Relative contribution of chemico-osmosis and electro-osmosis to the experimental determination of the reflection coefficient in semipermeable clay soils

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ABSTRACT

The containment performance of bentonite-based barriers is known to be influenced by the semipermeable membrane behaviour of the bentonite, which arises from the electrical interactions between the clay particles and the ionic species dissolved in the pore solution. Most of the experimental research conducted to date has provided evidence of the clay membrane behaviour, the extent of which is typically quantified through the reflection coefficient, \( \omega \), when the permeant (electrolyte) solution contains a monovalent or divalent salt. Under such conditions, the osmotic counter-flow of solution is controlled to a great extent by the solute exclusion, which is also referred to as the chemico-osmotic effect. However, theoretical simulations of coupled solute transport and solvent flow suggest that, when two or more cations with different diffusivities are contained in the permeant solution, the electro-osmotic effect, which stems from the condition of null electric current density, can be comparable or even greater than the chemico-osmotic effect. The relative importance of the aforementioned contributions to multi-electrolyte systems is examined herein through the interpretation of laboratory test results from the literature pertaining to a bentonite-amended clay soil permeated with aqueous mixtures of potassium chloride (KCl) and hydrochloric acid (HCl).

Keywords: bentonite, coupled fluxes, geosynthetic clay liner, landfill, membrane potential, osmosis

1 INTRODUCTION

Coupled flow phenomena are relevant for a number of geotechnical engineering applications, and the mechanisms that underlie such phenomena have therefore been the subject of both experimental and theoretical research (e.g. Medved and Černý, 2013). Among other coupled flow phenomena, mention can be made of the electrokinetic remediation of polluted fine-grained soils, whereby contaminants are removed through the generation of a direct electric current, or the enhancement of the mechanical properties of low-strength active clays as a result of consolidation, which can be induced either via chemico-osmosis or electro-osmosis (Shackelford et al., 2019).

With respect to engineered clay barriers (e.g. geosynthetic clay liners and soil-bentonite mixtures), which are widely used for chemical containment purposes in municipal and hazardous solid waste landfills, surface impoundments and deep geological repositories of high-level radioactive wastes, coupling among the hydraulic, ionic and electrical fluxes and non-conjugated driving forces has been shown to provide a more accurate simulation of the movement of solvent and solutes through clay membranes relative to that based on classical transport theories that simply relate the fluxes to their conjugated forces (Guarena et al., 2020; Manassero, 2020). In fact, as a consequence of the net negative electrical surface charge associated with smectite minerals (e.g. montmorillonite), which represent the primary mineralogical components of such clay barriers, anion migration through pores that are freely accessible to the water molecules is partially restricted. This anionic partitioning effect has been identified as being responsible for the semipermeable properties of smectitic clays and, as a result, the occurrence of coupled fluxes.

A review of the literature pertaining to clay membrane behaviour 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 (H₂O) 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.

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 and Kobatake, 1968; Sasidhar and Ruckenstein, 1982). 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,” \( \alpha < 0 \) (Kemper and Quirk, 1972; Bresler, 1973; Elrick et al., 1976; Röttger and Woermann, 1993).

The soil science and geotechnical engineering literature provides experimental evidence of such anomalous osmotic phenomena in active clays. Kemper and Quirk (1972) measured the \( \alpha \) 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 Cl ions (i.e. Ag/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, or streaming potential, to be estimated. After an initial period in which positive \( \alpha \) values were obtained, a reversal of the osmotic flow direction occurred at higher salt concentrations, with lower negative \( \alpha \) values generally being detected in the presence of salts that had dissociated into low-mobility multivalent cation species (CaCl\(_2\) and LaCl\(_3\)). Interestingly, this reversal occurred approximately at the same salt concentration at which the membrane potential changed sign.

