

Semi-permeable membrane behaviour of conventional and enhanced Geosynthetic Clay Liners

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Abstract. The semipermeable membrane behavior of conventional and enhanced Geosynthetic Clay Liners (GCLs) is viewed with great interest in pollutant containment applications, as the consequent reduction of diffusive flow and the onset of chemical osmosis improves the containment properties. In this context, an experimental apparatus was developed to characterize the semipermeable membrane behavior of GCLs. Preliminary results were obtained on conventional GCLs and a Dense PreHydrated and polymer-enhanced (DPH) GCL. The measured values of the chemico-osmotic efficiency coefficient ω are comparable with literature data. In addition, owing to the possibility of monitoring the total vertical stress, the equipment allows determining the at the same time the swelling coefficient $\bar{\omega}$. In this way, a complete picture of the behavior of the charged porous medium in response to chemical exposure is obtained and it is possible to determine on the same specimen the relevant parameters for the application of advanced theoretical models of chemical-osmotic phenomena in clays and GCLs.

1 Introduction

The ability of the bentonite layer in GCLs to exhibit semipermeable membrane behaviour, i.e. to limit the transport of solutes (ions) while allowing that of water, is well recognized [1-3] and attributed to the electrostatic repulsion exerted by negatively charged surface of the clay on anions. The restriction on ion migration is usually partial and the degree of ion entry restriction has traditionally been quantified by the chemico-osmotic efficiency coefficient, ω . Chemico-osmotic diffusion tests have been widely used to determine the ω coefficient of soils and GCL. The most adopted experimental approach is the closed-system approach [1] which consists in generating a steady-state chemical gradient through a saturated sample while preventing the hydraulic flow. If the medium has semipermeable membrane properties, a differential pressure arises across the sample due to the onset of chemical osmosis. The

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absence of volume change in closed-system tests is ensured by using rigid-wall cells and by preventing vertical swelling of the soil specimen by means of a locked rigid piston [1,4]. However, in rigid-wall cells, specimen shrinkage is possible, resulting in risk of hydraulic short-circuiting between the two ends of the specimen and destruction of the semipermeable membrane behavior [5]. The article presents an experimental apparatus based on a rigid-wall cell recently developed for the execution of chemical-osmotic diffusion tests on soils or GCLs, which allows applying a controlled strain condition to the sample, either by means of a locked piston, in a similar way to the approach adopted in [1], or by using a load cell, according to the approach described in [6]. The latter configuration allows monitoring the total vertical stress acting on the specimen during the diffusion test while keeping the vertical deformations at a negligible level ($< 1\%$). The article also reports the results of tests performed on different GCLs, to highlight the influence of the product type on the determined membrane properties. It also illustrates a first application of an advanced theoretical model for the description of chemical-osmotic phenomena to the results obtained on GCLs.

2 Materials and methods

2.1 Testing apparatus

Figure 1 shows a scheme of the apparatus, conceptually similar to the one described in [1]. The principle of the test is to induce a steady-state chemical gradient across a saturated soil (or GCL) sample while preventing hydraulic flow. The chemical gradient is induced by circulating equal amounts of electrolyte solutions at different concentrations at the ends of the specimen. This is achieved by attaching a dual syringe pump to two metal cylinders. The syringe plunger separates each cylinder into two compartments, hydraulically connected to a porous disk placed in contact with the specimen boundary, such that the solution is infused into the porous disk at a given flow rate by moving the plunger through one of the drainage lines connected to the disk and aspirated at the same rate through the other line. A third drainage line connects the porous disk to a differential pressure transducer. The hydraulic pressures generated at the top and base of the specimen are monitored separately by means of gauge pressure transducers placed along the drainage lines.

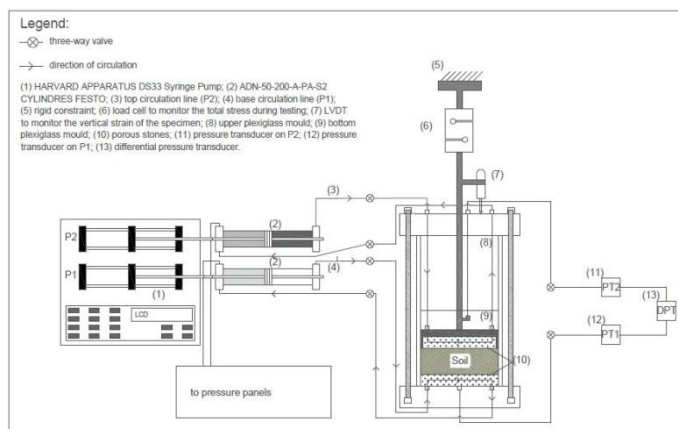


Fig. 1. Schematic of the solution recirculation system and the rigid-wall acrylic cell for the execution of chemico-osmotic diffusion tests (redrawn from [7])

