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## Assessing the leakage rate through semipermeable bentonite-based barriers permeated with multi-electrolyte solutions

Évaluation du taux de fuite à travers des barrières semi-perméables à base de bentonite imprégnées de solutions multi-électrolytes

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**ABSTRACT:** Most of the experimental research conducted to date on the semipermeable membrane behaviour of bentonites, which are used as part of pollutant containment systems, has involved permeant (electrolyte) solutions containing a single salt, thus not accounting for the simultaneous presence of two or more electrolytes. In view of the significance of the latter issue when bentonites are permeated with real contaminated liquids, the results of a multi-stage membrane test carried out on a powdered sodium bentonite in equilibrium with aqueous mixtures of sodium chloride (NaCl) and potassium chloride (KCl) are interpreted via a theoretical model, whereby the overall osmotic counter-flow of water in multi-electrolyte systems is decomposed into a chemico-osmotic effect, which arises from the partial exclusion of anions from the bentonite pores and also occurs in single-electrolyte systems, and an electro-osmotic effect, which stems from the condition of null electric current density in the presence of cationic species with different diffusivities and causes the measured reflection coefficient,  $\omega$ , to assume values both larger than unity ( $\omega = 1.064$ ) and lower than zero ( $\omega = -1.168$ ). While positive anomalous osmosis ( $\omega > 1$ ) correlates with an enhanced osmotic counter-advection of contaminants and, hence, with an improved containment performance of bentonite-based barriers, the occurrence of negative anomalous osmosis ( $\omega < 0$ ) causes such barriers to behave worse than non-semipermeable clay liners.

**RÉSUMÉ :** La plupart des recherches expérimentales menées à ce jour sur le comportement des membranes semi-perméables des bentonites, qui sont utilisées dans le cadre des systèmes de confinement des polluants, ont impliqué des solutions de perméation (électrolyte) contenant un seul sel, ne tenant donc pas compte de la présence simultanée de deux ou plusieurs électrolytes. Compte tenu de l'importance de ce dernier problème lorsque les bentonites sont imprégnées de vrais liquides contaminés, les résultats d'un essai membranaire en plusieurs étapes effectué sur une poudre de bentonite de sodium en équilibre avec des mélanges aqueux de chlorure de sodium (NaCl) et de chlorure de potassium (KCl) sont interprétés via un modèle théorique, dans lequel le contre-courant osmotique global de l'eau dans les systèmes multi-électrolytes est décomposé en un effet chimico-osmotique, qui résulte de l'exclusion partielle des anions des pores de la bentonite et se produit également dans un seul électrolyte, et un effet électro-osmotique, qui découle de la condition de densité de courant électrique nulle en présence d'espèces cationiques avec des diffusivités différentes et amène le coefficient de réflexion mesuré,  $\omega$ , à prendre des valeurs à la fois supérieures à l'unité ( $\omega = 1.064$ ) et inférieure à zéro ( $\omega = -1.168$ ). Alors que l'osmose anormale positive ( $\omega > 1$ ) est en corrélation avec une contre-advection osmotique améliorée des contaminants et, par conséquent, avec une performance de confinement améliorée des barrières à base de bentonite, l'apparition d'une osmose anormale négative ( $\omega < 0$ ) fait que ces barrières se comportent moins bien que les revêtements en argile non semi-perméable.

**KEYWORDS:** anomalous osmosis, coupled fluxes, geosynthetic clay liner, membrane behaviour, reflection coefficient.

### 1 INTRODUCTION

Engineered clay barriers wholly or partly consisting of bentonite (e.g. geosynthetic clay liners and soil-bentonite mixtures) are widely used for chemical containment purposes in municipal and hazardous solid waste landfills, surface impoundments, deep geological repositories of high-level radioactive wastes and groundwater remediation systems. As a consequence of the net negative electrical surface charge associated with smectite minerals (e.g. montmorillonite), which represent the primary mineralogical components of bentonites, migration of anions through the pores that are freely accessible to the water molecules is partially restricted, so that smectitic clays behave as semipermeable membranes (Musso et al. 2017; Manassero et al. 2018). The semipermeable properties of bentonites macroscopically result in the coupling among the hydraulic, ionic and electrical fluxes and non-conjugated driving forces, with the term “osmosis” being used to refer broadly to the movement of water that is induced by gradients in intensive properties of the bulk solutions other than hydraulic head (Mitchell 1991; Medved & Černý 2013; Shackelford et al. 2019; Guarena et al. 2020).

