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# Polymer-treated bentonite clay for chemical-resistant geosynthetic clay liners

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**ABSTRACT:** The purpose of hydraulic barriers, such as geosynthetic clay liners (GCLs), is to isolate waste liquids from the environment. Bentonite clay is widely used in GCLs because of its elevated sealing capacity in the presence of water and its ability to restrict the migration of solutes (chemico-osmotic efficiency or semi-permeable membrane behaviour). However, exposure to high concentrations of inorganic solutions can change the clay fabric increasing its hydraulic conductivity and degrading its membrane behaviour, with a consequent harm to the environment. The aim of this research was to study the hydraulic and chemico-osmotic performance of amended clays. For this purpose, an engineered clay (HYPER clay) was developed through treatment of a natural bentonite with an anionic polymer and the results were compared with two amended clay materials [multi-swellaable bentonite (MSB) and a dense prehydrated GCL (DPH GCL)]. To demonstrate the potential benefits of polymer treatment, material characterisation through x-ray diffraction analysis, density of solid particles, Atterberg limits, and swelling tests was performed on treated and untreated samples. Subsequently, hydraulic conductivity and chemico-osmotic tests were performed with CaCl<sub>2</sub> solutions on treated and untreated clays, to evaluate the modified clays resistance to chemical attack. The results of this research showed that the present amendment technology has a great potential for future GCL applications. x-ray diffraction analysis demonstrated the intercalation of the polymer in the interlayer region of the clay inducing a dispersed clay structure. The swell index and the liquid limit of the clay increased with increasing polymer dosage suggesting a potential benefit of the polymer on preserving the hydraulic performance of the clay. Unlike the untreated clay, HYPER clay treatment maintained low hydraulic conductivity of the clay to CaCl<sub>2</sub> even in the long term and protected the clay against the destructive role of diffusion, maintaining the initial osmotic efficiency in the long term. Test results were also compared with other amended clays MSB and DPH GCL. These two amended clay materials displayed a chemico-osmotic behaviour at the steady state similar to that observed on untreated clay. On the other hand, the preservation of the chemico-osmotic efficiency of the HYPER clay with time suggests that the carboxymethyl cellulose was not flushed out during the long period of permeation with deionised water.

**KEYWORDS:** Geosynthetics, Landfill, Liners, Geosynthetic clay liner, Bentonite, Polymer

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## 1. INTRODUCTION

Modified bentonites have been recently introduced in barrier applications to improve the chemical resistance of the bentonite to aggressive permeants (Kondo 1996; Onikata *et al.* 1996; Flynn and Carter 1998; Onikata *et al.* 1999; Ashmawy *et al.* 2002; Simon and Müller 2005; Di Emidio 2010; Razakamanantsoa *et al.* 2012). Some examples are: clays treated with cationic polymers, organoclays, multiswellable bentonites (MSB), dense prehydrated (DPH) geosynthetic clay liners (GCL), and HYPER clay.

Among these treated soils, the clays treated with cationic polymers showed higher or similar permeability compared with that of untreated clays. For instance, the permeability to water of this type of treated clays is between  $3.0 \times 10^{-9}$  and  $1.0 \times 10^{-7}$  m/s compared with that of untreated clays ranging between  $3.0 \times 10^{-9}$  and  $1.0 \times 10^{-8}$  m/s (Ashmawy *et al.* 2002). Cationic polymers dissolved in solution may easily be adsorbed onto clay surfaces (Stumm 1992). Such adsorption can be irreversible and entropy-driven. Cationic polymers are able to protect the clay from cation exchange because a cationic polymer chain contains thousands of cations that would need to be exchanged simultaneously (Theng 1982; Ashmawy *et al.* 2002). However, as shown above, the treatment with cationic polymers provides no decrease of the hydraulic conductivity of bentonites likely because the cationic polymer tends to aggregate clay particles, with a consequent compression of the diffuse double-layer thickness, which is not beneficial for the hydraulic performance of the clayey barrier.

Organoclays are bentonite clays treated with organic molecules. This treatment improves the ion retention capacity. Extensive research has been conducted to characterise the sorption of organic compounds onto clay surfaces (Lo *et al.* 1997; Lo and Yang 2001; Lorenzetti *et al.* 2005; Bartelt-Hunt *et al.* 2005; Bate and Burns 2010; Zhao and Burns 2011). Organoclays are bentonites, typically amended by exchanging quaternary ammonium groups for the naturally occurring cations. This process renders the modified clay hydrophobic and highly organophilic. Organoclays have sorption capacities for organic compounds that are four to five times higher than untreated clays. However, the hydraulic conductivity of these clays may increase significantly upon modification with this type of organics. Organoclays show, in fact, similar or higher permeabilities compared with untreated clays. Lorenzetti *et al.* (2005) showed permeabilities for organoclays ranging from  $3.4 \times 10^{-11}$  to  $2.3 \times 10^{-8}$  m/s in comparison with untreated clays with permeabilities ranging between  $4.3 \times 10^{-11}$  and  $6.8 \times 10^{-11}$  m/s.

Multi-swellable bentonite (MSB), developed by Kondo (1996), is modified with propylene carbonate (PC), which is an organic compound able to activate the osmotic swelling capacity of the clay. PC is placed in the interlayer of the smectite and attracts numerous water molecules. This results in an improved swelling ability even when the permeant contains polyvalent cations or a high concentration of monovalent cations. Most values of the hydraulic conductivity of MSB are one to two orders of magnitude

lower than those of the untreated clay for the same concentration levels (Katsumi *et al.* 2008; Mazzieri *et al.* 2010; Di Emidio 2010). On the other hand, after prolonged permeation, this material showed free swell, hydraulic conductivity and chemico-osmotic efficiency similar to those of the untreated bentonite. Prolonged permeation with water might have contributed to release of the organic additive from the clay (Mazzieri *et al.* 2010).

Dense prehydrated GCL (DPH GCL) is a manufactured patented geosynthetic clay liner densified by calendaring after the clay has been prehydrated with a polymeric solution containing sodium carboxymethyl cellulose (Na-CMC), sodium polyacrylate and methanol (Flynn and Carter 1998). DPH GCL showed excellent performance in various aggressive solutions (Schroeder *et al.* 2001; Kolstad *et al.* 2004; Di Emidio *et al.* 2008; Katsumi 2010; Di Emidio 2010; Mazzieri *et al.* 2010; Mazzieri and Di Emidio 2011). However, the polymer adsorption onto the clay may not last permanently. Mazzieri and Pasqualini (2008) studied the permeability of the DPH GCL subjected to dry/wet cycles and using a 12.5 mmol/L  $\text{CaCl}_2$  solution as hydrating liquid. They observed that the additives were partially removed during the tests. In addition, long-term testing suggested that this type of amendment was not completely durable after prolonged permeation with water, the chemico-osmotic efficiency and the permeability after the chemico-osmotic test were, in fact, comparable to those of an untreated clay (Di Emidio 2010; Di Emidio 2012).

Adsorption of anionic polymers onto the clay surface is promoted by the presence of polyvalent cations, which act as bridges between the anionic groups on the polymer and the negatively charged sites on the clay (Mortensen 1960; Theng 1982). Qiu and Yu (2007) modified a bentonite with CMC; x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses on a montmorillonite-treated with CMC, showed that these polymer chains had intercalated into the clay sheets, and the strong chemical interaction between the ether bonds from the polymer and Si-O bonds from the clay was the driving force for intercalation. They demonstrated that treating clay with CMC increases its water absorption and water retention ability.

Given their high water retention capacity, Di Emidio (2010) evaluated the pollutant-containment ability of clays treated with such anionic polymer, Na-CMC. This clay, named HYPER clay, is mixed with a polymeric solution containing Na-CMC then dehydrated in an oven at 105°C. Dehydration at temperatures higher than 60°C have been proven to enhance the irreversible adsorption of the polymer on the clay surface (Ruehrwein and Ward (1952). Stutzmann and Siffert 1977) stated that the adsorption of anionic polymers onto clays occurs through ionic exchange. On the other hand, Michaels and Morelos (1955) suggested that adsorption is mainly conditioned by hydrogen bonding. A third possible adsorption mechanism would originate from the interaction between polyvalent cations acting as crosslinking agents between the clay negative surface and the anionic polymer (Stutzmann and

Siffert 1977). In the presence of salts and cations naturally present at the clay surface, the negative charges of the clay and the anionic polymer are shielded from one another allowing the polymer to coil and collapse on the clay surface (Breen 1999).

