transport of solutes against their concentration gradients (Yaroshchuk et al., 1993).

Most experimental studies concerning the assessment of the reflection coefficient of clays have been devoted to analysing the extent to which membrane behaviour is affected by the soil porosity and the salt concentration of the permeating solution (Musso et al., 2017; Dominijanni et al., 2018), the valence of the ion species (Kemper and Rollins, 1966), the effective confining stress (Malusis et al., 2013) and the degree of water saturation (Sample-Lord and Shackelford, 2018). However, all the aforementioned studies dealt with aqueous solutions of a single electrolyte, and thus did not account for the influence of the simultaneous presence of two or more different electrolytes in the pore solution. In this regard, the biological and chemical literature provides evidence of both negative and positive large osmotic volume flows under isobaric conditions in electrically charged fine-porous membranes (e.g. Grim and Sollner, 1960), which separate aqueous solutions of two electrolytes with different counter-ions (i.e. charge polarity opposite to that of the membrane) and the same co-ion (i.e. charge polarity equal to that of the membrane). Yaroshchuk et al. (1993) were the first to measure larger values of the reflection coefficient than unity for a cation exchange membrane, namely a phenol-sulfonic acid-formaldehyde condensation product, which separated two aqueous solutions containing sodium chloride and hydrochloric acid.

As smectite clays are characterised by the same osmotic properties as the typical ones of cation exchange membranes, this study has been aimed at discussing the conditions under which clay soils are expected to exhibit anomalous membrane behaviour, when the permeating solution consists of a mixture of different electrolytes. The scope of the discussion is therefore to stimulate further experimental research in order to verify the

existence and magnitude of such anomalous osmotic phenomena, which can be of relevance for many geotechnical and geoenvironmental applications that deal with pollutant control in the subsoil.

2 Transport equations for a semipermeable membrane

On the basis of pioneering models that were developed to simulate the movement of solvent and solutes through fine-porous charged diaphragms, such as biological tissues, reverse-osmosis membranes and polyelectrolyte gels, Dominijanni and Manassero (2012) derived the macroscopic transport equations of a porous medium that behaves as a selectively permeable membrane by upscaling (i.e. volume-averaging over the capillary cross-section) the Navier-Stokes equation for the volumetric flux of the solution and the Nernst-Planck equations for the mass fluxes of the ion species at the microscopic scale. Such an upscaling procedure, which is equivalent to neglecting the dispersive effect that is caused by the pore-scale fluctuation of the state variables, yields the following equations:

$$q = -\frac{k_\varphi}{\gamma_w}\left(\frac{\partial \bar{u}}{\partial x} + F\frac{\partial \bar{\varphi}}{\partial x}\sum_{i=1}^{n} z_i \bar{c}_i\right) \tag{1}$$

$$J_i = q\bar{c}_i - n_m D_i^* \frac{\partial \bar{c}_i}{\partial x} - n_m z_i \frac{F}{RT} D_i^* \bar{c}_i \frac{\partial \bar{\varphi}}{\partial x} \qquad \text{for } i = 1,...,n \tag{2}$$

where q is the macroscopic volumetric flux of the solution, k_φ is the hydraulic conductivity at zero electric potential gradient, γ_w is the water weight per unit volume (9.81 $kN \cdot m^{-3}$), $\bar{u}$ is the hydraulic pressure within the pore solution, x is the position along the macroscopic transport direction, F is Faraday's constant (96,485 $C \cdot mol^{-1}$), $\bar{\varphi}$ is the electric potential within the pore solution, z_i is the electrochemical valence of the i-th ion species, $\bar{c}_i$ is the concentration of the i-th ion species within the pore solution, J_i is the macroscopic mass flux of the i-th ion species, n_m is the soil porosity associated with the conductive pores, D_i^* is the effective diffusion coefficient of the i-th ion species ($D_i^* = \tau_m \cdot D_{0,i}$), τ_m is the matrix tortuosity factor, $D_{0,i}$ is the free-solution or aqueous-phase diffusion coefficient of the i-th ion species, R is the universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$) and T is the absolute temperature.