A review of the literature pertaining to the semipermeable membrane behaviour of clays has demonstrated that, in the

absence of an externally applied electric potential difference, the non-hydraulic component of the water movement in porous media, as driven by a gradient in the ionic concentrations, is referred to as “chemical osmosis,” which suggests that the different resistance against the passage of water (H<sub>2</sub>O) molecules and dissolved ionic chemical species is the only cause of the coupled phenomenon. Accordingly, the extent to which clay soils exhibit membrane behaviour is quantified through the laboratory measurement of the so-called “chemico-osmotic efficiency coefficient,” represented by  $\omega$ , which ranges from zero, for non-semipermeable membranes, to unity for ideal or perfect semipermeable membranes that prevent all anions from entering the pores (Fritz 1986; Keijzer et al. 1999; Malusis & Shackelford 2002a, 2002b; Bader and Kooi 2005; Malusis et al. 2003, 2020).

In terms of uncharged porous media, the aforementioned rationale provides a comprehensive understanding of the microscale mechanisms that govern osmotically induced water movement, since the selective restriction of the solutes can be attributed only to steric hindrance, which arises when the molecules have a larger size than the physical size of the membrane pores. However, this interpretation does not explain several particular features that are observed in the flow behaviour

when an electrically charged porous medium is interposed between electrolyte solutions of different concentrations (Fujita & Kobatake 1968; Woermann 1968; Sasidhar & Ruckenstein 1982; Hijnen & Smit 1995). For instance, if the ratio of the diffusivity of cations to that of anions is less than unity, the liquid flux may take place from the more concentrated to the dilute solution under isobaric conditions, resulting in the so-called “negative anomalous osmosis,”  $\omega < 0$  (Grim & Sollner 1957; Röttger & Woermann 1993).

The soil science and geotechnical engineering literature provides experimental evidence of such anomalous osmotic phenomena in active clays. Kemper & Quirk (1972) measured the  $\omega$  parameter for bentonite, illite and kaolinite clays permeated with aqueous solutions of a single salt, adopting a test configuration that is referred to as an “open hydraulic control system” (Shackelford 2013; Dominijanni et al. 2019a). In addition to the osmotic liquid flux, their testing apparatus allowed the electromotive force (EMF) of the system to be measured through a pair of silver-coated electrodes reversible to  $\text{Cl}^-$  ions (i.e.  $\text{Ag}/\text{AgCl}$  electrodes), while the known chloride concentration difference allowed the portion of the total EMF due to the electric potential difference established across the specimen to be estimated (Bader & Heister 2006). After an initial period in which positive  $\omega$  values were obtained, a reversal of the osmotic flow direction occurred at higher salt concentrations, with lower negative  $\omega$  values generally being detected in the presence of salts that had dissociated into low-mobility multivalent cation species ( $\text{CaCl}_2$  and  $\text{LaCl}_3$ ). Interestingly, this reversal occurred approximately at the same salt concentration at which the electric potential difference changed sign.

The results of the aforementioned study indicate that anomalous osmotic phenomena may be related to an electro-osmotic effect. In fact, because of the presence of non-equivalent concentrations of cations and anions within the pore solution, the generation of an electric potential difference across the specimen leads to a net momentum transfer to the water molecules and a resulting liquid flux in the direction of cation migration, i.e., from the anode to the cathode (Acar & Alshawabkeh 1996; Alshawabkeh & Acar 1996; Mitchell & Soga 2005; Delgado et al. 2007). When a short-circuiting of the clay boundaries is absent, as is the case of the laboratory tests conducted by Kemper & Quirk (1972) and of most geoenvironmental containment scenarios, the electric potential difference builds up in response to the different diffusivities and electrochemical valences of the ionic species, and the magnitude is such that the condition of a null electric current density is satisfied (Helfferich 1962; Groenevelt & Bolt 1969; Kemper et al. 1972; Appelo & Wersin 2007). Considering this, the measured  $\omega$  parameter includes both a chemico-osmotic and a diffusion induced electro-osmotic component, and the terms “membrane efficiency coefficient” and “reflection coefficient” may therefore be regarded as being more appropriate when referring to the aforementioned phenomenological parameter.