The main purpose of this research was to study a clay treated with an anionic polymer with enhanced hydraulic performance (HYPER clay). This study was set up to investigate the influence and mechanisms through which the amendment used in HYPER clay can improve the hydraulic and chemico-osmotic efficiency of bentonites for barrier applications. To evaluate the improved performance of polymer treatment, material characterisation, swelling, hydraulic conductivity and chemico-osmotic tests were executed on treated and untreated clays.

## 2. MATERIALS

The reference untreated clay used in this investigation was a natural sodium bentonite provided by Hojun Corporation, Japan. This material was treated with an anionic polymer, CMC, to obtain HYPER clay. CMC is a cellulose derivative with carboxymethyl groups and it is used in food science as a viscosity modifier or thickener, and to stabilise emulsions in various products including ice cream. It is also a constituent of many non-food products, such as toothpaste, paints, detergents and various paper products. It is used primarily because it has high viscosity, is non-toxic, and is non-allergenic.

The clay was treated with various polymer dosages (from 2 up to 16% by dry weight). The clay was poured in a polymeric solution containing CMC while stirring using a mechanical stirrer. The clay and the polymeric solution were mixed for about 30 min. These slurries of clay, polymers and water were then oven dried at 105°C. After drying, the treated clays were ground, first using a mortar and pestle and later using a Retsch Mortar Grinder RM 200. The physical and chemical properties of these clays are summarised in Table 1.

The solutions used are deionised water and a series of KCl and CaCl<sub>2</sub> solutions with concentration varying from 0.001 to 0.5 mol/L. These solutions were chosen to study the impact of concentration and valence on the swelling performance of the polymer-treated bentonite. A

0.005 mol/L CaCl<sub>2</sub> solution was selected to study the hydraulic and chemico-osmotic performance of the polymer-treated clay to allow comparison with published data concerning a similar test on untreated bentonite (Shackelford and Lee 2003). They selected that solution to determine whether a GCL would exhibit membrane behaviour when exposed to the divalent Ca<sup>2+</sup> cation, as opposed to the previous studies that used the monovalent K<sup>+</sup> cation (Malusis *et al.* 2001; Malusis and Shackelford 2002). The chemical properties of the solutions used here are shown in Table 2.

## 3. METHODS

### 3.1. Material characterisation

The specific gravity of soil solids ( $G_s$ ) and Atterberg limits were determined following ASTM standards (ASTM D854 and ASTM D4318). XRD analyses were performed on oriented samples. The cation exchange capacity (CEC) of the bentonites analysed was measured following the ammonium acetate method (Sumner and Miller 1996). Swell index tests were performed following the ASTM D5890 using deionised water, KCl and CaCl<sub>2</sub> solutions with concentrations varying from 0.001 to 0.5 mol/L.

### 3.2. Hydraulic conductivity

Falling-head hydraulic conductivity tests were conducted in rigid wall permeameters in a 20°C-conditioned room following suitable ASTM standards (ASTM D6766; ASTM D5856). The falling-head method is more suitable for soils with very low hydraulic conductivities, such as clays, where the flow rate is small and needs to be precisely measured. The specimen was first permeated with deionised water to measure the reference hydraulic conductivity. After prehydration, the specimen was tested with a chemico-osmotic apparatus (as described in the next paragraph). At the end of the chemico-osmotic test, the specimen was permeated with a 5 mmol/L CaCl<sub>2</sub> solution. The hydraulic conductivity tests were performed on samples, 7.1 cm in diameter, with porosity  $n = 0.718$ . Thin clay specimens were prepared, with the purpose of

Table 1. Physical and chemical properties of the materials

Property	Clay	HYPER clay (2% CMC)	HYPER clay (4% CMC)	HYPER clay (8% CMC)	HYPER clay (16% CMC)
Specific gravity (-)	2.66	2.53	2.47	2.25	2.40
Dry clay content (kg/m <sup>2</sup> )	4.5	4.5			
Swell index (ml/2 g)	26	37	55		
Liquid limit (%)	654.63	650.45	659.18	741.83	743.25
Plastic limit (%)	44.56	56.22	58.62	61.03	70.55
CEC (meq/100 g)	44.51	47.29	44.26	46.69	42.92
Exchangeable cations:					
Na <sup>+</sup> (meq/100 g)	26.30	34.15	35.46	44.47	53.40
Ca <sup>2+</sup> (meq/100 g)	5.58	11.43	12.23	12.71	12.03
Mg <sup>2+</sup> (meq/100 g)	7.89	6.16	5.45	5.47	5.39
K <sup>+</sup> (meq/100 g)	0.17	0.25	0.17	0.18	0.21

**Table 2. Chemical properties of the electrolyte solutions**

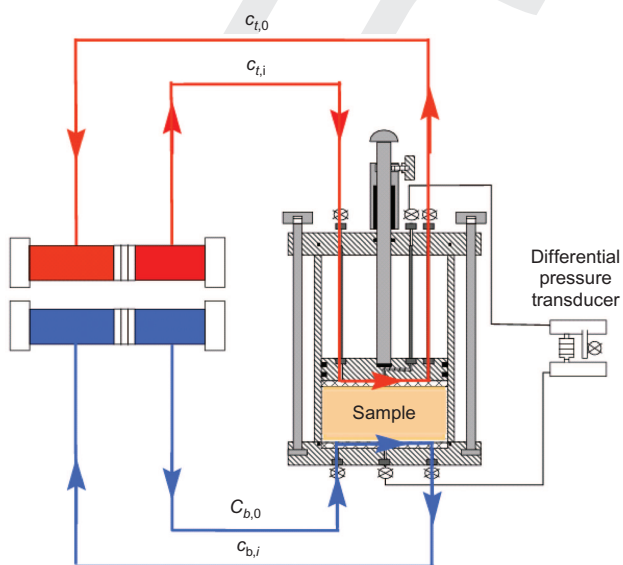
Solution	Concentration (mol/L)	EC (mS/cm)	Salinity (-)	pH (-)	Eh (mV)
Deionised water		0.0039	0.0	7.57	293
	KCl	0.0001	0.0142	0.0	258
		0.001	0.143	0.0	243
		0.01	1.392	0.5	304
		0.1	12.760	7.3	324
CaCl <sub>2</sub>		112.9			
		0.0001	0.0253	0.0	297
		0.001	0.251	0.0	330
		0.005	1.211	0.4	262
		0.01	2.220	0.9	238
		0.1	18.540	11	260
		1	144.5		

simulating the bentonite core of a standard GCL using 0.45 g/cm<sup>2</sup> of dry soil.

### 3.3. Chemico-osmotic test

To measure chemico-osmotic efficiency and diffusion coefficient, a special apparatus was employed following the testing methods of previous studies (Olsen 1969; Malusis *et al.* 2001; Mazzieri *et al.* 2003). The complete setup consists essentially of two main parts: the pumping system and the rigid-wall testing cell (used also to measure the hydraulic conductivity) provided with pressure transducers (Figure 1).

The pumping system consists of a dual syringe pump (model 33; Harvard Apparatus) equipped with two stainless steel cylinders aimed to circulate separate electrolyte solutions of different concentrations at the top ( $C_{t,i}$ ) and at the base ( $C_{b,i}$ ) of the soil specimen in order to induce and maintain a chemical gradient across the soil. If membrane behaviour occurs, a differential pressure ( $\Delta P$ ) between the top and the base of the sample should be measured. Circulation outflow from these boundaries is simultaneously collected on the opposite end of the cylinder



**Figure 1. Chemico-osmotic test experimental setup**

actuator at the same rate in order to maintain a constant volume inside the cell and prevent liquid flux through the specimen (perfect flushing conditions).

Measured solute concentrations in the outlet solutions are used to evaluate the solute mass flux entering the soil from the higher concentration boundary ( $C_{t,i}-C_{t,0}$  in Figure 1) and exiting the soil into the lower concentration boundary ( $C_{b,0}-C_{b,i}$ ), due to diffusion. The measured concentrations are used to compute the solute transport parameters (such as diffusion,  $D^*$  and retardation factor,  $R_d$ ).