Elrick et al. (1976) measured \( \alpha \) for a sodium (Na) homo-ionic bentonite after having permeated the specimen with NaCl solutions, and adopting a test configuration that can be classified as a “closed hydraulic control system,” since the net liquid flux was forced to be null (Maluis et al., 2013; Shackelford, 2013; Musso et al., 2017; Dominijanni et al., 2018; Dominijanni et al., 2019a). The testing procedure consisted of a first stage, in which the EMF was measured through a pair of Ag/AgCl electrodes under non short-circuited conditions, and a second stage, wherein the specimen boundaries were electrically connected by short-circuiting the reversible electrodes and providing a preferential pathway for the passage of electrons, in a similar way to what happens within a galvanic cell. Although “normal” osmotic behaviour was observed during the first stage, with the osmotic component of the liquid flux being directed towards the more concentrated side, the short-circuiting annulled the EMF and, accordingly, a change in sign of the membrane potential, which in turn caused the occurrence of a strong negative osmosis.

The results of the aforementioned studies 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 (Groenevelt and Bolt, 1969). When a short-circuiting of the clay boundaries is not present, as is the case of most geoenvironmental containment scenarios, the membrane potential 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. Considering this, the measured \( \alpha \) parameter includes both a chemico-osmotic and an 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.

An alternative interpretation of the Kemper and Quirk (1972) and Elrick et al. (1976) experimental results was proposed by Olsen et al. (1990), who postulated that “diffusion-osmosis,” or the viscous drag exerted on the molecular water (H\(_2\)O) by solutes diffusing in response to a chemical potential gradient, was the additional mechanism responsible for the movement of pore water in the direction of decreasing solute concentration. Despite the straightforward explanation for negative osmosis, this interpretation appears to be inconsistent with the dependence of the reflection coefficient on the average salt concentration of the bulk solution that was observed by Kemper and Quirk (1972), as \( \alpha \) values asymptotically approaching zero were measured at the highest salt concentrations. Under such conditions, wherein the semipermeable properties of clays are almost completely suppressed and chemico-osmosis no longer affects the measured \( \alpha \), the occurrence of diffusion-osmosis would lead to increasingly higher absolute values of the (negative) reflection coefficient with increasing difference in the salt concentration across the clay specimen, as diffusion-osmosis is hypothesised to be driven only by the chemical potential gradient regardless of the anionic
partitioning effect. A consistent interpretation of the Kemper and Quirk (1972) results can be provided based on electro-osmosis, which is annulled similarly to chemico-osmosis when the ionic strength of the permeant solution is sufficiently high so as to cancel out the anionic partitioning effect.

All of 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, reference is made to the study by Yaroshchuk et al. (1993), who measured reflection coefficient values greater than unity ($\alpha > 1$), which reflects evidence of "positive anomalous osmosis."

The laboratory test conducted by Yaroshchuk et al. (1993) was performed using a phenolsulfonic acid-formaldehyde cation exchange membrane that separated two reservoirs containing aqueous solutions of both NaCl and HCl. The concentration of NaCl, referred to as the background electrolyte, was maintained the same in both reservoirs and was increased stepwise from 0 to 500 mM, while a constant difference in HCl concentration of 15 mM was imposed by maintaining reservoir HCl concentrations of 5 mM and 20 mM. A hydraulic pressure difference was applied across the membrane and adjusted to suppress the volumetric liquid flux, so that the reflection coefficient could be determined according to the approach which is commonly adopted for closed hydraulic control systems.

As shown in Fig. 1, the measured $\alpha$ first increased with increasing NaCl concentration, $c_{\text{NaCl}}$, up to a maximum value of about 2.4 at $c_{\text{NaCl}} \approx 50$ mM, and then decreased and reached values close to unity at $c_{\text{NaCl}} \approx 500$ mM. This observed flow behaviour clearly cannot be explained by chemico-osmosis alone, and not even by the existence of an additional diffusion-osmotic effect as suggested by Olsen et al. (1990), but only by the build-up of an electro-osmotic effect which is related to the different diffusion coefficients of H$^+$ and Na$^+$ ions in aqueous solution.