The rigid-wall cell consists of a plexiglass cylinder (internal diameter 100 mm) that houses the soil specimen (or GCL) and an upper pressure chamber, hydraulically isolated from the specimen housing by a rigid piston laterally sealed by a rubber o-ring. Plexiglass was preferred to stainless steel because it is not conductive. The rigid piston is free to move downwards or upwards during the consolidation or swelling phase of the specimens. During the circulation phase, the piston can be locked against a rigid steel frame ("No Strain" condition) or connected to a load cell (LCM411-500-USBH Load Cell, AEP Transducers, Italy) located between the piston rod and the steel frame, which allows the total stress acting on the specimen to be monitored. Since the load cell undergoes minimal deformation (≈ 0.2 mm/KN) for the measurement of the applied force, in principle very small volume changes can occur with the latter test condition ("small strain" condition). A displacement transducer (LVDT) attached to the piston rod allows to monitor volume changes during the preliminary consolidation or swelling phase of the specimen as well as during the chemical-osmotic diffusion phase.

2.2 Chemico-osmotic diffusion tests

A closed-system chemico-osmotic diffusion test consists of measuring the pressure difference generated across a soil specimen (or GCL) by the inhibition of the volumetric flow of solution, q . The chemical-osmotic efficiency coefficient ω (or reflection coefficient) is then determined as:

$$\omega = \left(\frac{\Delta P}{\Delta \pi} \right)_{q=0} \quad (1)$$

where ΔP = hydraulic pressure difference across the sample, $\Delta \pi$ = theoretical osmotic pressure difference across an ideal semipermeable membrane separating two dilute solutions of a single electrolyte, which can be calculated by the van't Hoff equation:

$$\Delta \pi = \nu RT \Delta C \quad (2)$$

where ν = number of ions per salt molecule, R = universal gas constant [$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$], T = absolute temperature, and ΔC = difference in solute concentration across the membrane (M). Since the restriction of solutes through the porous medium is usually partial, a diffusive flow occurs in response to the induced concentration gradient, until a steady-state diffusion condition is reached. Monitoring of the inlet and outlet solute concentrations allows to determine the molar diffusive flux at steady state, J [1], and the chemico-osmotic diffusion coefficient is determined experimentally as:

$$D_s^\omega = H \frac{J}{n(C_{i,av} - C_{b,av})} \quad (3)$$

where $C_{i,av}$ = average solute concentration at the top, $C_{b,av}$ = average solute concentration at the base, H = sample thickness and n = total porosity. In the case of electrolyte solutions, for zero electric current density and in the absence of membrane behaviour, the diffusion coefficient measured at steady state is the effective diffusion coefficient of the salt D_s^* . In the presence of membrane behaviour, the diffusion coefficient D_s^ω , can be related to the

effective diffusion coefficient of the salt as follows [8]):

$$D_s^\omega = (1 - \omega)D_s^* = (1 - \omega)\tau_m D_{so} \quad (4)$$

where τ_m = geometric or matrix tortuosity of the porous medium and D_{so} = diffusion coefficient of the salt in free solution.

