

Comparison between the beneficial impact of polymer treatment and sodium-activation on Calcium bentonites

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ABSTRACT

The hydraulic conductivity of Geosynthetic Clay Liners for the confinement of waste disposal facilities mainly depends on the hydraulic conductivity of the core bentonite clay encased between the two geotextiles. Bentonite clay is the most common material for Geosynthetic Clay Liners. Even though sodium bentonite has the lowest hydraulic conductivity to water, calcium bentonite is widely used because of low cost and availability. This research concerns the evaluation of the treatment of calcium bentonite with an anionic polymer, Sodium CarboxyMethyl Cellulose (Na-CMC) with HYPER clay technology. Permeability tests were performed in order to compare HYPER clay behaviour to the standard sodium activation treatment of calcium bentonite. Increasing concentrations of calcium dichloride, 5 mM – 100 mM – 200 mM, were used as hydrating solutions. Test results showed the beneficial effect of the anionic polymer treatment on the hydraulic performance of the clay analysed in the long term.

Keywords: Bentonite, Chemical Compatibility, Hydraulic Conductivity, Ion Exchange, Polymer

1 INTRODUCTION

To isolate contaminants leaching from waste disposal facilities, hydraulic barriers, such as Compacted Clay Liners (CCLs) and Geosynthetic Clay Liners (GCLs), are largely used. GCLs are factory-manufactured clay liners consisting of a thin layer of bentonite sandwiched between two geotextiles or glued to a geomembrane. Sodium bentonite has higher quality compared to calcium bentonite, because of its low hydraulic conductivity to water and favourable swelling properties (Mitchell, 1993; Schackelford et al., 2000; Egloffstein, 2001; Bouazza, 2001; Bouazza et al., 2006). Ca-bentonites have higher hydraulic conductivity compared to Na-bentonites, but Ca-bentonites are more readily available and may be enhanced by sodium activation (i.e., saturating the exchange complex of the Ca-bentonite with sodium ions). However, the bentonite is prone to cation exchange in presence of liquid other than water, and sodium cations are easily replaced by multivalent cations (e.g., Ca^{2+} , Mg^{2+}). In fact, long term exposure to high concentrations of organic and inorganic compounds, largely present in landfill leachates, can change the bentonite behaviour, causing a loss of hydraulic performance (Norrish, 1954; Mitchell, 1993). Another critical disadvantage of the sodium activation is the consequent formation of calcium carbonate precipitates into the soil. This calcium carbonate may re-dissolve during contact with a dilute permeant, releasing calcium ions that exchange with sodium in the clay (Guyonnet et al., 2005).

With the attempt to overcome this problem, modified clays have been recently introduced in barrier applications to improve their chemical resistance to aggressive permeants (Kondo, 1996; Onikata et al., 1996, 1999; Flynn and Carter, 1998; Schroeder et al., 2001; Simon and Müller, 2005; Katsumi et al., 2008; Mazzieri et al., 2010; Di Emidio, 2010a&b; Scalia et al., 2011; Bohnhoff et al., 2012; Mazzieri et al., 2013; Zhao et al., 2014). In terms of pollutant containment applications, nowadays it is of great interest to evaluate the potential benefits of these treated clays to highly concentrated electrolyte solutions.

This study deals with a newly-developed polymer treated clay (HYPER clay), that showed a reduction of its hydraulic conductivity compared to the non-amended clay (Di Emidio, 2010a&b; Bohnhoff et al., 2012; Malusis & Di Emidio, 2013). With this treatment, the anionic polymer penetrates irreversibly the interlayer region between clay platelets enhancing the osmotic swell of the clay. Intercalation of the anionic polymer in the interlayer space between clay platelets tends to protect the clay from chemical attack, by preventing the contraction of the interlayer and the consequent increase of the hydraulic conductivity in presence of exchangeable cations.

The objective of this paper is to show the comparison between the hydraulic efficiency of the treated, the untreated calcium clay and a sodium activated clay permeated to highly concentrated CaCl₂ solutions. In a previous study, it was found that the treatment with the anionic polymer improved the swelling ability of the calcium clay compared to the sodium activation method (Di Emidio et al., 2013a; Di Emidio et al., 2014). It was also shown preliminary promising results in terms of hydraulic conductivity. That research was followed by the present study with the purpose to evaluate the effect of the treatments on the hydraulic conductivity in the long term, after chemical equilibrium, and with higher CaCl₂ concentrations.

