EVALUATION OF THE CHEMICO-OSMOTIC BEHAVIOUR OF A NATURAL BENTONITE

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Summary

The paper presents an introduction to the chemico-osmotic phenomenon, which characterizes semi-permeable soils . Subsequently the preliminary experimental results relative to the chemico-osmotic behaviour of a natural bentonite, used in a manufactured geosynthetic clay liner (GCL), are reported. The results were obtained at Politecnico di Torino, using an innovative apparatus, reproduced on the basis of the design of Ghent University.

1. Introduction

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

Clay membrane barriers, CMBs, are soil made barriers that act as selective membranes that represent an innovative answer to the relevant issue of pollution control and waste management that concerns industrialised countries.

The ability of clays to act as CMBs is affected, among others, by the types and amounts of clay minerals in the soil. In particular, membrane behaviour is significant in clay soils containing an appreciable amount of sodium montmorillonite, such as Na-bentonite (Shackelford et al., 2001).

CMBs are characterized by the ability to generate coupled liquid, solute and electrical current fluxes due to the application of hydraulic pressure, solute concentration and electrical potential gradients. The ability of these barriers to create suitable conditions to hinder the passage of pollutants more than the traditional barriers is a consequence of the coupled flux

phenomena.

Geosynthetic Clay Liners (GCLs) are the most popular manifactured CMBs used in landfill applications. GCLs generally contain a thin layer of sodium bentonite that ensures excellent containment performances in the short term regarding both advective and, if coupled with an attenuation layer, diffusive contaminant transport.

The extent to which clay soils act as semi-permeable membranes traditionally has been quantified in terms of a reflection or chemico-osmotic efficiency coefficient, σ (Staverman, 1952). In cases where σ represents stress, the chemico-osmotic efficiency coefficient has been designated by ω. The chemico-osmotic efficiency coefficient is one of the parameters of the phenomenological mass flux equations that may derived using the formalism of the Thermodynamics of Irreversible Processes for solutions containing a salt supposed completely dissociated, in the absence of electric current (Dominijanni and Manassero, 2005a). Based on such an approach, the clay membrane may be considered as a transition region or a "discontinuity" between two homogeneous compartments having the same temperature, and the differences in the thermodynamic potentials across the membrane that represent the driving forces responsible for the corresponding flows are assumed to be small. Using the phenomenological parameters proposed by Malusis and Shackelford (2002) and Dominijanni and Manassero (2005a), the volumetric flux, q, and the salt mass flux, J_s, are given by:

$$q = \frac{k_h}{\gamma_w L_h}\left(\Delta P - \omega \Delta \Pi\right) \tag{1a}$$

$$J_s = (1-\omega)q\overline{C}_s + \frac{nD_\omega^*}{L_h}\Delta C_s \tag{1b}$$

Where: q = volumetric flux or Darcy's velocity of the solution;

$k_h = k_h(n, C_s)$ = hydraulic conductivity depending on the porosity, n, and on the salt concentration, C_s;

L_h = thickness of the clay membrane;

γ_w = unit weight of the solvent;

$\Delta P = P' - P''$ = difference of hydraulic pressure, P, between the compartment (') and the compartment ('');

$\omega = \omega(n, C_s)$ = chemico-osmotic efficiency coefficient;

$\Delta \Pi = (\nu_1 + \nu_2)RT\Delta C_s$ = difference of osmotic pressure;

ν_1 = stoichiometric coefficient of the cation; ν_2 = stoichiometric coefficient of the anion;

R = universal gas constant; T = absolute temperature;

$\Delta C_s = C_s' - C_s''$ = difference of salt concentration, $C_s = C_1/\nu_1 = C_2/\nu_2$, where C_1 is the cation concentration and C_2 is the anion concentration;

$J_s = J_1/\nu_1 = J_2/\nu_2$ = salt mass flux, being J_1 the mass flux of the cation and J_2 the mass flux of the anion;

$\overline{C}_s = (C_s' + C_s'')/2$ = average salt concentration;

n = porosity of clay membrane;

$D_\omega^* = D_\omega^*(n, C_s)$ = osmotic effective salt diffusion coefficient.