2.3 Materials and testing procedure

To illustrate the use of the equipment, this article reports the results of chemico-osmotic diffusion tests performed on three different GCL products currently on the market, hereinafter called GCL-1, GCL-2 and GCL-3. GCL-1 (Bentofix[®]BFG5000; NAUE, Germany) is a needle-punched product containing 4.5 kg/m² of sodium bentonite powder. Further details on the GCL-1 are reported in [9]. GCL-2 is a needle-punched product (Bentomat[®] SS, CETCO, USA), which contains a nominal unit mass of 4.2 kg/m² of granular sodium bentonite. The main properties of the product are reported in [10]. GCL-3 (Rawmat[®], Rawell, UK) is a product known as prehydrated and high-density (DPH) GCL. The type used in this study includes a 5.0 kg/m² layer of prehydrated and vacuum-extruded bentonite, 4.6 mm thick, interposed between a perforated polyester geotextile and an HDPE layer, which was removed before performing the test. It is known that the bentonite of GCL3-3 is amended with polymers (Na-polyacrylate and Na-carboxymethylcellulose) during the production process. Further details on GCL-3 are reported in [9]. The liquids used in this study are distilled water (DW) and potassium chloride (KCl) solutions. The solutions were prepared by dissolving analytical grade solid KCl in DW. Circular GCL specimens (diameter = 100 mm) were carefully cut, hydrated and permeated with DW to reduce the concentration of soluble salts, increase the degree of saturation and measure the initial hydraulic conductivity (k). Preliminary hydration and permeation were performed in flexible-wall permeameters (ASTM D5887), under an average effective isotropic stress $\sigma'_i=34.5$ kPa. After 4-6 months of permeation, each specimen was transferred to the rigid-wall cell, taking care to avoid gaps in the contact with the rigid walls. Then, the specimens were re-consolidated by pressurizing the upper chamber ($\sigma=34.5$ kPa) and subsequently permeated with DW (hydraulic gradient, $i = 90-120$), mainly to check for sidewall leakage. After permeation, the confining piston was blocked on the steel frame in the "no strain" testing approach, while in the case of the "small strain" testing approach the load cell was interposed between the piston rod and the steel frame, to allow the total stress to be monitored in the subsequent testing steps. At this point, the upper chamber was depressurized and DW was circulated as the inlet solution on both ends of the sample to establish the baseline differential pressure. The circulation rate was set at 4.8×10^{-10} m³/s (41.5 mL/day) in all tests to allow comparison with previous studies [10-11]. After about 7 days of circulation with DW, the chemical-osmotic phase of the test was started by circulating the chosen electrolyte solution as the inlet solution at the top while continuing the circulation of DW at the base. During the circulation phase, regular cylinder recharges were carried out (on average every 48 hours), and at the same time the outlet solutions were sampled to monitor the electrical conductivity, EC, and for the subsequent analysis of concentrations. At the end of the chemico-osmotic phase, the GCL specimens were again permeated with the electrolyte solution, to verify the possible shrinkage of the sample through the increase in k , compared to the permeation with DW. Finally, the moisture content of the specimen was measured to verify the final degree of saturation.

3 Results and discussion

3.1 Typical result of a chemico-osmotic test

A typical result of a chemical-osmotic diffusion test, in terms of the trend of the differential pressure, $\Delta P (=P_{top}-P_{base})$ over time is shown in Figure 2a. The average value of differential pressure during circulation with distilled water, ΔP_{DW} , was assumed as representative of the entire phase, while the representative value of ΔP for circulation with the electrolyte solution, ΔP_{KCl} , was determined by the overall trend, considering also the disturbance induced by the sampling and recharging operations (i.e. "jumps" of the plot in Fig 2a). The coefficient ω has been calculated as follows:

$$\omega = \frac{\Delta P_e}{\Delta \pi_{av}} \tag{5}$$

where ΔP_e is the effective differential pressure (Fig.2), defined as:

$$\Delta P_e = \Delta P_{KCl} - \Delta P_{DW} \tag{6}$$

and $\Delta \pi_{av}$ is the theoretical chemico-osmotic differential pressure, calculated by Eq.2 considering the difference of average concentrations at the specimen boundaries. Fig. 2b shows the trend of the total vertical stress (σ) measured during the chemical-osmotic diffusion test, carried out with the small-strain test mode. The initial value of the vertical stress (σ_0) was generated in the load cell as a result of the depressurization of the upper hydraulic chamber and the consequent tendency of the specimen to swell. In the subsequent phase of circulation with DW, it is possible to observe an increasing trend of σ , consistent with the reduction of the concentration of soluble salts at the specimen boundaries, indicated by the progressive decrease in the EC of the outlet solutions (data not shown). This decrease leads to an increase in the osmotic pressure difference between the specimen pore water and the external circulation solution, which contributes to an increase in the swelling pressure, detected by the load cell [6]. On the contrary, the circulation of the 20 mM KCl solution at the top of the specimen induces a decreasing trend of σ , due to the reduction of the chemical-osmotic component of the swelling pressure.

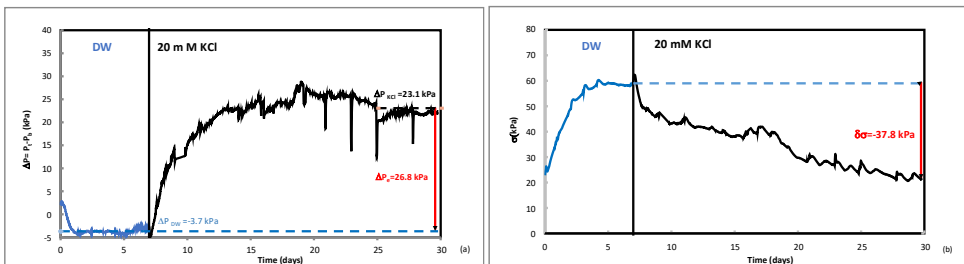


Fig. 2 - Examples of differential pressure (a) and of total stress (b) trend measured during a chemical-osmotic diffusion test conducted with the small-strain mode.