When the chemico-osmotic efficiency is measured, an error can occur neglecting the influence of solute diffusion across the sample during the test. This error can be reduced choosing an optimal circulation rate ( $4.2 \times 10^{-10}$  m<sup>3</sup>/s, Malusis *et al.* 2001) sufficiently rapid to minimise changes in the boundary solute concentrations due to diffusion, but sufficiently slow to allow a measurable accumulation of solute mass into the base to determine the transport parameters.

The chemico osmotic efficiency coefficient,  $\omega$ , is defined as follows (Staverman 1952; Katchalsky and Curran 1965)

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

where  $\Delta P$  is the measured pressure difference induced across the specimen as a result of prohibiting chemico-osmotic flux of solution ( $q = 0$ ), and  $\Delta \pi$  is the theoretical chemico-osmotic pressure difference across an ideal membrane ( $\omega = 1$ ) subjected to an applied difference in solute concentration (Olsen *et al.* 1990).

The value for  $\Delta \pi$  in Equation 1 is calculated based on the salt concentrations at the specimen boundaries in accordance with the van 't Hoff expression as follows

$$\Delta \pi = RT \sum_{j=1}^N (C_{b,j} - C_{t,j}) \quad (2)$$

where  $R$  is the universal gas constant (8.314 J/mol per K),  $T$  is the absolute temperature (K). Under perfect flushing conditions,  $C_{b,j} (= 0)$  is the initial concentration of solute species  $j$  at the bottom (b) of the specimen [mol/L],  $C_{t,j}$  is

the source concentration of solute species  $j$  at the top ( $t$ ) of the specimen (mol/L), and  $N$  is the total number of solute species. For simple salt solutions, such as  $\text{CaCl}_2$ . Equation 2 may be written more conveniently as

$$\Delta\pi = \nu RT\Delta C \quad (3)$$

where  $\nu$  is the number of ions per molecule of salt, and  $\Delta C = C_{b,t} - C_{t,i}$  is the salt concentration gradient. The induced pressure difference,  $\Delta P$ , in Equation 1 is measured using a differential pressure transducer that is connected to the top and the base of the specimen, as shown in Figure 1.

The top plate of the permeameter can be fixed to a specific height to avoid swelling of the sample during the test. Due to the considerable soluble salt content of bentonite clays, the specimen is first permeated with deionised water to remove soluble salts, improve the saturation and measure the reference hydraulic conductivity.

After permeation, the testing cell is connected to the cylinders' actuators and the pumping system. Then purified water is first circulated for about 7 days at both ends of the specimen to establish a steady baseline differential pressure and to remove residual salts from the porous plates.

The chemico-osmotic/diffusion phase of the experiment is then initiated by circulating the first source solution ( $\Delta C_1 = 1 \text{ mmol/L CaCl}_2$ ) in the top piston while continuing circulation of deionised water in the base, to induce a chemical gradient across the soil.

Multiple-stage chemico-osmotic tests were conducted in this study. These tests consisted of two individual stages for every sample in which differential pressures corresponding to two different source  $\text{CaCl}_2$  solutions (i.e.  $\Delta C_1 = 1 \text{ mmol/L CaCl}_2$  and  $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$ ) introduced sequentially through the top piston were measured across the same specimen. Each stage was conducted until steady-state conditions were achieved (e.g. steady-state differential pressure, electrical conductivity and solute concentrations at both ends of the specimen).

Permeation with  $5 \text{ mmol/l CaCl}_2$  was carried out at the end of the chemico-osmotic stage of test in order to assess the impact of the electrolyte solution on the hydraulic conductivity of the clay after prehydration.

### 3.4. Transport parameters determination: time-lag method

The differences in solute ( $\text{Cl}^-$  and  $\text{Ca}^{2+}$ ) concentrations between the top and bottom boundaries of the specimen cause solute diffusion from the higher concentration boundary (top) to the lower concentration boundary (bottom), such that a steady-state solute flux through the bottom of the specimen is eventually established and maintained. This scenario is commonly referred to as the steady-state approach for diffusion testing (Shackelford 1991).

In the steady-state approach, the measured concentrations for a given solute in the circulation outflow (i.e. from the base) are typically converted to cumulative mass

per unit area,  $Q_t$ , using the following expression (Malusis *et al.* 2001)

$$Q_t = \frac{1}{A} \sum_{j=1}^N \Delta m_j = \frac{1}{A} \sum_{j=1}^N C_{b,0,j} \Delta V_j \quad (4)$$

where  $A$  is the cross-sectional area of the specimen,  $\Delta m_j$  is the incremental mass of the solute species collected (output from the base of the sample) over a time increment ( $\Delta t$ ),  $C_{b,0,j}$  is the concentration of the solute species in the incremental volume,  $\Delta V_j$ , of the circulation outflow from the base of the sample corresponding to the same  $\Delta t$ , and  $N$  is the number of incremental samples corresponding to the total elapsed time,  $t$ . The results are plotted in terms of  $Q_t$  against cumulative time. The curved portion of the plot represents transient diffusion, whereas the linear portion of the data, corresponding to a constant slope,  $\Delta Q_t/\Delta t$ , represents steady-state diffusion.

Two characteristic times can be defined on a plot of  $Q_t$  against time: the time to steady state,  $t_{ss}$ , and the time lag,  $t_L$ . The time lag is the time corresponding to the intersection of the extension of the steady-state slope of  $Q_t$  with the time axis (Shackelford 1991). The value of  $t_L$  can be used to determine the retardation factor,  $R_d$ , which reflects the adsorption behaviour of the solute during transient diffusion, as shown further on in this paragraph (Crank 1975; Shackelford 1991).

The time to steady state,  $t_{ss}$ , is the time corresponding to the intersection of the initial curved portion of the plot, representing the transient diffusion stage, and the linear portion of the example plot, representing steady-state diffusion.

The effective diffusion coefficient,  $D^*$ , of the given solute species is determined from the slope of the steady-state portion of the response,  $\Delta Q_t/\Delta t$ , in accordance with the following expression

$$D^* = - \left( \frac{\Delta Q_t}{\Delta t} \right) \left( \frac{L}{n\Delta C} \right) \quad (5)$$

where  $n$  is the specimen porosity and  $L$  is the specimen thickness. The value of  $D^*$  determined according to Equation 5 is a coupled effective diffusion coefficient that includes a coupling term associated with the prevention of solution flow in accordance with the principles of irreversible thermodynamics Malusis and Shackelford (2002). In the limit, as the membrane efficiency of a clay approaches zero, the coupled effective diffusion coefficient given by Equation 5 converges to the true effective diffusion coefficient represented by Fick's first law for diffusion in soil as defined by Shackelford and Daniel (1991).

The analytical solution for  $Q_t$  at steady state based on one-dimensional diffusion with a constant source concentration,  $C_{t,i}$ , in the top piston and a perfectly flushing boundary condition in the base pedestal (i.e.  $C_{b,i} = 0$ ) can be written as follows (Crank 1975; Shackelford 1991)

$$Q_t = \frac{nD^*C_{t,i}}{L}t - \frac{nR_dLC_{t,i}}{6} \quad (6)$$

where  $n$  is the specimen porosity,  $D^*$  is the effective diffusion coefficient,  $L$  is the specimen thickness and  $R_d$  is

the retardation factor. The retardation factor of the solute,  $R_d$ , is evaluated by determining the time tag,  $t_L$ . The intercept,  $t_L$ , is related to  $R_d$  by setting  $Q_t = 0$  in Equation 6 and rearranging the resulting expression for  $R_d$  as follows (Shackelford 1991)

$$R_d = \frac{6D^*t_L}{L^2} \quad (7)$$

For the second stage ( $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$ ), the transport equation is solved for the case of non-zero initial concentrations at the top and at the bottom of the specimen ( $C_{t,1}$  and  $C_{b,1}$ , final concentrations of the first stage). Assuming a linear initial concentration and an instantaneous increase of the boundary concentrations, the analytical solution for  $R_d$  can be written as follows

$$R_{d2} = \frac{6D^*t_L}{L^2} \cdot \left( \frac{C_{t,2} - C_{b,2}}{(C_{t,2} - C_{b,2}) - (C_{t,1} - C_{b,1})} \right) \quad (8)$$

where  $C_{t,1}$  and  $C_{b,1}$  are the steady-state concentrations at the top and base as a result of the first diffusion stage; and  $C_{t,2}$  and  $C_{b,2}$  are the steady-state concentrations at the top and base as a result of the second diffusion stage.