The available experimental evidence concerning clay membrane behaviour under non short-circuited conditions shows a relatively limited, if not negligible, contribution of electro-osmosis compared to chemico-osmosis. However, such membrane efficiency tests were carried out on clay specimens permeated with single-electrolyte solutions and, thus, did not account for the influence of the simultaneous presence of two or more different electrolytes in the pore solution. In order to shed some light on this latter condition, which is of the utmost relevance to evaluate the field performance of bentonite-based barriers, the objective of this paper is to present the results of a multi-stage membrane test conducted on a natural sodium bentonite in contact with aqueous mixtures of sodium chloride and potassium chloride. The obtained results are interpreted through a physically-based theoretical model, which was derived according to the uniform potential assumption, to assess the

extent to which the measured reflection coefficient deviates from predictions based on pure chemico-osmosis when two monovalent cations, which diffuse at different rates in water, are simultaneously present in the pore solution. Besides negative anomalous osmosis, the possible occurrence of the so-called “positive anomalous osmosis,”  $\omega > 1$  (Yaroshchuk et al. 1993), as driven by the different mobilities of sodium and potassium cations is also investigated.

## 2 THEORETICAL FRAMEWORK

On the basis of pioneering models that were developed with the aim of simulating coupled transport phenomena in fine-porous charged diaphragms, such as track-etched membranes and polyelectrolyte gels (Yaroshchuk 1995), Dominijanni & Manassero (2012) were able to identify the pore-scale interactions that govern the behaviour of chemically active clays at the macroscopic scale, thus allowing a complete characterisation of the osmotic properties of bentonites to be obtained in the frame of a purely mechanistic approach. If the reflection coefficient of clays is determined according to a test configuration which is referred to as “closed hydraulic control system” (Shackelford 2013; Dominijanni et al. 2019a), whereby the hydraulic head difference,  $\Delta h$ , or conjugated force, across the specimen is measured in the presence of an applied osmotic pressure difference,  $\Delta \Pi$ , or non-conjugated force, while the volumetric liquid flux,  $q$  (direct flux), is hindered, the aforementioned mechanistic approach yields the following physical identification of  $\omega$  (Eq. 1) for an aqueous mixture of  $n \geq 2$  ionic species (Guarena et al. 2021a, 2021b):

$$\omega = \left[ \frac{\gamma_w (\Delta h)_{ss}}{\Delta \Pi} \right]_{q=0; I=0} = \left( 1 - \frac{\Delta \bar{\Pi}}{\Delta \Pi} \right) - F \frac{\bar{c}'_{sk,0}}{e} \frac{\Delta \bar{\varphi}}{\Delta \Pi} \quad (1)$$

where  $\gamma_w$  is the water unit weight ( $9.81 \text{ kN/m}^3$ ),  $(\Delta h)_{ss}$  is the difference in steady-state hydraulic head across the specimen,  $\Delta \Pi = RT \sum_{i=1}^n \Delta c_i$  and  $\Delta \bar{\Pi} = RT \sum_{i=1}^n \Delta \bar{c}_i$  are the differences in osmotic pressure of the external and pore solution across the specimen, respectively,  $R$  is the universal gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  $T$  is the absolute temperature,  $c_i$  and  $\bar{c}_i$  are the concentrations of the  $i$ -th ionic species within the external and pore solution, respectively,  $I = F \sum_{i=1}^n z_i J_i$  is the electric current density,  $F$  is Faraday’s constant ( $9.6485 \cdot 10^4 \text{ C}\cdot\text{mol}^{-1}$ ),  $z_i$  is the electrochemical valence of the  $i$ -th ionic species,  $J_i$  is the molar flux of the  $i$ -th ionic species,  $\bar{c}'_{sk,0}$  is the solid charge coefficient, which depends both on the surface charge density carried by the solid skeleton and the soil fabric (Dominijanni et al. 2018, 2019b; Manassero 2020),  $e$  is the void ratio and  $\Delta \bar{\varphi}$  is the difference in electric potential of the pore solution across the specimen, also referred to as diffusion potential.