In view of the similarities between such cation exchange membranes and smectitic clays, the objective of this paper is to present a theoretical framework that allows the osmotic phenomena in clay soils to be studied, for the case of a permeant (electrolyte) solution containing an unspecified number of ionic species. The ability of the proposed theory to capture the effect of the different mobilities of the cation species contained in the pore solution is verified through the interpretation of laboratory test results published in the geotechnical literature.

![Fig. 1. Theoretical interpretation (continuous line) of the $\alpha$ values measured by Yaroshchuk et al. (1993) on a synthetic cation exchange membrane permeated with aqueous mixtures of NaCl and HCl (open symbols).](image)

2 THEORETICAL FRAMEWORK

Almost all of the mechanistic models developed for the simulation of transport phenomena through charged porous media rely on the Navier-Stokes equation to determine the volumetric liquid flux, $q$, the Nernst-Planck equation to determine the molar flux of the $i$-th ionic species, $J_i$, and the Poisson-Boltzmann equation to determine the distribution of the electrostatic potential over the pore cross-section. Two different approaches may be pursued to find a solution to the non-linear differential system of equations. According to the first approach, which has come to be known as the space-charge model, the aforementioned set of equations is solved numerically, without any additional simplifying assumption. This approach is, at least potentially, applicable to a wide range of scenarios (Gross and Osterle, 1968; Sasidhar and Ruckenstein, 1982). The second approach, which has come to be known as the uniform-potential model, dates back to the work of Schlögl (1955) and assumes that the electrostatic potential does not vary over the pore cross-section, thus neglecting the dispersive effect that is caused by the microscopic fluctuation of the state variables. Although the assumption of a uniform potential profile leads to some errors for high ionic concentrations, this does not seriously limit the applicability of such an approach which, unlike the previous one, allows solutions to be obtained with a relatively little computational effort (Cwirko and Carbonell, 1989).

2.1 Physical interpretation of the reflection coefficient of clays

The reformulation of the uniform-potential model...
proposed by Dominijanni and Manassero (2012), who treated the porous medium as an assembly of conductive capillaries with a slit-like geometry, enclosed between parallel-aligned solid particles or tactoids, is used hereafter to provide a theoretical interpretation of the reflection coefficient of clays with high specific surface (e.g. bentonites). If the aforementioned phenomenological parameter is determined via a testing apparatus that allows the hydraulic pressure difference, $\Delta u$, or conjugated force, across the clay specimen to be measured in the presence of an applied osmotic pressure difference, $\Delta \Pi$, or non-conjugated force, while the volumetric liquid flux (direct flux) is hindered, the following physically-based expression is obtained under steady-state and fully saturated conditions (Dominijanni et al., 2019a):

$$\omega = \left( \frac{\Delta u}{\Delta \Pi} \right)_{q=0,I=0} = \left( 1 - \frac{\Delta \Pi}{\Delta \Pi} \right) - F \frac{\Delta \Phi}{\Delta \Pi}$$

where $u$ is the hydraulic pressure within the external bulk solution, $\Pi$ is the osmotic pressure within the external bulk solution ($\Pi = RT \sum_{i=1}^{n} c_i$). $\bar{\Pi}$ is the osmotic pressure within the pore solution ($\bar{\Pi} = RT \sum_{i=1}^{n} \bar{c}_i$), $I$ is the electric current density ($I = F \sum_{i=1}^{n} z_i F_1$), $F$ is Faraday’s constant (9.6485-10$^4$ C-mol$^{-1}$), $\bar{c}_i$ are the molarity of the solid skeleton electric charge per unit volume of the conductive pores (Dominijanni et al., 2019b), $\bar{\Phi}$ is the electric potential within the pore solution, $R$ is the universal gas constant (8.314 J-mol$^{-1}$-K$^{-1}$), $T$ is the absolute temperature, which is assumed equal to 293.15 K for all of the subsequent analyses, $\bar{c}_i$ is the concentration of the $i$-th ionic species within the pore solution, $c_i$ is the concentration of the $i$-th ionic species within the external bulk solution and $z_i$ is the electrochemical valence of the $i$-th ionic species.