## 4. RESULTS

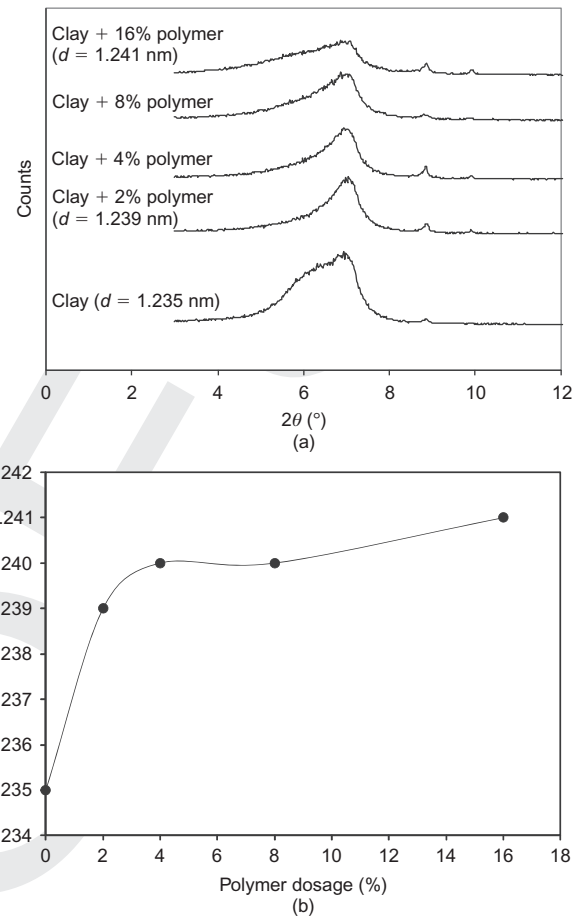
### 4.1. Material characterisation

Table 1 shows an overview of the characterisation of the treated and untreated clays. The specific gravity decreased with increasing polymer dosage. These results may depend not only on the lower specific gravity of the polymer alone (about 1.59), but also on a dispersed structure of the treated clay, supporting the hypothesis that the presence of the polymer maintains the interlayer between clay platelets open.

Figure 2 shows the results of XRD analysis in which the basal spacing,  $d$ , increased with increasing polymer dosage (Figure 2b) indicating that the polymer has intercalated in the interlayer region between platelets and that the interplatelets spacing increases with increasing polymer dosage. As indicated in Figure 2b, the basal spacing showed a sudden increase up to a polymer dosage of 4%, followed by a gradual increase.

Figures 3a and 3b show that the liquid limit and plasticity index of the clay increased with increasing polymer dosage for different solutions. Furthermore, the plastic limit increased with polymer dosage, the values ranged between 44.56% (of the natural clay) to 70.55% (for the clay treated with 16% Na-CMC). This demonstrates that the polymer addition improves the water adsorption capacity of the untreated clay, which in turn suggests a possible improved barrier performance, in particular in seawater.

It should be stressed out that Figures 3a and 3b show that the beneficial effect of the Na-CMC polymer treatment was more pronounced for high concentrated solutions than for diluted solutions. The effect of the polymer for diluted solutions was negligible probably because for diluted solutions the diffuse double layer (DDL) thickness



**Figure 2. (a) Shift of the basal spacing,  $d$ , with increasing polymer dosage. (b) Increase of the basal spacing with increasing polymer dosage**

is already sufficiently thick. On the other hand, for concentrated solutions the DDL thickness was compressed with consequent aggregation between platelets. The clay platelets are distant in deionised water or diluted solutions and the interlayer region is sufficiently open in either case, with or without the intercalated polymer. On the other hand, in concentrated solutions the untreated clay particles aggregate; whereas the polymer-treated clays maintain the interlayer open.

The swell index ( $SI$ ) to deionised water of the untreated clay was  $SI = 26 \text{ ml/2g}$ . After treating the clay with CMC, an increased swell index was observed. In fact, the swell index was  $SI = 37 \text{ ml/2g}$  for the HYPER clay (treated with 2% CMC) and  $SI = 55 \text{ ml/2g}$  for the HYPER clay treated with 4% CMC. This result shows that the addition of the polymer improved the swelling capacity of the clay. Figure 4 shows that the addition of the polymer improved the swelling ability of the clay also in the presence of electrolyte solutions. The increase of the swell index for the treated clay agreed with the increase in water adsorption.

Based on the well-known inverse relationship between liquid limit, swell index and the hydraulic performance of clays (Jo *et al.* 2001; Lee *et al.* 2005), it is relevant to also evaluate the hydraulic conductivity of polymer-treated clays in view of their potential benefits in field applications.

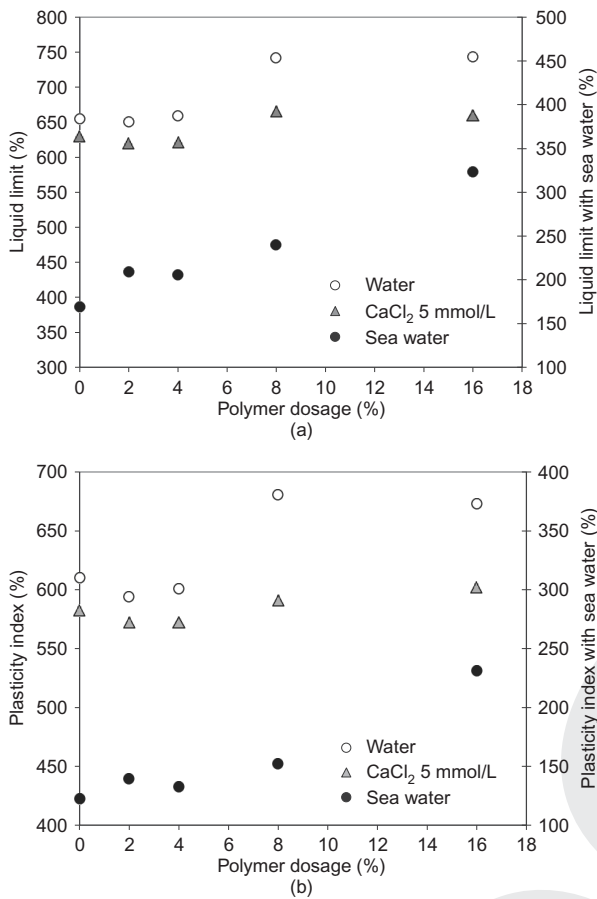


Figure 3. (a) Liquid limit increase with increasing CMC polymer dosage. (b) Plasticity index increase with increasing polymer dosage

4.2. Hydraulic conductivity

Figure 5 shows that the hydraulic conductivity to deionised water of the untreated clay and the HYPER clay were comparable ( $k = 6.4 \times 10^{-12}$  versus  $k = 6.5 \times 10^{-12}$  m/s, respectively). The hydraulic conductivity to water was not influenced by the presence of the polymer, probably because the diffuse double layer of the two clays hydrated with water were both sufficiently thick.

After about 300 days of prehydration with deionised water, the samples were tested in the chemico-osmotic apparatus. At the end of the chemico-osmotic test, the sample was then permeated with a 5 mmol/L CaCl<sub>2</sub> solution. The hydraulic conductivity ( $k$ ) of the untreated clay increased from  $k = 6.4 \times 10^{-12}$  m/s (deionised water) to  $k = 4.0 \times 10^{-11}$  m/s (5 mmol/L CaCl<sub>2</sub> solution) (Figure 5a). Whereas, the hydraulic conductivity of the HYPER clay to 5 mmol/L CaCl<sub>2</sub> remained mostly constant ( $k = 6.5 \times 10^{-12}$  m/s with deionised water and  $k = 5.3 \times 10^{-12}$  m/s with CaCl<sub>2</sub>) as shown in Figure 5b.

The chemical equilibrium of the prehydrated HYPER clay permeated with the 5 mmol/L CaCl<sub>2</sub> solution was established after 607 days of permeation with the solution, which is an indication that the exchange reactions were concluded.