As a consequence of the negative electric charge of the solid phase, a discontinuity is established in the concentration of the  $i$ -th ionic species between the pore and external solutions (Eq. 2):

$$\bar{c}_i = c_i \exp \left( -z_i \frac{F}{RT} \bar{\Psi} \right) \quad (2)$$

where  $\bar{\Psi}$  is the so-called phase-boundary or Donnan potential, which can be determined by coupling Eq. 2 with the statement of macroscopic electroneutrality in the pore ( $\bar{c}'_{sk,0}/e = \sum_{i=1}^n z_i \bar{c}_i$ ).

Eq. 1 allows the different mechanisms that contribute to determining the measured reflection coefficient to be appreciated. The first contribution to  $\omega$  is represented by the chemico-osmotic component,  $\Omega_c = 1 - \Delta \bar{\Pi}/\Delta \Pi$ , which is solely related to the ionic partition effect and tends to drive solvent from the dilute solution side to the concentrated solution

side. The second contribution to  $\omega$  is represented by the electro-osmotic component,  $\Omega_e = -F(\bar{c}'_{sk,0}/e)(\Delta\bar{\varphi}/\Delta\Pi)$ , and is controlled by the diffusion potential, which arises to enforce the condition of null electric current density when the mobilities of the ionic species differ from each other.

The diffusion potential can be expressed as follows (Eq. 3):

$$\Delta\bar{\varphi} = -\frac{RT}{F} \int_0^L \frac{\sum_{i=1}^n z_i D_{0,i} d\bar{c}_i}{\sum_{j=1}^n z_j^2 \bar{c}_j D_{0,j}} dx \quad (3)$$

where  $L$  is the length of the clay specimen and  $D_{0,i}$  is the free-solution or aqueous-phase diffusion coefficient of the  $i$ -th ionic species.

Although an antiderivative of the integrand that appears in Eq. 3 is easily found in the case of single-electrolyte solutions (Dominijanni et al. 2019a), such a calculation is not straightforward for electrolyte mixtures. A general solution that holds for an arbitrary number of ionic species was proposed by Helfferich (1962), but assessment of the diffusion potential by this method is quite cumbersome and time consuming. Nevertheless, approximate analytical solutions can be obtained through the introduction of simplifying hypotheses, as the one based on the so-called ‘‘constant-field assumption’’ (Goldman 1943). According to this latter approach,  $\bar{\varphi}$  is assumed to vary linearly over the length of the porous medium, so that an explicit closed-form analytical solution for the diffusion potential is obtained when two monovalent cations (i.e.  $\text{Na}^+$  and  $\text{K}^+$  ions) and a single monovalent anion (i.e.  $\text{Cl}^-$  ion) are simultaneously present in the system (Eq. 4):

$$\Delta\bar{\varphi} = \frac{RT}{F} \cdot \ln \left( \frac{D_{0,\text{Na}} \bar{c}_{\text{Na},B} + D_{0,\text{K}} \bar{c}_{\text{K},B} + D_{0,\text{Cl}} \bar{c}_{\text{Cl},T}}{D_{0,\text{Na}} \bar{c}_{\text{Na},T} + D_{0,\text{K}} \bar{c}_{\text{K},T} + D_{0,\text{Cl}} \bar{c}_{\text{Cl},B}} \right) \quad (4)$$

where  $\bar{c}_{\text{Na},B}$ ,  $\bar{c}_{\text{K},B}$  and  $\bar{c}_{\text{Cl},B}$  are the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  ions in the pore solution at the bottom specimen boundary, respectively, and  $\bar{c}_{\text{Na},T}$ ,  $\bar{c}_{\text{K},T}$  and  $\bar{c}_{\text{Cl},T}$  are the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  ions in the pore solution at the top specimen boundary, respectively.

### 3 EXPERIMENTAL EVIDENCE

#### 3.1 Materials and laboratory apparatus

The powdered bentonite tested in this study was an Indian sodium bentonite, whose physicochemical properties have already been described by Dominijanni et al. (2018). The cation exchange capacity was found to vary in the 97 to 104 meq/100g range and the mineralogical composition, assessed through the X-ray diffraction technique, was observed to mainly consist of smectite (> 98%). The salt solutions were prepared with sodium chloride ( $\text{NaCl}$ ) and potassium chloride ( $\text{KCl}$ ), using deionised water as solvent.