3.2 Influence of the GCL type

Fig.3a shows a comparison between the effective differential pressure, ΔP_e , measured during the circulation phase with 20 mM KCl on the three different products considered in this study,

of which two are classifiable as "conventional" (GCL-1 and GCL-2) and one with "enhanced" performance (GCL-3 or DPH GCL). It is possible to highlight that the type of GCL significantly influences the chemico-osmotic behaviour as the two "conventional" products substantially similar in configuration (i.e. needle-punched) and bentonite state (anhydrous), showed a very different behaviour. The lack of osmotic response of GCL-1 (i.e., $\Delta P_c \approx 0$) could be attributed to the characteristics, nature and origin of bentonite (activated sodium bentonite vs. natural sodium bentonite), as well as to the different technologies and operating sequences (e.g. fineness of bentonite, type and density of needle-punched fibers, etc.) during production. Further investigation is underway to investigate the factors underlying the different behaviour of GCL-1 compared to GCL-2. GCL-3 showed, under the same testing conditions, the highest values of ΔP_c and of ω compared to the other products. The factors underlying the better performance of GCL-3 mainly lie in the quality of the bentonite and in the production process of the prehydrated bentonite layer, as well as in the amendment with polymers. The results obtained for ω and D_s^o in this study are compared with those by [11] obtained on a similar DPH GCL product in Fig. 3b and Fig. 3c, respectively. The lower ω values and higher D_s^o observed in this study can be ascribed mainly to the higher specimen porosity ($n=0.74$) with respect to those reported ($n=0.53-0.64$) in the study by [11], besides possible differences in the GCL initial properties (e.g., polymer content).

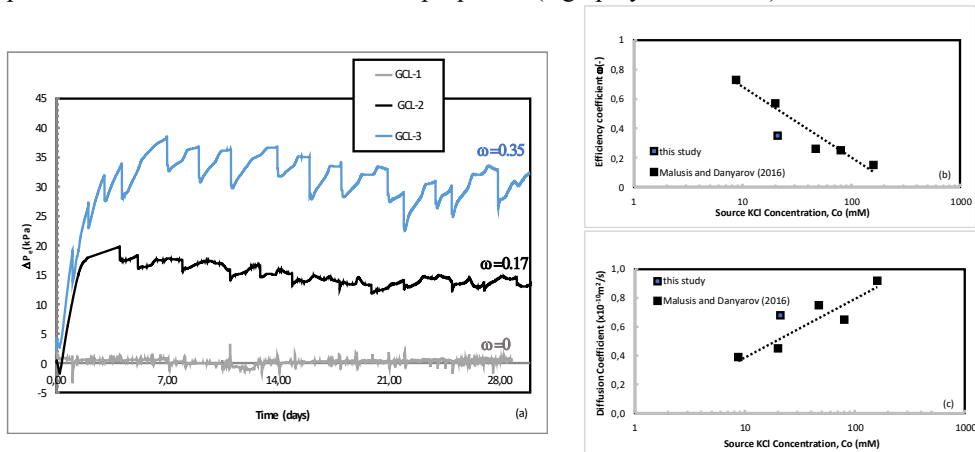


Fig. 3 Trend of the effective differential pressure (a) upon circulation of 20 mM KCl solution during the chemical-osmotic diffusion tests on the three GCLs used in this study (no strain mode). Comparison between the results of this study for GCL-3 and those by [11]: (b) chemico-osmotic coefficients; (c) chemico-osmotic diffusion coefficients

3.3 Multistage tests and theoretical interpretation

"Multistage" tests allow evaluating the influence of the electrolyte concentration on the coefficients ω and D_s^o . In addition, if carried out with the small strain mode, they also allow monitoring the trend of s as the concentration varies, which, in the absence of volume change, depends on the variation in the swelling pressure of the bentonite. Figure 4a shows the differential pressure values measured during the multistage test on GCL-2, during which the concentration of the KCl solution circulated at the top of the sample was increased in three stages (20 mM, 40 mM, 80 mM), while Fig.4b shows the corresponding values of s . The ability to monitor the total vertical stress allows to determine the swelling coefficient $\bar{\omega}$ [12], which expresses how efficient a change in boundary concentration is to produce a change in the chemical-osmotic swelling pressure, u_{sw} , which develops in response to the ion

partitioning mechanism within the charged porous medium. In the absence of volume variations, the coefficient $\bar{\omega}$ is determined as:

$$\bar{\omega} = -\frac{\delta u_{sw}}{\delta \pi} = -\frac{(\delta \sigma - \delta \bar{u})}{\delta \pi} \quad (7)$$