The hydraulic conductivity of the HYPER clay to seawater remained one order of magnitude lower in comparison with the untreated clay even after 1800 days of

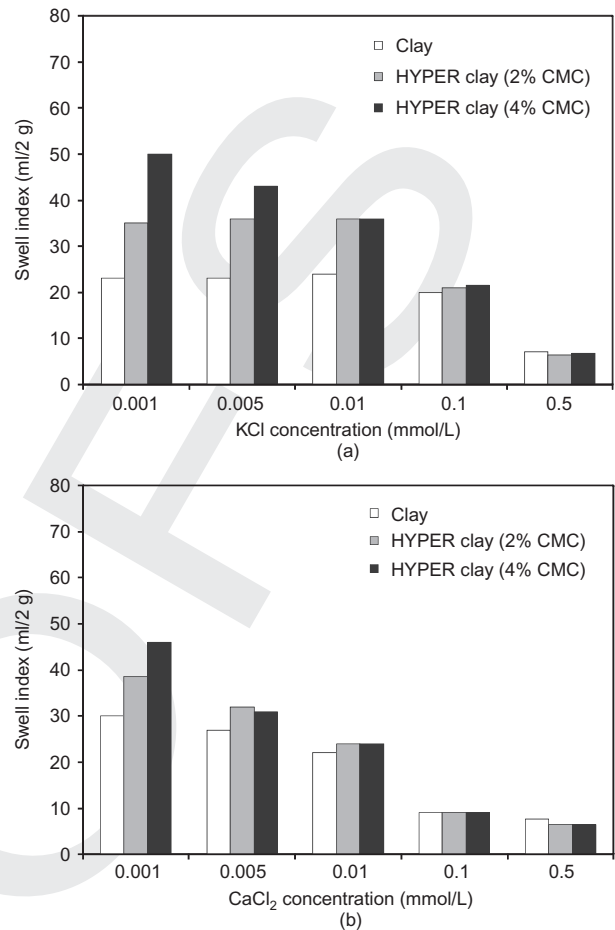


Figure 4. The addition of CMC to the clay improved its swelling ability in: (a) KCl solutions and (b) CaCl<sub>2</sub> solutions

permeation (as reported by Di Emidio 2010; De Saegher 2011; Seurnyck 2012; De Jaegher 2013). This test is still on-going to further demonstrate the long-term adsorption of the amendment into the clay. If this low permeability is extended in the long term, it may suggest that the chemico-osmotic efficiency of the HYPER clay will also be maintained with time even in the presence of electrolyte solutions.

4.3. Chemico-osmotic performance

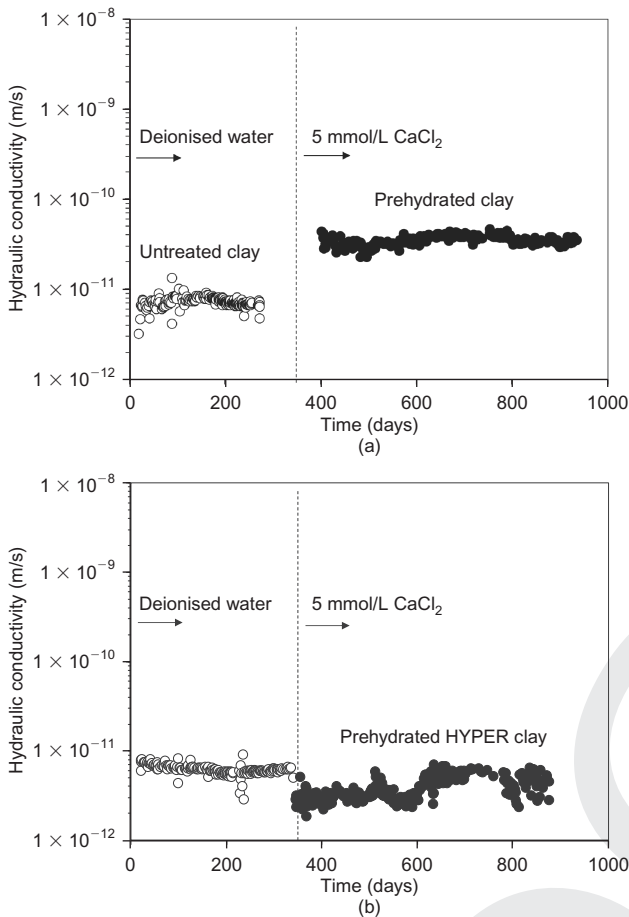
4.3.1. Chemico-osmotic efficiency of untreated bentonite clay

The initial stage of every test consists of circulation of deionised water through both porous stones at the opposite ends of the specimen in order to measure a reference differential pressure and to remove residual soluble salts. Although a concentration gradient was not yet applied, a slight induced pressure difference was observed. In this study the baseline pressure difference was of the order of  $-\Delta P_{ref} = 1$  to 5 kPa. These values were similar to those observed by Olsen (1969) and Malusis *et al.* (2001). This baseline pressure difference has been attributed not only to possible residual salt content in the porous stones but also to different hydraulic resistances of the two porous stones and/or to slight differences in the dimensions of the cylinder actuators.

The measured differential pressures induced across the

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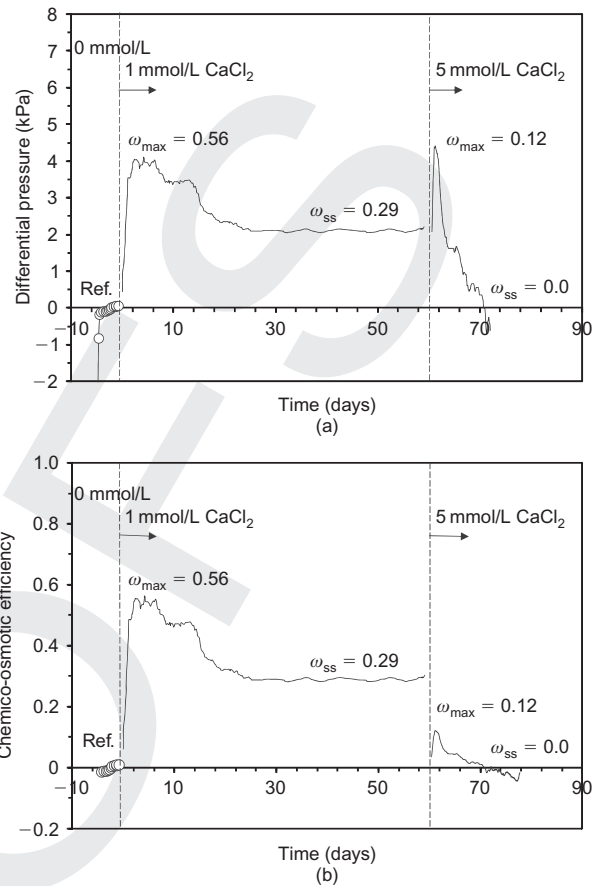




**Figure 5.** Hydraulic conductivity to 5 mmol/L CaCl<sub>2</sub> solution of: (a) untreated clay and (b) the HYPER clay after prehydration with water

untreated clay sample are presented in Figure 6a. The corresponding chemico-osmotic efficiencies ( $\omega$ ) are plotted against time in Figure 6b. After replacing the purified water circulating across the top of the specimen with the first 1 mmol/L CaCl<sub>2</sub> electrolyte solution (at  $t = 0$  in Figure 6), the induced pressure difference increased immediately and continued to increase gradually to a maximum value,  $-\Delta P_{\max} = 4.1$  kPa, corresponding to an  $\omega_{\max} = 0.56$ . Subsequently, the induced pressure difference and corresponding  $\omega$  gradually decreased to steady-state (ss) values,  $-\Delta P_{\text{ss}} = 2.1$  kPa and  $\omega_{\text{ss}} = 0.29$ , that remained constant up to 60 days when the next stage started. As expected, the maximum differential pressure value increased from  $-\Delta P_{\max 1} = 4.1$  kPa to  $-\Delta P_{\max 2} = 4.4$  kPa as the CaCl<sub>2</sub> concentration source solutions circulated on the top of the specimen increased from  $\Delta C_1 = 1$  mmol/L to  $\Delta C_2 = 5$  mmol/L CaCl<sub>2</sub>.