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The chemico-osmotic efficiency of a clay membrane is a measure of its effectiveness in causing hydraulic flow under an osmotic gradient (see Eq.1a) and of its ability to prevent the passage of ions (see Eq.1b). The values of ω are frequently assumed to vary from zero to unity, although there are not thermodynamic restrictions to such a variation and, actually, also low negative values have been measured (Kemper and Quirk, 1972). When the clay soil does not exhibit membrane behavior, $\omega = 0$ and $D_\omega^* = D^* = \tau_m D_0$, where D^* is the effective salt diffusion coefficient, τ_m is the matrix tortuosity factor and D_0 is the free-solution salt diffusion coefficient. τ_m represents the tortuous nature of the actual diffusive pathways through the porous medium due to the geometry of the interconnected pores. The clay membrane is "ideal" or "perfect" if $\omega = 1$ and $D_\omega^* = 0$: in this case, the clay membrane completely restricts the movement of the ion species.

This paper reports the preliminary results, obtained at Politecnico di Torino, relative to the chemico-osmotic behaviour of a natural bentonite, used in a manufactured GCL.

2. Materials and methods

2.1 Natural sodium bentonite

The bentonite used in this study is a powdered sodium bentonite (NaB), provided by Laviosa. This bentonite is characterized by a cation exchange capacity (CEC, measured using methylene blue adsorption method) equal to 105 meq/100g.

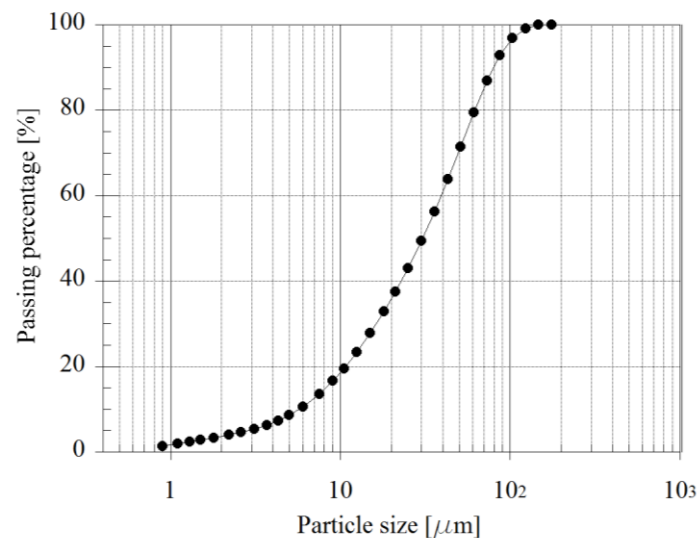In Figure 1 the sodium bentonite particle size distribution performed by Laviosa is reported.

Figure 1. Particle size distribution of the powdered NaB.

The mineralogical composition, evaluated through the x-ray diffraction analysis performed by Laviosa and shown in Figure 2, gives a bentonite mainly composed by smectite (> 98%) and calcite, quartz, mica and gypsum in trace.