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 bulk solutions:

$$\bar{c}_i = c_i \exp \left[ -z_i \frac{F}{RT} (\bar{\Phi} - \phi) \right]$$

where $\phi$ is the electric potential within the external bulk solution. The $\bar{\Phi} - \phi$ difference, which is known as the Donnan potential, can be determined by coupling Eq. 2 with the statement of macroscopic electroneutrality in the pore ($\bar{c}_{sk} = \sum_{i=1}^{n} z_i c_i$).

Eq. 1 allows the different physical mechanisms that contribute to determining the measured reflection coefficient to be appreciated, which is interpreted as the superposition of a chemico-osmotic component

$$\Omega_c = 1 - \frac{\Delta \Pi}{\Delta \Pi}$$

and an electro-osmotic component

$$\Omega_e = - F \frac{\Delta \Phi}{\Delta \Pi}$$

The membrane potential, $\Delta \Phi$, stems from the condition of null electric current density, and can be expressed as follows:

$$\Delta \Phi = - \frac{RT}{F} \int_{0}^{L} \sum_{i=1}^{n} \frac{z_i D_{0,i}}{\bar{c}_i} \frac{\partial \bar{c}_i}{\partial x} dx$$

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.

According to Revil (1999), the membrane potential can, in turn, be decomposed into a “liquid junction potential,” which compensates for the separation of the charge due to the different mobilities of cations and anions in aqueous solution and, therefore, generates regardless of the membrane behaviour of the porous medium, and an “exclusion potential” which, as the term suggests, arises from the exclusion of anions and the excess of cations within the pore solution due to the development of the diffuse double layers. However, electro-osmosis should be regarded as a distinctive feature of semipermeable clay soils, i.e., since an imbalance in the ion concentrations within the membrane phase (i.e. $\bar{c}_{sk} \neq 0$) is a necessary condition for electro-osmosis to occur.

### 2.2 Calculation of the membrane potential

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 multi-electrolyte systems which, in general, require a numerical procedure to solve. Nevertheless, approximate analytical solutions to the latter case can be obtained through the introduction of simplifying assumptions.

As a first working hypothesis, the membrane potential can be evaluated for the condition in which anions are completely excluded from the pore solution, and only two different cation species are dissolved in the permeant solution (Yaroshchuk et al., 1993):

$$\Delta \Phi = - \frac{RT}{F} \left[ \frac{z_1 D_{0,1}}{z_1^2 D_{0,1} - z_1 z_2 D_{0,2}} \frac{\partial \bar{c}_{1,0}}{\partial x} + \frac{z_2 D_{0,2}}{z_2^2 D_{0,2} - z_1 z_2 D_{0,1}} \frac{\partial \bar{c}_{2,0}}{\partial x} \right]$$

where the subscripts 1 and 2 represent the first and second cation species, respectively.
As a second working hypothesis, the Nernst-Planck equation can be linearised with respect to the electric potential gradient, thus assuming that \( \bar{\phi} \) varies linearly over the length of the membrane. Such an approach, commonly known as the “constant field assumption,” was first proposed by Goldman (1943) with the aim of studying the electrical properties of cell membranes and biological tissues, and allows the Nernst-Planck equation to be integrated with the method of the separation of variables. Substitution of the steady-state molar flux of the \( i \)-th ionic species into the condition of vanishing electric current density then yields the following implicit solution for the membrane potential:

\[
\sum_{i=1}^{n} z_i^2 D_{0,i} \exp \left( \frac{z_i F}{RT} \bar{\phi} \right) - \bar{c}_{i,0} = 0
\]  

(5)

The accuracy of these approximate solutions can be checked by referring to the testing conditions considered by Yaroshchuk et al. (1993). Under such experimental conditions, an exact analytical solution can be derived as follows:

\[
\Delta \bar{\pi} = -\frac{RT}{F} \int_{\bar{c}_{0,0}}^{\bar{c}_{0,1}} \left[ \bar{c}_{0,0} \frac{z_{i,1} D_{0,1}}{z_{i,3} D_{0,3} + \bar{c}_B} \sqrt{\frac{z_{i,3} (\bar{c}_{i} + \bar{c}_{i,3})}{z_{i,3} (\bar{c}_{0,1} - \bar{c}_{0,2})}} \left( \frac{D_{0,1} - D_{0,2}}{D_{0,0} + D_{0,3}} \right) \right] d\bar{c}_3
\]  