The primary components of the laboratory apparatus, which was used for the multi-stage membrane test, include an osmotic cell, a flow-pump accumulator, a differential pressure transducer and a data acquisition system. The osmotic cell, which is schematically illustrated in Figure 1, consists of a modified rigid-wall permeameter (70.57-mm inner diameter), where the top piston and the bottom pedestal are endowed with three drainage lines. The two peripheral lines allow different electrolyte solutions to circulate at the osmotic cell boundaries, so that a chemical potential gradient is established across the clay specimen and is maintained constant throughout the testing

stages. The central line is connected to the differential pressure transducer, which enables the difference in hydraulic head to be measured between the porous stones. The flow-pump accumulator prevents the liquid volumetric flux from occurring through the specimen by simultaneously injecting into and withdrawing from the osmotic cell boundaries the same volume of solution.

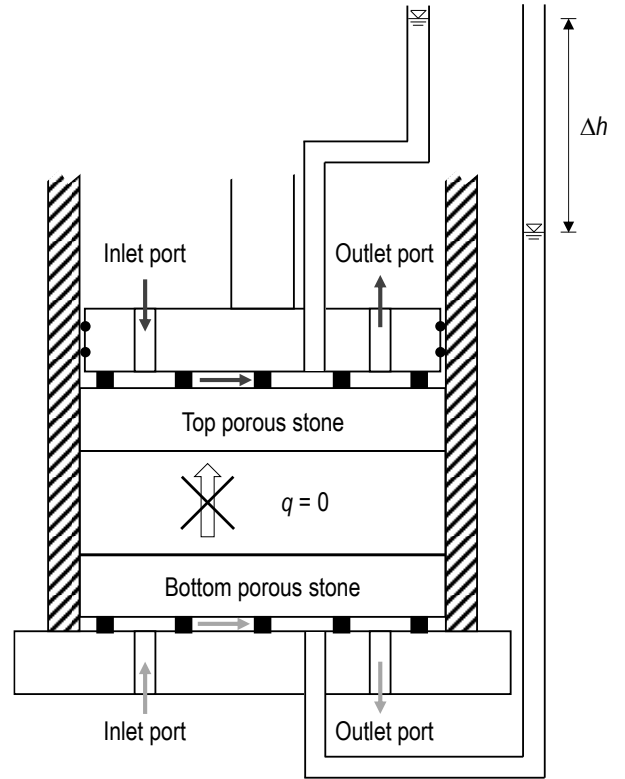


Figure 1. Schematic of the modified rigid-wall permeameter and the associated circulation system used to measure the transport properties of active clays.

#### 3.2 Testing procedures and results

Prior to membrane testing, the sodium bentonite was subjected to the same ‘‘squeezing’’ procedure that was described in detail by Dominijanni et al. (2018), aiming to remove the excess soluble salts that are naturally contained in the powdered material. At the end of the above treatment procedure, the electrical conductivity of the sampled pore solution reached stable values in the 500 to 600  $\mu\text{S}/\text{cm}$  range, corresponding to a salt concentration lower than 5 mM. The squeezed sodium bentonite, oven-dried at 105  $^{\circ}\text{C}$  and sifted through as ASTM No. 200 mesh sieve, was hydrated with DW up to a water content close to the liquid limit and the mixture was then worked with a spatula until a gel-like structure was obtained. A known amount of the clay-water mixture (dry mass equal to 21.94 g) was uniformly distributed inside the modified rigid-wall permeameter and enclosed between the sintered porous stones. A vertical load was applied to the shaft of the top piston by means of a pneumatic actuator, and gradually increased to consolidate the bentonite specimen up to a total vertical stress of 400 kPa. At the end of consolidation, the specimen height and its void ratio were equal to 10.27 mm and 3.85, respectively. After the piston was locked in place and the drainage lines were connected to the ports of the osmotic cell, membrane testing was initiated.