2.2 Testing solutions

Sodium solutions were prepared with sodium chloride (ACS reagent, purity $\geq$ 99%) using de-ionized water (DW). Sodium solutions, prepared at different molarity values in the range between 5 mM and 100 mM, were used to investigate the effect of monovalent cations on the osmotic behavior of natural bentonite.
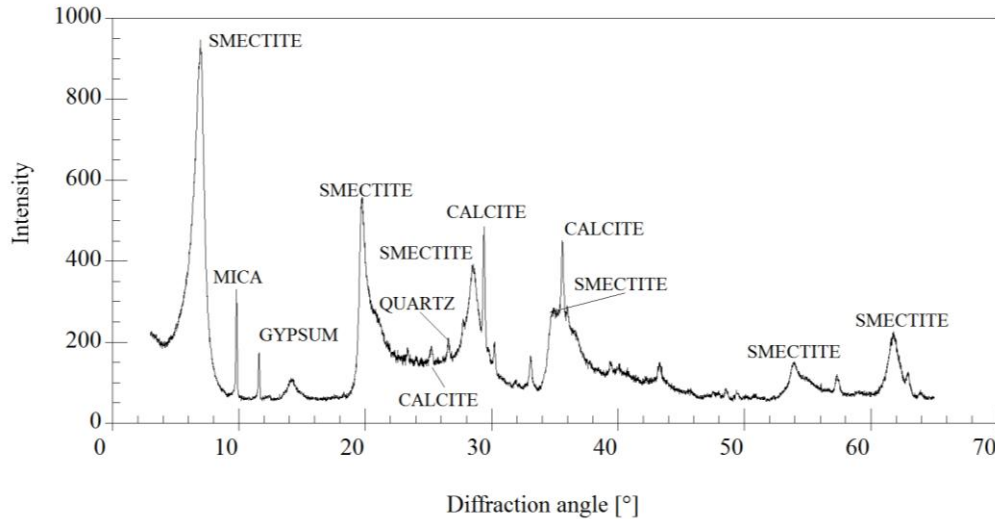
Figure 2. XRD mineralogical composition of powdered NaB contained in the studied GCL.

2.3 Testing Apparatus

The laboratory apparatus for measuring the chemico-osmotic efficiency of clay soils in the presence of electrolytes was used for testing NaB. The chemico-osmotic test was performed by maintaining a constant difference in the NaCl concentration across the bentonite specimen and hindering the flow of the solution through the specimen, while the chemico-osmotic efficiency is derived from the differential pressure measured across the specimen and due to the applied concentration gradient.

Figure 3 shows a scheme of the laboratory apparatus used to perform the osmotic test.

The main components of the apparatus are: (1) the osmotic cell; (2) the flow-pump system, (3) a pressure trasducer aimed at measuring the differential pressure developed across the specimen during the test, (4) the data acquisition system.
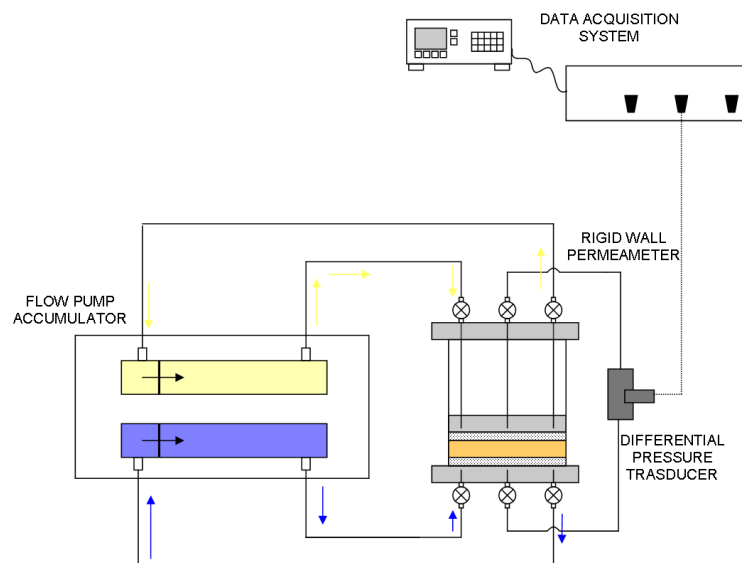

Figure 3. Scheme of the osmotic test apparatus used during the laboratory activity.

In particular, the osmotic cell consists of a modified rigid wall permeameter, in which the top piston and the base pedestal are equipped with three ports each: two of them enable

circulation of separate electrolyte solutions through the top and the base porous stones to establish a constant concentration difference across the specimen; the third one is installed in both the top piston and the base pedestal to allow for the measurement of the differential pressure across the specimen.