(6)

where \( c_B \) is the concentration of NaCl, which represents the background electrolyte within the external bulk solution, and the subscripts 1, 2 and 3 stand for the H\(^+\) cation, the Na\(^+\) cation and the common Cl\(^-\) anion, respectively (\( D_{0,H} = 9.31 \times 10^{-9} \text{ m}^2/\text{s}; D_{0,Na} = 1.33 \times 10^{-9} \text{ m}^2/\text{s}; D_{0,Cl} = 2.03 \times 10^{-9} \text{ m}^2/\text{s} \)).

As shown in Fig. 1, a best-fitting value of the fixed charge concentration, \( \bar{c}_{sk} \), equal to 95 mM has firstly been determined in such a way that the predicted peak value of the reflection coefficient compares well with the measured one. Despite a shift between the Yaroshchuk et al. (1993) experimental data and the simulated trend relative to the background electrolyte concentration, which is probably due to the inability of the proposed theory to properly account for the microstructural properties that are typical of the tested synthetic cation exchange membrane, electro-osmosis appears to be confirmed as the additional mechanism which causes the anomalous osmotic behaviour to occur.

On the basis of the previously calibrated \( \bar{c}_{sk} \) value, the electric potential difference calculated according to the anion exclusion and constant field assumptions has been compared against the exact analytical solution (Fig. 2). In addition to the ability to model the membrane potential in the presence of aqueous solutions consisting of an unspecified number of ions, the constant field assumption results in a theoretical prediction that is close to the exact one, while the hypothesis of a porous medium that is perfectly impermeable to anions, albeit acceptable for very low electrolyte concentrations, is evidently erroneous for medium to high concentrations.

3 INTERPRETATION OF THE TANG ET AL. (2014, 2015) EXPERIMENTAL DATA

Tang et al. (2014) performed a multi-stage membrane test on a specimen that was obtained by mixing a locally available natural clay with 5% powdered sodium bentonite (by dry weight). The bentonite-amended clay was tested by circulating deionised water (DW) at the bottom of the specimen, while injecting aqueous solutions with KCl concentrations of 0.5, 1, 5, 10 and 50 mM at the top of the specimen under a null volumetric liquid flux condition. The measured steady-state \( \omega \) values, plotted in Fig. 3 as a function of the average KCl concentration at the top boundary, \( c_{KCl} \), have been interpreted, via the theoretical model described in the previous section, for a value of the fixed charge concentration, \( \bar{c}_{sk} \), equal to 5 mM. This value of \( \bar{c}_{sk} \) compares well with the one obtained by Dominijanni et al. (2018) for an unmixed pure sodium bentonite (\( \bar{c}_{sk} \approx 30 \text{ mM} \)), and allows for the expected decrease in the reflection coefficient with increasing KCl concentration. Furthermore, the osmotic behaviour in the presence of a single electrolyte that dissociates into monovalent ionic species with similar diffusivity (\( D_{0,K} = 1.96 \times 10^{-9} \text{ m}^2/\text{s} \)) is dominated by chemico-osmosis, as the electro-osmotic effect is negligible for the investigated salt concentrations.
Tang et al. (2015) repeated the above membrane test adding HCl to the aqueous solution circulating at the top of the specimen in order to maintain a pH of 4, while leaving all of the other testing conditions unchanged. The measured \( \omega \) values, shown in Fig. 4, reveal that the addition of HCl did not cause any appreciable variation in the osmotic behaviour for the lowest \( c_{KCl} \approx 1 \text{ mM} \) and highest \( c_{KCl} \approx 40 \text{ mM} \) salt concentrations, while a decrease in \( \omega \), i.e. with respect to the neutral conditions, occurred for the intermediate salt concentrations. Tang et al. (2015) explained such a detrimental effect on the membrane behaviour as being due to a partial dissolution of the bentonite crystalline structure in acidic conditions, which in turn resulted in larger void spaces and a reduced influence of the diffuse double layers. Although the aforementioned process cannot be excluded, calculations based on the evidence presented by Amram and Ganor (2005) demonstrate that, even assuming a uniform pH profile equal to 4 across the specimen, the bentonite mass loss resulting from this pH probably was only about 0.1% relative to the initial mass of bentonite, thus producing a negligible impact on the macroscopic semipermeable properties. Hence, the dissolution mechanism does not explain the concentration dependent decrease in \( \omega \). This conclusion is consistent with that of Shackelford (1994), who reported on the basis of the literature that clay dissolution is not likely until the pH decreases below a value of about 2.