Table 1. Measured values of hydraulic head difference and reflection coefficient during the multi-stage membrane test on the natural sodium bentonite.

| Stage | Values at steady state |                    |                     |                    |                   |          |
|-------|------------------------|--------------------|---------------------|--------------------|-------------------|----------|
|       | $c_{\text{NaCl},L}$    | $c_{\text{KCl},L}$ | $c_{\text{NaCl},0}$ | $c_{\text{KCl},0}$ | $(\Delta h)_{ss}$ | $\omega$ |
|       | (mM)                   | (mM)               | (mM)                | (mM)               | (m)               | (-)      |
| 1     | 0                      | 10                 | 0                   | 1                  | 1.733             | 0.694    |
| 2     | 0                      | 10                 | 5                   | 1                  | 1.121             | 0.989    |
| 3     | 0                      | 10                 | 8                   | 1                  | 0.510             | 1.064    |
| 4     | 0                      | 10                 | 12                  | 1                  | 0.306             | -1.168   |
| 5     | 0                      | 10                 | 20                  | 1                  | -0.204            | 0.139    |
| 6     | 0                      | 10                 | 40                  | 1                  | -0.510            | 0.133    |

The multi-stage membrane test was carried out by circulating different salt solutions through the upper and lower boundaries of the osmotic cell. A constant difference in KCl concentration of 9 mM was imposed throughout the entire duration of the membrane test by maintaining the KCl concentrations of the solutions injected into the upper,  $c_{\text{KCl},L}$ , and lower,  $c_{\text{KCl},0}$ , boundaries equal to 10 and 1 mM, respectively. While KCl was the only salt present in the solution circulating through the upper boundary (i.e.  $c_{\text{NaCl},L} = 0$ ), the NaCl concentration of the solution injected into the lower boundary,  $c_{\text{NaCl},0}$ , was increased stepwise from 0 to 40 mM (Table 1), so that the latter solution corresponded to the hypotonic solution for the first three testing stages and, on the contrary, to the hypertonic solution for the last three testing stages.

The hydraulic head difference induced across the specimen,  $\Delta h$ , and the electrical conductivity of the solutions exiting from the upper and lower boundaries were measured during all the stages. While  $\Delta h$  was continuously monitored at time increments of 120 s, samples of the solutions exiting from the osmotic cell boundaries were collected for measurement of the electrical conductivity when the flow-pump system was briefly halted to refill the hydraulic actuators. Once steady-state conditions were deemed to be achieved for each testing stage based on the measured  $\Delta h$  and electrical conductivity, the subsequent testing stage was initiated.

### 3.3 Discussion

The best-fitting of the experimental  $(\Delta h)_{ss}$  values, which are listed in Table 1, with the theoretically predicted  $(\Delta h)_{ss}$  using the mechanistic model outlined in Section 2 allowed  $\bar{c}'_{sk,0}$  to be determined for the tested bentonite. The free-solution or aqueous-phase diffusion coefficients of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  ions were set equal to  $1.33 \cdot 10^{-9}$ ,  $1.96 \cdot 10^{-9}$  and  $2.03 \cdot 10^{-9}$   $\text{m}^2/\text{s}$ , respectively (Shackelford & Daniel 1991), and a high value of the coefficient of determination ( $R^2 = 0.957$ ) was observed in correspondence of  $\bar{c}'_{sk,0} = 180$  mM.

The aforementioned good agreement between experimental data and model predictions, highlighted in Figure 2, suggests that neglecting the pore-scale fluctuations in electric potential, hydraulic head and ionic concentrations is acceptable to model the osmotic properties of smectitic clays, also when they are permeated with aqueous electrolyte mixtures. Furthermore, the proposed theoretical model is suitable to appreciate the different mechanisms that contributed to the build-up of the measured hydraulic head difference under null volumetric liquid flux conditions. The presence of a single salt (i.e. KCl), which dissociated into cations and anions with similar diffusivities, was associated to the predominant contribution of chemico-osmosis during the first testing stage, as the diffusion potential that was necessary to enforce the electric current density to be null was

negligibly small. However, the presence of NaCl in the solution circulating through the lower boundary caused  $\text{Na}^+$  ions to diffuse upward from the bottom to the top porous stone during the subsequent testing stages, i.e., in the opposite direction to that of  $\text{K}^+$  ions, with the system approaching a condition of pure counterdiffusion due to the low permeability of the bentonite specimen to  $\text{Cl}^-$  ions (Shackelford & Daniel 1991). If any other driving force had not been superimposed to the ionic concentration gradients, a surplus of positive and negative electric charge would have been accumulated at the lower and upper boundaries, respectively, as a result of the purely diffusive transport. A negative diffusion potential, with the cathode corresponding to the top specimen boundary and the anode to the bottom specimen boundary, was thus generated to “speed up” the slower  $\text{Na}^+$  ions and “slow down” the faster  $\text{K}^+$  ions, so that any charge unbalance was prevented from occurring. Such an electrically driven migration of cations towards the cathode was responsible for a net momentum transfer to the water molecules in the direction of more negative potential and, on account of the  $q = 0$  condition, for the build-up of an electro-osmotic contribution to the measured hydraulic head difference, whose magnitude was observed to increase upon an increase in  $c_{\text{NaCl},0}$ .