In the multiple-stage test conducted on the untreated clay, the maximum chemico-osmotic efficiency,  $\omega_{\max}$ , decreased from 0.56 to 0.12 increasing the concentration of the solution circulated on the top solution, whereas the chemico-osmotic efficiency at the steady state,  $\omega_{\text{ss}}$ , decreased from 0.29 to 0.0. This last observation confirms the results described in Shackelford and Lee (2003). They also observed a gradual destruction of the  $\omega_{\max}$  to  $\omega_{\text{ss}}$  on a Bentofix GCL after circulation of a 5 mmol/L CaCl<sub>2</sub>



**Figure 6.** (a) Chemico-osmotic induced differential pressures and (b) chemico-osmotic efficiency of the specimen for multiple-stage test (concentration gradients  $\Delta C_1 = 1$  mmol/L CaCl<sub>2</sub> and  $\Delta C_2 = 5$  mmol/L CaCl<sub>2</sub>) on the untreated clay

probably due to a compression of the diffuse double layer of the clay due to diffusion of the Ca<sup>2+</sup> source through the specimen (Barbour and Fredlund 1989; Shackelford and Lee 2003).

The time required to reach steady-state diffusion was evaluated by performing sequential linear regression analyses.  $D^*$  and  $R_d$  were determined by the time-lag method. Table 3 shows the parameters obtained. The higher  $t_L$  for Ca<sup>2+</sup> relative to the  $t_L$  for Cl<sup>-</sup> is attributed to the tendency for cation exchange associated with the divalent calcium cation. At steady state, electroneutrality requires that the charge flux  $J(\text{Cl}^-)$  of Cl<sup>-</sup> has the same magnitude as the charge flux  $J(\text{Ca}^{2+})$  of Ca<sup>2+</sup>. Based on the results, this theoretical requirement was satisfied, suggesting that steady-state diffusion was essentially established. The  $D^*$  of the solutes (Cl<sup>-</sup> and Ca<sup>2+</sup>) were similar, which is consistent with the electroneutrality requirement at steady-state diffusion. Furthermore,  $D^*$  for a concentration gradient  $\Delta C_2 = 5$  mmol/L were similar for both solutes.

Based on the calculated  $R_d$  values, both Cl<sup>-</sup> and Ca<sup>2+</sup> were retarded in both stages of the chemico-osmotic test. The main retarding process for Ca<sup>2+</sup> was the cation exchange with Na<sup>+</sup> onto the soil surface. The chemico-osmotic effect and the electrostatic interaction among the diffusing ions also influence the transport of Ca<sup>2+</sup>. Cl<sup>-</sup> is usually considered a conservative tracer in soil diffusion

**Table 3. Chemico-osmotic/diffusion test results**

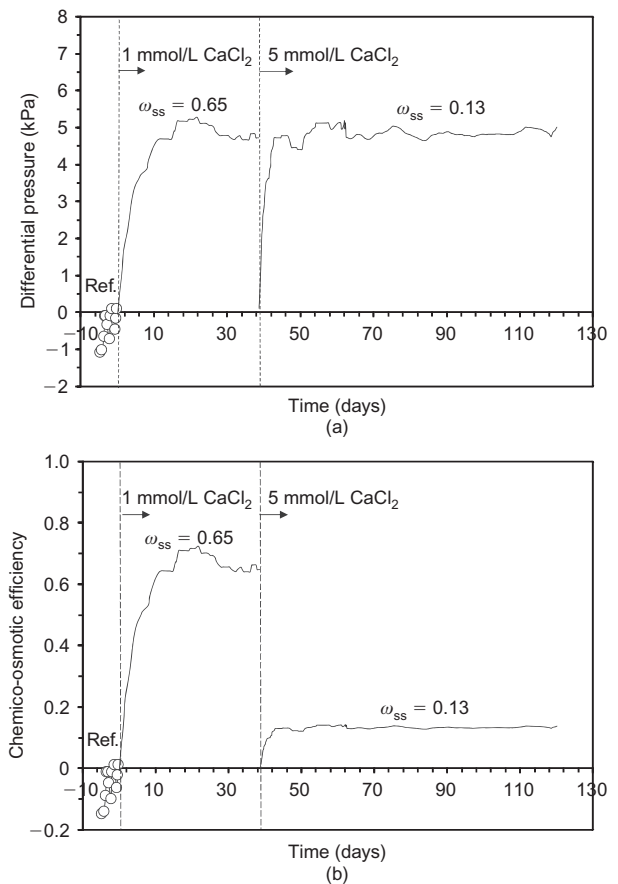
Sample	CaCl <sub>2</sub> (mMol/L)	Solute	<i>t<sub>L</sub></i> (days)	<i>t<sub>ss</sub></i> (days)	<i>D</i> *·10 <sup>-10</sup> (m <sup>2</sup> /s)	<i>R<sub>d</sub></i> (-)	<i>ω<sub>max</sub></i> (-)	<i>ω<sub>ss</sub></i> (-)
Clay	ΔC <sub>1</sub> = 1	Cl <sup>-</sup>	12.87	28.21	0.40	7.65	0.56	0.29
		Ca <sup>2+</sup>	23.47	36.29	0.41	13.49	0.56	0.29
	ΔC <sub>2</sub> = 5	Cl <sup>-</sup>	7.83	19.38	2.22	36.21	0.12	0.0
		Ca <sup>2+</sup>	15.68	26.02	2.22	68.60	0.12	0.0
	ΔC <sub>3</sub> = 10	Cl <sup>-</sup>	4.40	18.78	3.80	24.11		
		Ca <sup>2+</sup>	3.68	21.72	3.77	19.99		
HYPER clay 2%	ΔC <sub>1</sub> = 1	Cl <sup>-</sup>	10.97	25	0.44	6.91	0.62	0.65
		Ca <sup>2+</sup>	22.58	28	0.39	11.54	0.62	0.65
	ΔC <sub>2</sub> = 5	Cl <sup>-</sup>	13.47	39.27	1.67	43.76	0.13	0.13
		Ca <sup>2+</sup>	16.81	39.27	1.35	43.28	0.13	0.13
	ΔC <sub>3</sub> = 10	Cl <sup>-</sup>	4.46	15.63	1.71	9.16		
		Ca <sup>2+</sup>	9.24	15.63	1.58	20.57		

studies as it tends to be repelled from negatively charged surfaces. Theoretically, a conservative tracer should have  $R_d = 1$ . In addition to solute restriction ( $\omega > 0$ ), the retardation of Cl<sup>-</sup> could be partly explained by the counter-diffusion of Na<sup>+</sup> into the top solution, which may have delayed the downward diffusion of Cl<sup>-</sup> due to electroneutrality requirements. For an overview of the transport parameters of the clays analysed, refer to Table 3.

As illustrated in Figure 6, the chemico-osmotic efficiency showed a maximum value, ( $\omega_{max}$ ), after a few hours of testing and a gradual decrease to a lower constant value, ( $\omega_{ss}$ ), at steady-state diffusion conditions. The results obtained here with a CaCl<sub>2</sub> concentration gradient  $\Delta C_2 = 5$  mmol/L qualitatively resemble the findings of Shackelford and Lee (2003). They also observed a variable osmotic efficiency, with a peak value followed by a gradual decrease to zero. Their conceptual explanation for the correlation between Ca<sup>2+</sup> diffusion and the destruction of the membrane behaviour can be formulated on the basis of the clay structure models described by Pusch and Schomburg (1999). In these models, bentonite clay consists of an intermingled structure of both unit particles and particle clusters, with the primary pores located between the unit particles and the clusters. In these models, bentonite clay consists of an intermingled structure of both unit particles and particle clusters, with the primary pores located between the unit particles and the clusters. At the measured porosity of the specimen  $n = 0.718$ , interlayer spacing of the particles will be controlled by surface hydration rather than by the diffuse double-layer interactions, such that the interlayer spacing of the unit particles will probably not have been affected much by the exchangeable cation (Van Olphen 1977). However, DDLs will probably have extended into the voids between both unit particles and particle clusters, thereby restricting the diffusive migration of the ions. In addition, the decrease of DDL thickness also causes particles aggregation, with a consequent decrease of the specific surface area of the clay contributing to surface hydration forces. As a consequence, not only the thickness of the DDL, but also the hydration forces of the water molecules on the clay surface decrease with a consequent decrease in chemico-osmotic efficiency.