An alternative interpretation of the observed phenomenon is proposed in Fig. 4, where the membrane potential is calculated according to Eq. 5 for the same value of the fixed charge concentration that has been calibrated with respect to the neutral conditions \( \gamma_{0k} = 5 \text{ mM} \). Such an interpretation suggests that electro-osmosis, which arises from the different mobilities of the H\(^+\) and K\(^+\) ions in aqueous solution, should be regarded as being responsible for the measured decrease in the reflection coefficient.
Science, 51: 51-73. doi:10.1016/j.jengsci.2011.11.001.
5) Dominijanni, A., Guarena, N. and Manassero, M. (2018): Laboratory assessment of semipermeable properties of a natural sodium bentonite, Canadian Geotechnical Journal, 55(11), 1611-1631. doi:10.1139/cgj-2017-0599.
6) Dominijanni, A., Guarena, N. and Manassero, M. (2019a): Phenomenological analysis and physical interpretation of the reflection coefficient of clays, Proceedings of the 8th International Congress on Environmental Geotechnics, Hangzhou, China, Vol. 3, 156-163. doi:10.1007/978-981-13-2227-3_19.
7) Dominijanni, A., Fratalocchi, E., Guarena, N., Manassero, M. and Mazzieri, F. (2019b): Critical issues in the determination of the bentonite cation exchange capacity, Géotechnique Letters, 9(3), 205-210. doi:10.1680/jgate.18.00229.
8) Elrick, D.E., Smiles, D.E., Baumgartner, N. and Groenevelt, P.H. (1976): Coupling phenomena in saturated homo-ionic montmorillonite: 1. Experimental, Soil Science Society of America Journal, 40(4), 490-491. doi:10.2136/sssaj1976.0361599500400040014x.
9) Fujita, H. and Kobatake, Y. (1968): Interpretation of anomalous osmosis, Journal of Colloid and Interface Science, 27(4), 609-615. doi:10.1016/0021-9797(68)90092-1.
10) Goldman, D.E. (1943): Potential, impedance, and rectification in membranes, Journal of General Physiology, 27(1), 37-60. doi:10.1085/jgp.27.1.37.
11) Groenevelt, P.H. and Bolt, G.H. (1969): Non-equilibrium thermodynamics of the soil-water system: Review paper, Journal of Hydrology, 7(4), 358-388. doi:10.1016/0022-1694(69)90092-4.
12) Gross, R.J. and Osterle, J.F. (1968): Membrane transport characteristics of ultrafine capillaries, Journal of Chemical Physics, 49(1), 228-234. doi:10.1063/1.1669814.
13) Guarena, N., Dominijanni, A. and Manassero, M. (2020): From the design of bottom landfill liner systems to the impact assessment of contaminants on underlying aquifers, Innovative Infrastructure Solutions, 5(1), Article number: 2. doi:10.1007/s41062-019-0251-y.
14) Kemper, W.D. and Quirk, J.P. (1972): Ion mobilities and electric charge of external clay surfaces inferred from potential differences and osmotic flow, Soil Science Society of America Journal, 36(3), 426-433. doi:10.2136/sssaj1972.03615995003600030019x.
15) Malusis, M., Kang, J.B. and Shackelford, C. (2013): Influence of membrane behavior on solute diffusion through GCLs, Proceedings of the 1st International Symposium on Coupled Phenomena in Environmental Geotechnics, Torino, Italy, 267-274. doi:10.1201/b15004-29.