The flow-pump system, which consists of a dual-carriage syringe pump and two stainless steel accumulators (*Model 33 - Twin syringe pump*, produced by Harvard), allows to have no solution flux through the specimen simply infusing and withdrawing the same volume of solution in each porous stone at the boundaries of the specimen. To obtain this result the syringes have to move at the same rate.

2.3 Testing Method

Since no standard methods exist to rule the test, it had been performed following the method described by Malusius et al. (2001).

In order to measure the chemico-osmotic efficiency coefficient, ω, in the top porous stone the solution, containing a certain concentration of electrolyte (NaCl), is circulated, while in the base porous stone the de-ionized water solution is circulated. The concentration difference across the specimen is maintained constant continuously infusing the two solutions at the boundaries of the specimen.

Since the same volume of solution is infused and withdrawn from the porous stones, the solution flux through the soil cannot occur. In these conditions ω is calculated using equation 2:

$$\omega = \frac{\Delta P}{\Delta \Pi}\bigg|_{q=0} \tag{2}$$

Applying a concentration gradient across the bentonite specimen, a chemico-osmotic flux of solution should occur through the membrane to balance concentrations. If this flux is hindered, a hydraulic pressure difference across the specimen is induced (ΔP). In equation 2 ΔP is measured and compared with the ideal pressure ($\Delta \Pi$) that would occur if an ideal (i.e. $\omega = 1$) membrane was used.

3. Results

The osmotic test was performed using a powdered sodium bentonite specimen prepared through the following two stages: (1) a squeezing stage, aimed at removing excess soluble salts, naturally contained into the NaB because of its formation process in the marine environment, in which the pore water is in thermodynamic equilibrium with the seawater; (2) a compaction phase, in which the squeezed sample (oven dried at 100°C) is rehydrated with DW at a water content lower than the liquid limit value and then statically compacted in a compaction mold, allowing excess water release.

After that, the specimen was transferred to the osmotic cell for the osmotic stage.

Prior to subjecting the specimen to a solute concentration gradient, DW was circulated through the top piston and base pedestal to establish a steady baseline differential pressure. Afterwards, the source concentrations of NaCl were injected in the top porous stone, while DW has continued to circulate in the lower porous stone. The multiple-stage osmotic test (i.e. source NaCl concentration: 1st step = 5 mM, 2nd step = 10 mM, 3rd step = 20 mM) was performed at a constant flow rate of 0.05 mL/min.

The results in terms of chemico-osmotic efficiency coefficient, derived from the chemico-osmotic pressure differences, are reported in Figure 4 referred to the average concentration measured across the specimen during the test.
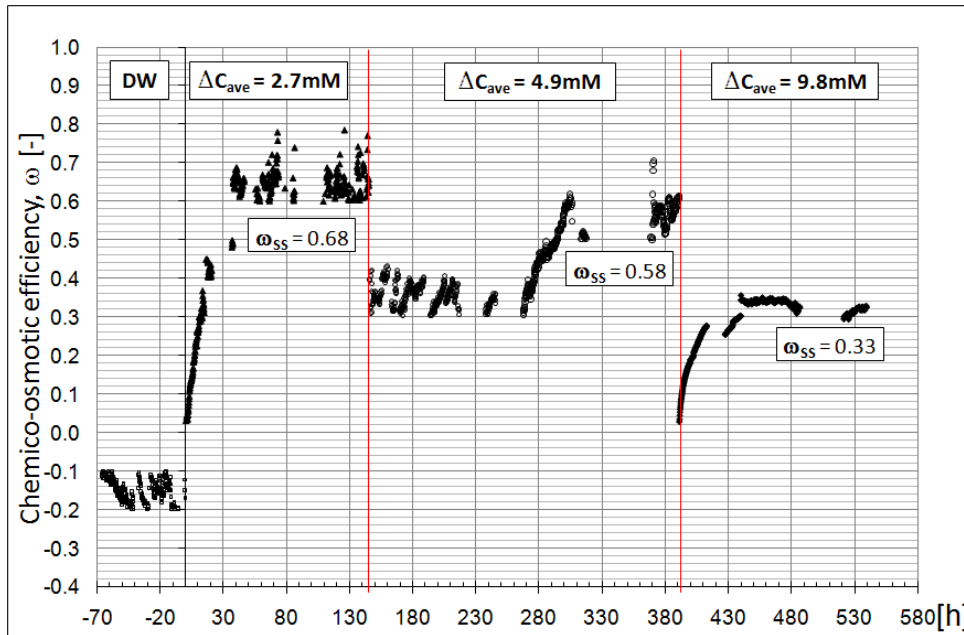
Figure 4. Membrane efficiency versus elapsed time referred to the average concentration across the specimen.