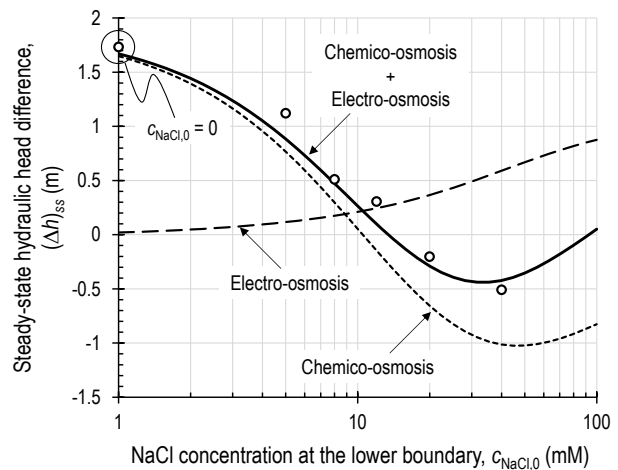


Figure 2. Steady-state hydraulic head difference across the bentonite specimen, as measured during the multi-stage membrane test (open symbols), and theoretical interpretation based on  $\bar{c}'_{sk,0} = 180$  mM (continuous line). The chemico-osmotic and electro-osmotic contributions to the measured  $(\Delta h)_{ss}$  are highlighted with short-dashed and long-dashed lines, respectively.

As a difference from the chemico-osmotic contribution, which changed in sign from positive to negative in correspondence of a null osmotic pressure difference across the specimen, the electro-osmotic contribution was always positive in sign and caused water movement in the same direction as that of chemico-osmosis during the second and third testing stages, i.e., when the solution circulating at the lower boundary corresponded to the hypotonic solution, and in the opposite direction to that of chemico-osmosis during the fourth, fifth and sixth testing stages, i.e., when the solution circulating at the lower boundary corresponded to the hypertonic solution.

Once  $\bar{c}'_{sk,0}$  had been determined for the tested bentonite, the reflection coefficient was obtained from the measured  $(\Delta h)_{ss}$  according to Eq. 1 (Table 1). The physical interpretation of the experimental values of  $\omega$ , as illustrated in Figure 3, shows that the occurrence of electro-osmosis during the second and third testing stages gave rise to an increase in the reflection coefficient relative to the (hypothetical) case of pure chemico-osmosis, which would have been observed if ions had diffused at the same rate in solution. In particular, the extent of the electro-osmotic contribution at  $c_{NaCl,0} = 8$  mM was such that  $\omega$  resulted to be greater than unity ( $\omega = 1.064$ ), which reflects evidence of positive anomalous osmosis in active clays. On the contrary, electro-osmosis caused the reflection coefficient to decrease relative to the case of pure chemico-osmosis during the fourth, fifth and sixth testing stages, being the value of  $\omega$  at  $c_{NaCl,0} = 12$  mM by far lower than zero ( $\omega = -1.168$ ) and, as such, a manifestation of negative anomalous osmosis.

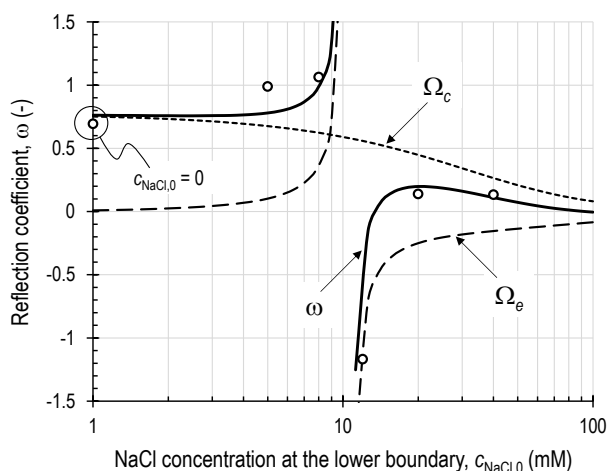


Figure 3. Reflection coefficient obtained from the multi-stage membrane test (open symbols), and theoretical interpretation based on  $\bar{c}'_{sk,0} = 180$  mM (continuous line). The chemico-osmotic and electro-osmotic contributions to  $\omega$  are highlighted with short-dashed and long-dashed lines, respectively.