As a consequence of the negative electric charge of the solid skeleton, the hydraulic pressure and the concentration of the ion species within the pore solution are discontinuous with respect to the corresponding state variables of the external bulk solutions, which are hypothesised to be in equilibrium with the porous medium at its boundaries. In particular, by combining the definitions of the electrochemical potentials of the components of both the pore and bulk solutions with the Donnan equations, the pore solution state variables can be expressed in the following form:

$$\bar{c}_i = c_i \Gamma_i = c_i \exp\left[-z_i \frac{F}{RT} \left(\bar{\varphi} - \varphi \right) \right] \qquad \text{for } i = 1, ..., n \tag{3}$$

$$\bar{u} = u - \Pi + \bar{\Pi} \tag{4}$$

where Γ_i is the partition coefficient of the *i*-th ion species, φ is the electric potential within the external bulk solution, c_i is the concentration of the *i*-th ion species within the external bulk solution, u is the hydraulic pressure within the external bulk solution, Π is the osmotic pressure within the external bulk solution ($\Pi = RT \sum_{i=1}^{n} c_i$) and $\bar{\Pi}$ is the osmotic pressure within the pore solution ($\bar{\Pi} = RT \sum_{i=1}^{n} \bar{c}_i$). Smectite clays behave like negatively charged semipermeable membranes, thus the partition coefficient results to be larger than one for cations (positive adsorption), while it is expected to range between zero and one for anions (negative adsorption). The introduced ion partition coefficients can be determined by coupling Eq. (3) with the statement of macroscopic electroneutrality in the pore ($\bar{c}_{sk} = \sum_{i=1}^{n} z_i \bar{c}_i$), where $\bar{c}_{sk}$ are the moles of the solid skeleton electric charge per unit volume of the conductive pores (Dominijanni et al., 2019a).

3 Reflection coefficient under closed-system boundary conditions

Dominijanni et al. (2019b) have shown that the test configuration which is commonly referred to as "closed hydraulic control system" allows a direct measurement of the global value of the reflection coefficient, ω_m, to be obtained. Briefly, the clay specimen is interposed between two compartments through which electrolyte solutions with different chemical composition are circulated, while the volumetric flux of water is hindered across the soil. When these conditions are maintained over time, a difference in hydraulic pressure arises between the specimen boundaries under steady-state conditions, and the measured global value of the reflection coefficient is therefore given by:

$$\omega_m = \left(\frac{\Delta u}{\Delta \Pi} \right)_{q=0; I=0} \tag{5}$$

where I is the electric current density ($I = F \sum_{i=1}^{n} z_i J_i$), and the finite differences are defined as the values in the first compartment solution, which are denoted by a prime, minus those in the second compartment solution, which are denoted by a double prime (i.e. $\Delta u = u' - u''$ and $\Delta \Pi = \Pi' - \Pi''$).

By imposing the condition of a null volumetric flux of solution (q = 0), Eq. (1) yields the following relationship:

$$\frac{\partial u}{\partial x} = \frac{\partial \Pi}{\partial x} - \frac{\partial \bar{\Pi}}{\partial x} - F \bar{c}_{sk} \frac{\partial \bar{\varphi}}{\partial x} \tag{6}$$

where the gradient in the electric potential of the pore solution is obtained by substitution of Eq. (2) in the condition of null electric current density ($I = 0$):

$$\frac{\partial \overline{\varphi}}{\partial x} = -\frac{RT}{F} \frac{\sum_{i=1}^{n} z_i D_i^* \frac{\partial \overline{c}_i}{\partial x}}{\sum_{i=1}^{n} z_i^2 \overline{c}_i D_i^*} \tag{7}$$

For the case in which the clay specimen is in equilibrium with solutions consisting of electrolyte mixtures, some qualitative conclusions about the conditions whereby anomalous osmotic phenomena may occur can be drawn directly from Eq. (6), by assuming that the partition coefficients of anions are close to zero (decreased concentrations within the pore solution), whereas the partition coefficients of cations are much larger than one (increased concentrations within the pore solution). In fact, if μ_i^c represents the chemical potential of the i-th ion species within the bulk solution, Eq. (6) can be rewritten in the following way (Yaroshchuk et al., 1995):

$$\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} = \frac{1}{\sum_{i=1}^{n} z_i^2 c_i \Gamma_i D_i^*} \sum_{i=1}^{n} \sum_{j=1}^{i-1} c_i \Gamma_i c_j \Gamma_j \left(z_j D_j^* - z_i D_i^* \right) \left(z_i \frac{\partial \mu_j^c}{\partial x} - z_j \frac{\partial \mu_i^c}{\partial x} \right) \tag{8}$$