2 MATERIALS

In this study three materials are compared: a natural calcium bentonite (Ca-bent), the same Ca-bent sodium activated (Na-act) and the same Ca-bent treated with the HYPER clay technology using 8% of polymer dosage (HYPER clay 8%). The latter treatment method consists of mixing a base clay with a polymeric solution (containing in this study 8% - by dry weight of clay - of Sodium Carboxymethyl Cellulose, Na-CMC) with a mechanical stirrer for 30 minutes. This slurry is then oven dried at 105° C for 16 hours. After drying, the HYPER clay is ground first manually using a mortar and pestle and then mechanically using a Retsch Mortar Grinder RM 200. This treatment method can also be applied to other types of clay with different polymer dosages (Di Emidio, 2010b). Some properties of the materials tested here are listed in Table 1. The electrolyte solutions used in this investigation are deionized water (DW) and calcium chloride (CaCl₂) solutions. Deionized water was used as base solution for the preparation of HYPER clay and of the electrolyte solutions. The deionized water was produced using a water purification system PURELAB Option-R 7/15. The electrical conductivity of the deionized water was EC=0.0039 mS/cm, the pH=7.57, and the redox potential was Eh=293 mV. The electrolyte solutions were used to test the hydraulic conductivity of the materials. The solutions were prepared by dissolving (>99.7% pure) CaCl₂ (5 mM, 100 mM, 200 mM, 500 mM), in deionized water. Some properties of the solutions are listed in the Table 2.

Table 1: Characteristics of tested soils: Ca-bent = calcium bentonite; Na-act = sodium activated calcium bentonite; HYPER clay 8% = Ca-bent treated with HYPER clay technology using 8% (by dry weight) of polymer dosage.

Parameter	Ca-bent	Na-act	HYPER clay 8%
Swell index (ml/2g)	12	19	42
Specific gravity (-)	2.5	2.5	2.2
Liquid limit (%)	309.53	414.16	831.60
Plastic limit (%)	64.03	64.83	199.39
Plasticity index (%)	245.50	349.33	632.21
Smectites - Mica (%)	82-0	82-0	82-0
Quartz - Opal (%)	2-0	2-0	2-0
Feldspar (%)	2	2	2

Table 2: Chemical properties of the electrolyte solutions

Solution	Concentration	Electrical conductivity	Salinity	pH	Eh
	mM	mS/cm	-	-	mV
Deionized water		0.0039	0.0	7.57	293
CaCl ₂	0.005	1.211	0.4	6.56	262
	0.100	18.54	11	6.77	260
	0.200	35.8	22.3	6.6	172
	0.500	78.8	55.5	7.32	184

3 METHODS

Thin clay specimens were prepared for the hydraulic conductivity tests in a swell pressure setup, to simulate the bentonite core of a standard GCL hydrated with the first testing solution (CaCl_2 5 mM) with the purpose to test the hydraulic efficiency of non pre-hydrated samples. The swelling pressure test apparatus used consisted of a stainless steel ring (7.1 cm diameter) accommodated in a one-dimensional cell (similar to a standard oedometer cell) located in a frame provided with a load cell connected to a computer. The specimen was prepared by spreading a thin layer of dry clay (0.45 g dry bentonite/cm²) into the stainless steel ring placed into the oedometer cell. The aim of this procedure was to obtain samples that represent the bentonite core of a standard GCL with typical dry bentonite per unit area of 4.5 kg/m². After assembly, the sample was inundated with the test solution (e.g., CaCl_2 5 mM). For these powder samples a fixed height ($h=0,665$ cm) was chosen to obtain a similar initial porosity (with a dry unit weight of 6.65 kN/m³) for all samples. The achievement of a steady maximum swelling pressure (measured by the load cell keeping the height of the sample constant) was chosen as termination criteria for this sample preparation phase.