4.3.2. Chemico-osmotic efficiency of a HYPER clay

The measured differential pressures induced across the HYPER clay sample and the chemico-osmotic efficiency in the multiple-stage test are presented in Figure 7. After replacing the purified water circulating across the top of the specimen with the first solution (1 mmol/L CaCl<sub>2</sub>), at  $t = 0$  days, as shown in Figure 7, the induced pressure difference increased immediately and continued to increase gradually to a maximum value of  $-\Delta P = 4.74$  kPa corresponding to a



**Figure 7. (a) Chemico-osmotic induced differential pressures and (b) chemico-osmotic efficiency of the HYPER clay for multiple-stage test (concentration gradients  $\Delta C_1 = 1$  mmol/L CaCl<sub>2</sub> and  $\Delta C_2 = 5$  mmol/L CaCl<sub>2</sub>)**

maximum chemico-osmotic efficiency coefficient  $\omega_{\max} = 0.65$ . Subsequently, the second concentration gradient was applied. After replacing the solution, the induced pressure difference due to  $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$ , increased and continued to increase gradually to a maximum value of  $-\Delta P = 4.81 \text{ kPa}$  corresponding to a maximum chemico-osmotic efficiency coefficient  $\omega_{\max} = 0.13$ . The chemico-osmotic efficiency of the HYPER clay was maintained at the steady state, in contrast to the gradual decrease observed for the untreated clay.

Figures 8a and 8b show a comparison between the gradual destruction of the membrane behaviour of the untreated clay due to diffusion and, on the contrary, the preservation of the membrane behaviour with time for the HYPER clay due to the shielding role of this polymer. The effect of the polymer became evident for higher concentrations. In fact, for a concentration gradient  $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$ , the HYPER clay breakthrough of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  were similar, suggesting that the exchange of  $\text{Ca}^{2+}$  with  $\text{Na}^+$  was shielded due to the presence of the polymer. The polymer blocks the compression of the DDL when the concentration increases, whereas for diluted concentrations the DDL is already sufficiently thick and the effect of the polymer is negligible.

Likewise, the time at the steady-state,  $t_{ss}$ , and the retardation factor,  $R_d$ , of  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  were comparable.

These results could in fact indicate that the exchange was restricted during the second stage. Furthermore, the diffusive molar flux ratio of  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  ( $J(\text{Cl})/J(\text{Ca})$ ) was nearly constant from the start of the stage with  $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$ , indicating that the two solutes moved together, as a result of limited exchange between  $\text{Ca}^{2+}$  and  $\text{Na}^+$  in the transient phase of the test. For the high concentration gradient ( $\Delta C_2 = 5 \text{ mmol/l CaCl}_2$ ), the HYPER clay breakthrough showed some delay with respect to the untreated clay, confirming that the impact of the polymer is emphasised for concentrated solutions with respect to diluted solutions. To further validate this hypothesis, it should be stressed that the retardation factor,  $R_d$ , of the HYPER clay was comparable to the untreated clay for  $\Delta C_1 = 1 \text{ mmol/L CaCl}_2$ , but it was higher for the higher concentration gradient ( $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$ ) (Table 3). In addition, the comparison of the effective diffusion,  $D^*$ , confirms that for the diluted solution ( $\Delta C_1$ ) the HYPER clay showed a  $D^*$  comparable to the untreated clay, whereas for the concentrated solution ( $\Delta C_2$ ) the HYPER clay showed a lower  $D^*$  compared to the untreated clay.

Figure 9 shows that for the untreated clay the diffusion coefficient increases with increasing the ionic strength and decreasing the chemico-osmotic efficiency. In contrast,

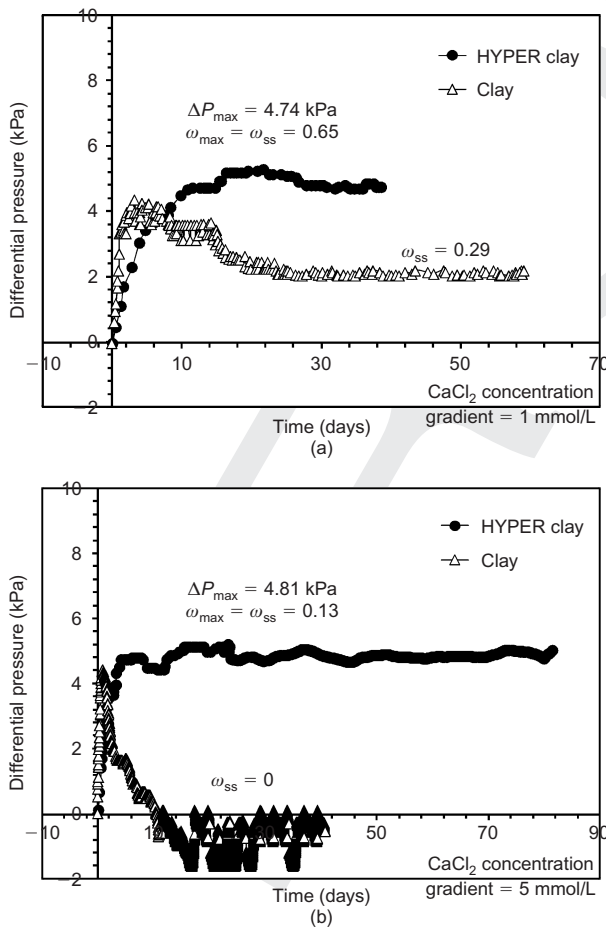


Figure 8. Enhancement due to the anionic polymer (CMC) on the chemico-osmotic efficiency of the HYPER clay with a concentration gradient: (a)  $\Delta C_1 = 1 \text{ mmol/L CaCl}_2$  and (b)  $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$

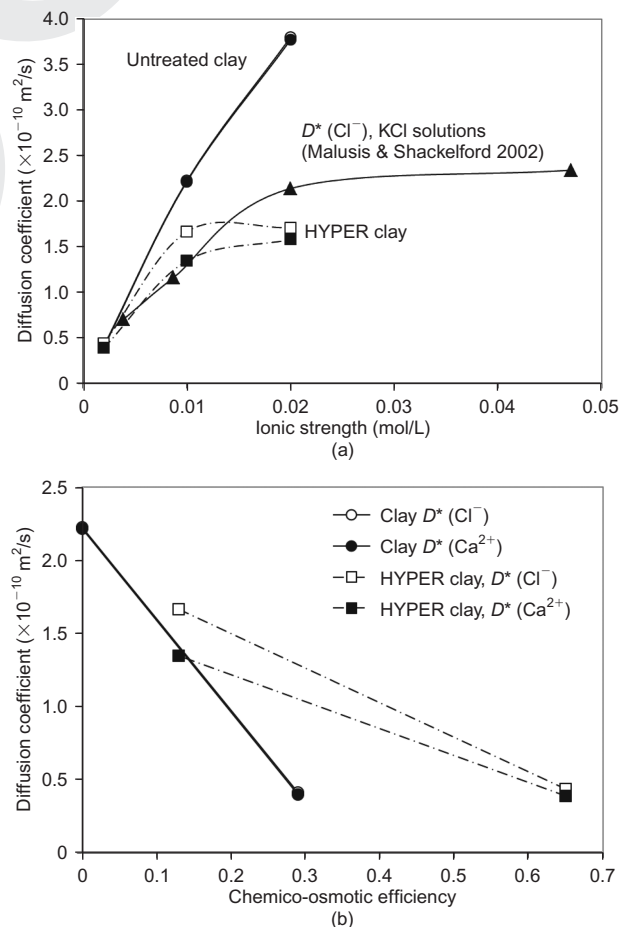


Figure 9. Effective solute diffusion coefficients plotted against: (a) ionic strength and (b) chemico-osmotic efficiency (data of HYPER clay with  $10 \text{ mmol/L CaCl}_2$ , ionic strength  $0.02 \text{ mmol/L}$ , from Seurynek 2012)

Figure 9a shows that for the HYPER clay a lower increase of the diffusion coefficient was observed, suggesting that the increase of diffusion coefficient with the ionic strength was softened by the presence of the polymer. In fact, the higher solute concentrations in the pore space associated with an increase in the concentration of the source solution, causes contraction of the diffuse double layers that results in a decrease in chemico-osmotic efficiency and a corresponding increase in  $D^*$  as more pores become available for solute transport. On the other hand, the polymer, maintaining the DDL open, restricts the availability of pores for solute transport with a consequent decrease of  $D^*$ . In fact, the degree of solute restriction is greatest when the double layers of adjacent clay particles overlap in the pore space, leaving no free solution for solute transport (Marine and Fritz 1981).