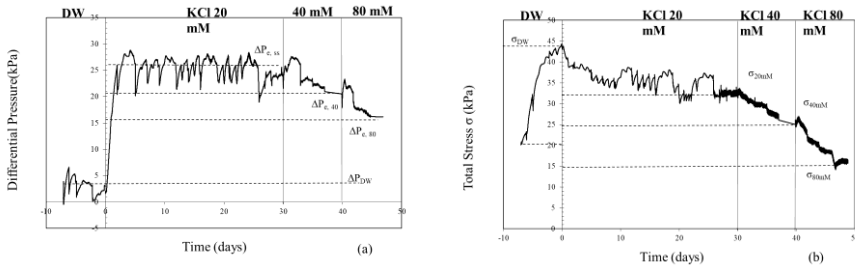


Fig. 4. Trend of differential pressure (a) and total stress (b) during a multistage test on GCL-2

where $\delta \sigma$ is the change in total stress, $\delta \bar{u}$ is the change in mean pore pressure, and $\delta \pi$ is the change in osmotic pressure at the boundary of the medium between two test stages. [12] proposed a theoretical model based on the physical approach for the description of chemical-osmotic phenomena in bentonites. According to this approach, the values of ω and $\bar{\omega}$ measured during an osmotic test (or "global" values) can be expressed as a function of the void ratio, e , of the ionic concentration at the boundaries of the porous medium, c_s , and of the coefficient of concentration of fixed charges, $c'_{sk,o}$, which expresses the concentration of the surface charges of the solid per unit volume of pores accessible for ion transport. This note presents the application of the above model, in the case of a 1:1 electrolyte (KCl) to the experimental data obtained in the multistage test, assimilating, in the first instance, the void ratio of bentonite to the GCL bulk void e_b . Fig.5 shows the excellent agreement between the theoretical prediction and the experimental values of ω and $\bar{\omega}$, obtained by assuming a single value of the fitting parameter, $c'_{sk,o} = 32$ mM [13]. The theoretical and experimental values of ω and $\bar{\omega}$ are plotted as a function of the dimensionless reference concentrations [14].

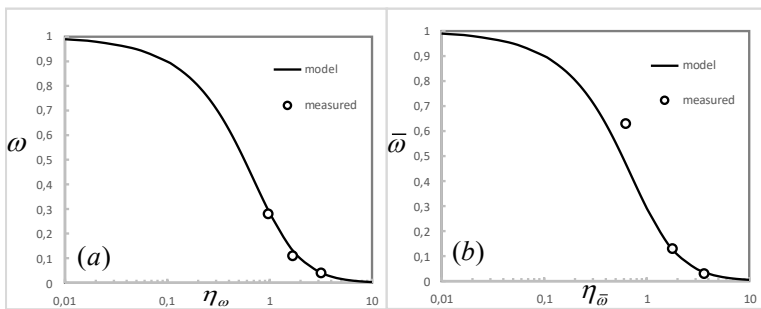


Fig. 5. Comparison between theoretical predictions and experimental data: (a) ω coefficient; (b) $\bar{\omega}$ coefficient

4 Conclusions

The semipermeable membrane behaviour of GCLs is viewed with great interest in pollutant containment applications as, if present, it can improve their performance. In this context, an

experimental apparatus has been developed that allows to highlight this behaviour through chemical-osmotic diffusion tests, which, unlike most of the equipment described in the literature for this purpose, offers the possibility of monitoring the total stress acting during the test owing to the introduction of a load cell. The measured osmotic efficiency and diffusion coefficient values are within the range of expected values for the selected materials. The data obtained indicate that the osmotic response of GCLs varies from product to product, depending on the characteristics and properties of bentonite; pre-hydrated and polymer-enhanced GCLs showed generally higher ω values than conventional products. The multistage test allowed to highlight the influence of the solute concentration on the efficiency coefficient and to determine the swelling coefficients. Finally, a theoretical model proposed in the literature by for the prediction of efficiency and swelling coefficients of bentonite has been applied for the interpretation of the results obtained on GCLs.

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