As we are here interested in large positive $\left(\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} \gg 0 \right)$ and negative $\left(\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} \ll 0 \right)$ osmotic anomalies, it should be pointed out that such phenomena are not likely to be observed if only one cation is present in the solution, regardless of the number of anions that are produced by the electrolyte dissociation, given that the product $\Gamma_i \cdot \Gamma_j$ is small. However, the presence of at least two cations with the same electrochemical valence ($z_i = z_j$) is not sufficient to give rise to anomalous membrane behaviour, as differences in both the cation mobilities ($D_i^* \neq D_j^*$) and the chemical potential gradients $\left(\frac{\partial \mu_i^c}{\partial x} \neq \frac{\partial \mu_j^c}{\partial x} \right)$ are necessary in the latter case.

Finally, the integration of Eq. (6) over the length of the clay specimen, L, allows a physical identification of the global reflection coefficient to be obtained:

$$\omega_m = \left(\frac{\Delta u}{\Delta \Pi} \right)_{q=0;I=0} = \left(1 - \frac{\Delta \overline{\Pi}}{\Delta \Pi} \right) - F \overline{c}_{sk} \frac{\Delta \overline{\varphi}}{\Delta \Pi} \tag{9}$$

where the difference in the electric potential of the pore solution results to be given by:

$$\Delta \overline{\varphi} = -\frac{RT}{F} \int_0^L \sum_{i=1}^{n} \frac{z_i D_i^*}{\sum_{j=1}^{n} z_j^2 \overline{c}_j D_j^*} \frac{\partial \overline{c}_i}{\partial x} dx \tag{10}$$

Eq. (9) allows the different physical mechanisms that contribute to determining the measured reflection coefficient to be appreciated. In particular, osmosis in clay soils can be interpreted as the superposition of a true chemico-osmotic component $\left(\Omega_c = 1 - \frac{\Delta\overline{\Pi}}{\Delta\Pi}\right)$, which originates from the electrostatic repulsion of the anions by the negatively charged clay particles, and an electro-osmotic component $\left(\Omega_e = -F\,\overline{c}_{sk}\,\frac{\Delta\overline{\varphi}}{\Delta\Pi}\right)$, whereby the gradient in the electric potential of the pore solution, under null electric current density conditions, builds up in response to the different diffusivities and electrochemical valences of the migrating cations.

A particularly interesting case is represented by the experimental conditions that were analysed by Yaroshchuk et al. (1993), namely when there are two electrolytes with the same anion and a difference in concentration of only one electrolyte is established across the porous medium. The concentration of the second electrolyte, which is referred to as the background electrolyte, is the same in both of the compartments that are separated by the porous medium. If the absolute values of the electrochemical valences of all the ion species are unitary, Eq. (3) shows that the partition coefficients of the two cations assume the same value and are equal to the reciprocal of the partition coefficient of the common anion. Under the aforementioned conditions, Eq. (10) can be rewritten as follows:

$$\Delta\overline{\varphi} = -\frac{RT}{F}\int_{\overline{c}_3'}^{\overline{c}_3} \frac{\left[\left(D_1^* - D_3^*\right) + \frac{\overline{c}_{sk}}{2\overline{c}_3}\frac{c_B}{\sqrt{\overline{c}_3\left(\overline{c}_3 + \overline{c}_{sk}\right)}}\left(D_1^* - D_2^*\right)\right]}{\left[\overline{c}_{sk}D_1^* + \overline{c}_3\left(D_1^* + D_3^*\right) + c_B\sqrt{1 + \frac{\overline{c}_{sk}}{\overline{c}_3}}\left(D_2^* - D_1^*\right)\right]} d\overline{c}_3 \qquad (11)$$

where c_B is the concentration of the background electrolyte within the bulk solution, and the subscripts 1, 2 and 3 stand for the cation associated with the electrolyte whose concentration is varied across the porous medium, the cation associated with the background electrolyte and the common anion, respectively.