Based on the above discussion, the obtained experimental evidence confutes the existence of the so-called “diffusion-osmosis,” which was invoked by Olsen et al. (1990) as an additional mechanism responsible for the observed deviations in the flow behaviour from chemico-osmosis when the clay soil is not subjected to an externally applied electric field. Olsen et al. (1990) supported this hypothesis through a qualitative interpretation of the Kemper & Quirk (1972) experimental data (see Section 1), stating that in the aforementioned study water movement in the direction of decreasing solute concentration was a consequence of the viscous drag exerted on the water molecules by solutes diffusing in response to chemical potential gradients. Despite providing an explanation for the occurrence of negative anomalous osmosis in single-electrolyte systems, this interpretation lacks to consider the origin of diffusion, which can be regarded as the macroscopic effect of the incessant thermal (Brownian) motion of the solutes at the molecular scale (Einstein 1956). Indeed, if the integral mean value of the momentum that

is exchanged between each randomly fluctuating solute and the surrounding solvent molecules were evaluated over a sufficiently long interval of time, i.e., after a sufficiently large number of collisions, the resulting net momentum transfer would be found equal to zero, proving that diffusion is not able to generate a macroscopic liquid volumetric flux. Furthermore, the occurrence of positive anomalous osmosis in aqueous solutions of mixed electrolytes, which drives the solution in the direction of increasing osmotic pressure, cannot be clearly ascribed to diffusion-osmosis, while a consistent interpretation has been provided based on diffusion induced electro-osmosis, the latter of which being a macroscopic effect of ion migration under the action of the diffusion potential.

#### 4 CONCLUSIONS

On the basis of a physically-based theoretical framework, which allows the macroscopic effect of the electrical interactions that occur at the pore scale to be modelled, the non-hydraulic component of the volumetric liquid flux through smectitic clays, as driven by a gradient in the chemical potential, has been shown to be dominated by chemico-osmosis whenever the permeant solution contains a single electrolyte, so that the measured reflection coefficient,  $\omega$ , is typically found to vary between 0 and 1. However, the same mechanistic model has also suggested that large osmotic anomalies (i.e. values of  $\omega$  outside the 0 to 1 range) may be observed in aqueous solutions of mixed electrolytes.

A multi-stage membrane test was thus conducted on a natural sodium bentonite using a closed-system testing apparatus, whereby the concentrations of potassium chloride (KCl) were kept constant at the boundaries of the testing cell throughout the experiment (equal to 1 and 10 mM at the lower and upper boundaries, respectively), while varying the concentration of sodium chloride (NaCl) at the lower boundary in the 0 to 40 mM range. Deviations in the measured hydraulic head difference across the specimen from the theoretical predictions based on pure chemico-osmosis became greater as the NaCl concentration was increased, due to the increasing influence of an electro-osmotic effect which was caused by the different diffusivities of  $Na^+$  and  $K^+$  ions dissolved in the pore solution. The build-up of such a diffusion induced electro-osmosis has thus been identified as the mechanism responsible for the occurrence of negative anomalous osmosis driving water in the direction of decreasing osmotic pressure, with values of  $\omega$  as low as -1.168, and positive anomalous osmosis driving water in the direction of increasing osmotic pressure, with values of  $\omega$  as high as 1.064.

An appreciable conclusion of this work is that the occurrence of these osmotic anomalies, which can be framed from a theoretical viewpoint based on the proposed mechanistic model, may be the norm rather than the exception when clay soils are permeated with solutions containing two or more cation species with different mobilities, as is the case with bentonite-based barriers used in geoenvironmental containment applications. Further experimental research is recommended to verify the significance of such an anomalous osmotic behaviour when bentonites are permeated with real leachates.

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