The  $D^*$  of the solutes ( $\text{Cl}^-$  and  $\text{Ca}^{2+}$ ) were similar, which is consistent with the electroneutrality requirement at steady-state diffusion. As observed for the untreated clay, also for the HYPER clay both  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  were retarded for a concentration gradient  $\Delta C_1 = 1 \text{ mmol/L CaCl}_2$ . For  $\Delta C_1 = 1 \text{ mmol/L CaCl}_2$ , release of  $\text{Na}^+$  cations during diffusion of  $\text{Ca}^{2+}$  suggested that cation exchange onto the soil surface was the main retarding process for  $\text{Ca}^{2+}$ . The chemico-osmotic effect and the electrostatic interaction among the diffusing ions also had a role in the retardation of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ . The retardation of  $\text{Cl}^-$  could be partly explained by electroneutrality requirements due to the counter-diffusion of  $\text{Na}^+$  into the top solution. The boundary concentrations vary during the test as a result of diffusion, with a consequent influence in the transport parameters.

For a concentration gradient  $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$ , the  $D^*$  of the solutes ( $\text{Cl}^-$  and  $\text{Ca}^{2+}$ ) were similar, which is consistent with the electroneutrality requirement at steady-state diffusion. In addition, for a concentration gradient  $\Delta C_2 = 5 \text{ mmol/L CaCl}_2$ , both  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  were delayed. Given that the cation exchange onto the soil surface was restricted, the retardation of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  are mainly due to the chemico-osmotic effect and the electrostatic interaction among the diffusing ions. The retardation of  $\text{Cl}^-$  could be partly explained by electroneutrality requirements due to the counter-diffusion of  $\text{Na}^+$  measured into the top solution.

Furthermore, the boundary concentrations vary during the test as a result of diffusion, with a consequent influence in the transport parameters. The steady-state diffusive molar flux of  $\text{Cl}^-$  theoretically should be twice the magnitude of the steady-state diffusive molar flux of  $\text{Ca}^{2+}$ . Based on the results, the observed ratio of the steady-state diffusive mass fluxes approached sufficiently this theoretical value suggesting that steady-state diffusion had essentially been established. Moreover, for the concentration gradient  $\Delta C_2$ , this ratio  $J(\text{Cl})/J(\text{Ca})$  was approximately 2.5 from the start of the test, suggesting that the adsorption of  $\text{Ca}^{2+}$  onto the clay due to cation exchange was restricted by the polymer, with a steady-state diffusive molar flux ratio from the start of the second stage.

As shown in Figure 6, the chemico-osmotic efficiency

showed a maximum value after few hours of testing and a gradual decrease to a lower constant value at steady-state diffusion conditions.

In contrast, the HYPER clay preserved its membrane efficiency with time due to the presence of the polymer that maintained the interlayer between particles open (Figure 8a and 8b). Ruehrwein and Ward (1952) stated that the adsorption of anionic polymers on to clays occurs through ionic exchange, Michaels and Morelos (1955) suggested that adsorption is mainly conditioned by hydrogen bonding, a third possibility would originate from the interaction between polyvalent cations (such as  $\text{Ca}^{2+}$ ), acting as crosslinking agents between the clay negative surface and the anionic polymer (Stutzmann and Siffert 1977). In the presence of salts and cations naturally present at the clay surface, the negative charges of the clay and the anionic polymer are shielded from one another allowing the polymer to coil and collapse on the clay surface (Breen 1999). The polymer and the adsorbed cation coat the clay surface, potentially forming a protective layer. The adsorption of polymer chains (such as CMC) in clay can be irreversible and entropy-driven because a polymer chain displaces many water molecules and attracts thousands of cations which would need to be displaced simultaneously (Theng 1982; Ashmawy *et al.* 2002). For these reasons polymers can protect the clay from cation exchange that is the main reason for the compression of the double layer and for the consequent decrease of chemico-osmotic efficiency.

Chemico-osmotic tests results were also reported on multi-swallowable bentonite (MSB) (Mazzieri *et al.* 2010; Di Emidio 2010) and a dense prehydrated GCL (DPH GCL) (Di Emidio 2010). Based on the improved hydraulic performance of MSB and DPH GCL, it was expected to also show an improved chemico-osmotic behaviour compared to the untreated clay. Conversely, Figure 10 shows that these two amended clay materials displayed a chemico-osmotic behaviour at the steady state similar to that observed on untreated clay, under the adopted experimental conditions (e.g. prolonged permeation to remove soluble salts). Different results may be obtained by adopting different testing conditions. On the other hand, the preservation of the chemico-osmotic efficiency of the

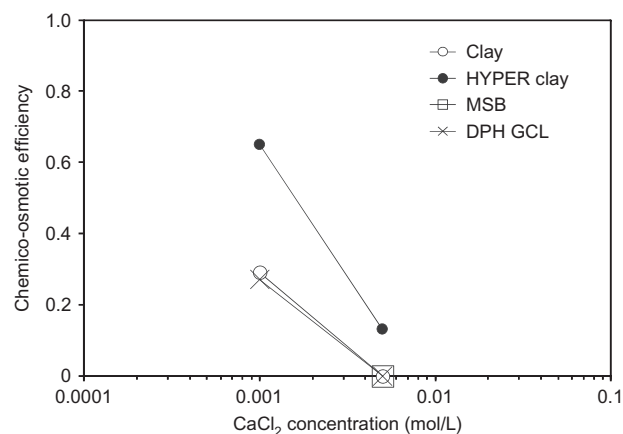


Figure 10. Chemico-osmotic efficiency overview: comparison with other modified clays from literature

HYPER clay with time suggests that the CMC was not flushed out during the long period of permeation with deionised water. These results suggest that the use of the HYPER clay in containment application may be very promising.

## 5. CONCLUSIONS

The main conclusions of this paper are summarised here. XRD analysis demonstrated the intercalation of the polymer in the interlayer region of the clay, inducing a dispersed clay structure. The swell index and the liquid limit of the clay increased with increasing polymer dosage suggesting a potential benefit of the polymer on preserving the hydraulic performance of the clay. The hydraulic conductivity of untreated clays increased after permeating the samples with electrolyte solutions due to the compression of the double layer thickness. Conversely, HYPER clay maintained low hydraulic conductivity to CaCl<sub>2</sub> and to seawater even in the long term. A decrease of membrane efficiency was observed in untreated clays due to diffusion. On the other hand, the polymer treatment protected the clay against the destructive role of diffusion, maintaining the initial osmotic efficiency in the long term. Polymer treatment modified the bentonite structure such that the double-layer thickness of the clay resisted collapse and the membrane efficiency was sustained. The diffusion coefficient of the HYPER clay was lower than that of the natural clay. This result suggests that the polymer protected the HYPER clay from cation exchange.

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## NOTATION

Basic SI units are given in parentheses.

$A$	cross-sectional area of the specimen (m <sup>2</sup> )
$C$	concentration (mol/l)
$C_{b,j}$	concentration of solute species $j$ at the bottom (mol/L)
$C_{t,j}$	concentration of solute species $j$ at the top (mol/L)
$D_0$	diffusivity in free solution (m <sup>2</sup> /s)
$D^*$	bulk diffusion coefficient (m <sup>2</sup> /s)
$d$	basal spacing (m)
$e$	void ratio (dimensionless)
$G_s$	specific gravity of soil solids (dimensionless)
$J$	diffusive flux (mol/s per m <sup>2</sup> )
$k$	hydraulic conductivity (m/s)
$L$	specimen thickness (m)
$m$	mass (kg)
$n$	porosity (dimensionless)
$Q_t$	cumulative mass per unit area (kg/m <sup>2</sup> )
$q$	volumetric flux (m <sup>3</sup> /s)
$R$	universal gas constant (J/mol per K)

$R_d$	retardation factor (dimensionless)
$T$	absolute temperature (K)
$t$	time (s)
$t_L$	time lag (s)
$t_{ss}$	time to steady state (s)
$V$	volume (m <sup>3</sup> )
$w$	water content (dimensionless)
$\Delta C$	salt concentration gradient (mol/L)
$\Delta P$	differential pressure (Pa)
$\Delta \pi$	theoretical chemico-osmotic pressure (kPa)
$\sigma'$	effective stress (Pa)
$\omega$	chemico-osmotic efficiency (dimensionless)

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