16) Manassero, M. (2020): Second ISSMGE R. Kerry Rowe Lecture: On the intrinsic, state, and fabric parameters of active clays for contaminant control, Canadian Geotechnical Journal, 57(3), 311-336. doi:10.1139/cgj-2019-0033.
17) Medved, I. and Černý, R. (2013): Osmosis in porous media: A review of recent studies, Microporous and Mesoporous Materials, 170, 299-317. doi:10.1016/j.micromeso.2012.12.009.
18) Musso, G., Cosentini, R.M., Dominijanni, A., Guarena, N. and Manassero, M. (2017): Laboratory characterization of the chemo-hydro-mechanical behaviour of chemically sensitive clays, Rivista Italiana di Geotecnica, 51(3), 22-47. doi:10.19199/2017.3.0557-1405.022.
19) Olsen, H., Yearsley, E., and Nelson, K. (1990): Chemico-osmosis versus diffusion-osmosis, Transportation Research Record No. 1288, Transportation Research Board, Washington, D.C., 15-22.
20) Revil, A. (1999): Ionic diffusivity, electrical conductivity, membrane and thermoelectric potentials in colloids and granular porous media: A unified model, Journal of Colloid and Interface Science, 212(2), 503-522. doi:10.1006/jcis.1998.6077.
21) Röttger, H. and Woermann, D. (1993): Osmotic properties of polyelectrolyte membranes: Positive and negative osmosis, Langmuir, 9(5), 1370-1377. doi:10.1021/la00029a034.
22) Sasidhar, V. and Ruckenstein, E. (1982): Anomalous effects during electrolyte osmosis across charged porous membranes, Journal of Colloid and Interface Science, 85(2), 332-362. doi:10.1016/0021-9797(82)90003-0.
23) Schlögl, R. (1955): Zur theorie der anomalen osmose, Zeitschrift für Physikalische Chemie, 3, 73-102. doi:10.1524/zpch.1955.3.1_2.073.
24) Shackelford, C. (1994): Waste-soil interactions that alter hydraulic conductivity, Hydraulic Conductivity and Waste Contaminant Transport in Soil, STP 1142, ASTM, West Conshohoken, Pennsylvania, 111-168. doi:10.1520/STP23887S.
25) Shackelford, C. (2013): Membrane behavior in engineered bentonite-based containment barriers: State of the art, Proceedings of the 1st International Symposium on Coupled Phenomena in Environmental Geotechnics, Torino, Italy, 45-60. doi:10.1201/b15004-7.
26) Shackelford, C., Lu, N., Malusis, M. and Sample-Lord, K. (2019): Research challenges involving coupled flows in geotechnical engineering, Geotechnical Fundamentals for Addressing New World Challenges, Springer International Publishing, AG, 237-274. doi:10.1007/978-3-030-06249-1_9.
27) Tang, Q., Katsumi, T., Inui, T. and Li, Z. (2014): Membrane behavior of bentonite-amended compacted clay, Soils and Foundations, 54(3), 329-344. doi:10.1016/j.sandf.2014.04.019.
28) Tang, Q., Katsumi, T., Inui, T. and Li, Z. (2015): Influence of pH on the membrane behavior of bentonite amended Fukakusa clay, Separation and Purification Technology, 141, 132-142. doi:10.1016/j.seppur.2014.11.035.
29) Yaroshchuk, A.E., Röttger, H. and Woermann, D. (1993): Osmotic properties of a cation exchange membrane: Reflection coefficients of a solute larger than 1 in a system with aqueous mixed electrolyte solutions, Berichte der Bunsegesellschaft für Physikalische Chemie, 97(5), 676-680. doi:10.1002/bpc.19930970506.