The electric potential difference, $\Delta\overline{\varphi}$, can be calculated both numerically and analytically, as the integrand that appears in Eq. (11) can be reduced to a rational function for which, by definition, an antiderivative always exists. Such a calculation has been performed for the case of the Wyoming Bentonite tested by Kemper and Rollins (1966) at a total porosity n = 0.8 (i.e. $\overline{c}_{sk}$ = 56.25 mM), by assuming that the clay specimen is placed between two aqueous solutions, which consist of sodium chloride (NaCl) and hydrochloric acid (HCl) mixtures, and that, alternately, sodium chloride (Fig. 1a) or hydrochloric acid (Fig. 1b) represents the background electrolyte ($D_{0,\mathrm{Na}}$ = $1.33\cdot10^{-9}$ m^2/s; $D_{0,\mathrm{H}}$ = $9.31\cdot10^{-9}$ m^2/s; $D_{0,\mathrm{Cl}}$ = $2.03\cdot10^{-9}$ m^2/s). The predicted positive (ω_m up to 1.5) and negative (ω_m down to -0.5) anomalous values of the reflection coefficient are due to the difference in diffusivity between the sodium and hydrogen ions.

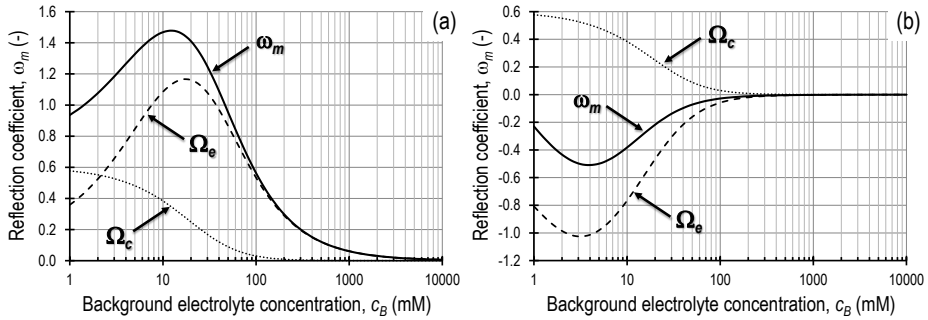

Fig. 1 Chemico-osmotic, Ω_c, and electro-osmotic, Ω_e, components of the measured reflection coefficient, ω_m. (a) $c'_{\mathrm{HCl}} = 5$ mM ; $c''_{\mathrm{HCl}} = 20$ mM ; $c'_{\mathrm{NaCl}} = c''_{\mathrm{NaCl}} = c_B$. (b) $c'_{\mathrm{NaCl}} = 5$ mM ; $c''_{\mathrm{NaCl}} = 20$ mM ; $c'_{\mathrm{HCl}} = c''_{\mathrm{HCl}} = c_B$.

4 Conclusions

The mechanistic model developed by Dominijanni and Manassero (2012) has here been adopted to provide insight into the physico-chemical mechanisms which, at the pore-scale, govern semipermeable membrane behaviour of smectite clays. In particular, when the clay specimen is tested under closed-system boundary conditions, the contribution of electro-osmosis to the measured membrane efficiency coefficient plays a major role for the case of electrolyte solutions containing two or more cations with different mobilities, whereas the aforementioned contribution is found to be negligible for single-electrolyte systems. On the basis of the theoretical predictions worked out in this paper, membrane behaviour in multi-electrolyte systems can cause both positive anomalous osmosis, which results in a better containment performance than expected for ideal semipermeable membranes, and negative anomalous osmosis which, on the contrary, results in a worse containment performance than expected for non-semipermeable porous media. As far as positive anomalous osmosis is concerned, in addition to the increased membrane efficiency, the persistency of membrane behaviour also seems to be enhanced in comparison to single-electrolyte systems, for which the threshold concentration (i.e. the average concentration across the specimen at which $\omega \sim 0$) was experimentally observed to be about 200 mM (Shackelford et al., 2016).

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