The chemico-osmotic efficiency value measured at the stady state is reported in Figure 4 for each concentration step. The steady state efficiency values tend to decrease with increasing salt concentration as a consequence of the progressive collapse of the diffusive double layer (DDL) surrounding bentonite lamellae. The reduction of DDL induces (1) an increase in the volume fraction of voids available for the passage of the solute and, correspondingly, (2a) an increase in solute diffusion across the specimen and (2b) a decrease in the ratio between the measured chemico-osmotic pressure difference (ΔP) and the ideal pressure ($\Delta \Pi$).

In Figure 5 the obtained results (red crossed symbols) are compared with the chemico-osmotic values founded for bentonite specimens by Kemper and Rollins (1966), closed symbols, and for a GCL by Malusis and Shackelford (2002), open symbols.
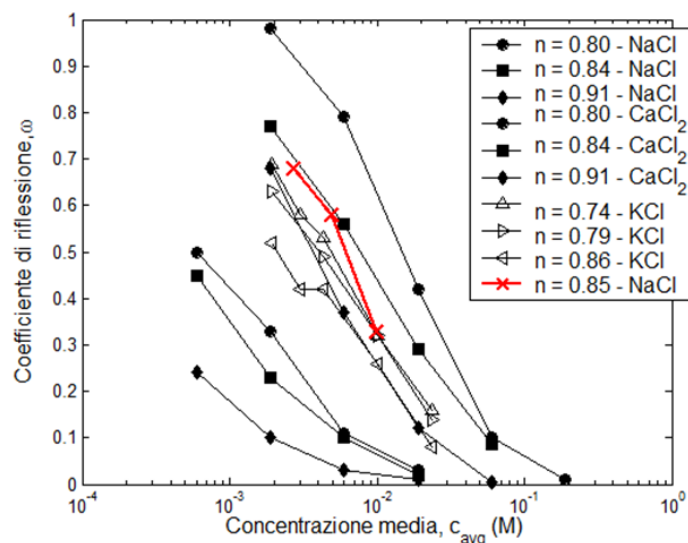

Figure 5. Chemico-osmotic efficiency coefficients as a function of the average salt concentration across the specimen and the specimen porosity (n) for (closed symbols) bentonite specimens (Kemper and Rollins, 1966), (open symbols) a GCL (Malusisand Shackelford, 2002) and (red crossed symbols) the results obtained in this study.

The test is still ongoing, a last two steps with 50 mM and 100 mM source NaCl concentration are planned.

4. Conclusions

The membrane behavior of a natural sodium bentonite, used in a GCL, was evaluated for different values of NaCl concentration.

The results of membrane testing a specimen of powdered NaB, preliminary submitted to a squeezing stage, aimed at removing excess soluble salts, and a compaction phase, indicate a significant value of the chemico-osmotic efficiency coefficient. The trend obtained as a function of the average concentration of salt across the sample is perfectly comparable with the results available in Literature.

The results suggest that the studied sodium bentonite and, consequently, the corresponding GCL are suitable for waste containment applications on the basis of both (1) the ability to achieve very low value of hydraulic conductivity and (2) the ability to hinder the passage of electrolyte pollutants and to generate a volumetric chemico-osmotic water flux.

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