The hydraulic conductivity tests were performed in flexible wall permeameters. The tests were executed with a hydraulic gradient of about 55 and an average effective stress of 30 kPa. This effective stress was chosen in order to simulate an extreme condition, such as the lowest effective stress expected in a landfill cover. In case the effective stress is increased (to represent, for instance, a landfill base liner), the hydraulic conductivity will decrease accordingly (Petrov and Rowe, 1997). The samples chosen for the hydraulic conductivity tests were: the calcium bentonite as base material, the sodium activated bentonite and the HYPER clay calcium bentonite, in order to compare the beneficial effects of the two treatments. A 5 mM CaCl_2 permeant solution was chosen as first solution in order to study the effect of cation ex-change on the hydraulic conductivity of the clays analyzed. After chemical equilibrium was established (ASTM D 6766) the solution concentration was increased to 100 mM; and later, after chemical equilibrium, up to 200 mM to analyze not only the effect of cation exchange with high concentrations of Ca^{2+} cations available to exchange, but also the effect of high concentrated ions on the diffuse double layer compression.

4 RESULTS AND DISCUSSION

This section shows the comparison of the results of the experimental work on the calcium clay treated with two enhancement methods: the standard sodium activation and the novel HYPER clay technology that consists, as seen above, in a treatment with an anionic polymer and dehydration to adsorb the polymer irreversibly.

Figure 1 shows the hydraulic conductivity of the three clays as a function of time. The hydraulic conductivity of both treated clays were lower than that of the untreated clay due to the typical thinner diffuse double layer between clay platelets in a calcium bentonite. The figure also illustrates that the hydraulic conductivity of the HYPER clay was lower than that of the sodium activated clay, indicating a higher hydraulic performance induced by the HYPER clay treatment.

The reference hydraulic conductivity to deionized water of a natural sodium bentonite is of the order of $6.4\text{E-}12$ m/s (as seen in Di Emidio, 2010a). The hydraulic conductivity to 5 mM and 100 mM CaCl_2 of the HYPER clay was of the same order ($8.76\text{E-}12$ m/s after 2.79 PVF of 5 mM CaCl_2 , $8.71\text{E-}12$ m/s after 3.31 PVF of 100 mM CaCl_2 , and it remained low after 1.6 PVF of 200 mM CaCl_2) whereas the hydraulic conductivity of the sodium activated clay was half order of magnitude higher ($2.96\text{E-}11$ m/s after 8.38 PVF of 5 mM CaCl_2 , $3.77\text{E-}11$ m/s after 14.72 PVF of 100 mM CaCl_2 , and $4\text{E-}11$ m/s after 6.14 PVF of 200 mM CaCl_2). The hydraulic conductivity of the calcium clay to 5 mM CaCl_2 was $1.38\text{E-}10$ m/s after 45.15 PVF, it was $1.43\text{E-}10$ m/s after 37.8 PVF to 100 mM CaCl_2 , and it was $1.28\text{E-}10$ m/s after 17.32 PVF to 200 mM CaCl_2 . All the tests shown above reached termination criteria and chemical equilibrium, with the exception of the HYPER clay permeated with 200 mM CaCl_2 . Currently the calcium bentonite (PVF = 13.66, $\text{EC}/\text{EC}_0 = 1.01$) and the sodium activated clay (PVF = 4.65, $\text{EC}/\text{EC}_0 = 0.95$) are being permeated with 500 mM CaCl_2 and reached already chemical equilibrium, whereas the HYPER clay continues the permeation with 200 mM CaCl_2 (PVF = 1.6) in order to reach

the chemical equilibrium (currently $EC/EC_0 = 0.56$) which is delayed by the very low permeability of the sample.

The lower hydraulic conductivity of the HYPER clay is likely due to its thick diffuse double layer that is maintained thick in the long term. This beneficial behavior is due to the irreversible adsorption of the polymer into the clay (Di Emidio, 2010b). Di Emidio, 2010a showed through X-Ray Diffraction analysis that the polymer intercalates between the clay particles maintaining the interlayer open and adsorbing lots of immobile water molecules and ions. This phenomenon restricts the pore space available for the flow and causes tortuous flow pathways, which are typical of dispersed structured low permeable clays. Given that the thickness of the adsorbed layer is inversely related to the ions concentration and valence, bentonites are particularly sensitive to changes in the composition of the pore fluid. In particular, electrolyte solutions with high valence (such as the $CaCl_2$ solution used in this work) cause the thickness of the diffuse double layer to collapse and therefore the hydraulic conductivity to increase.

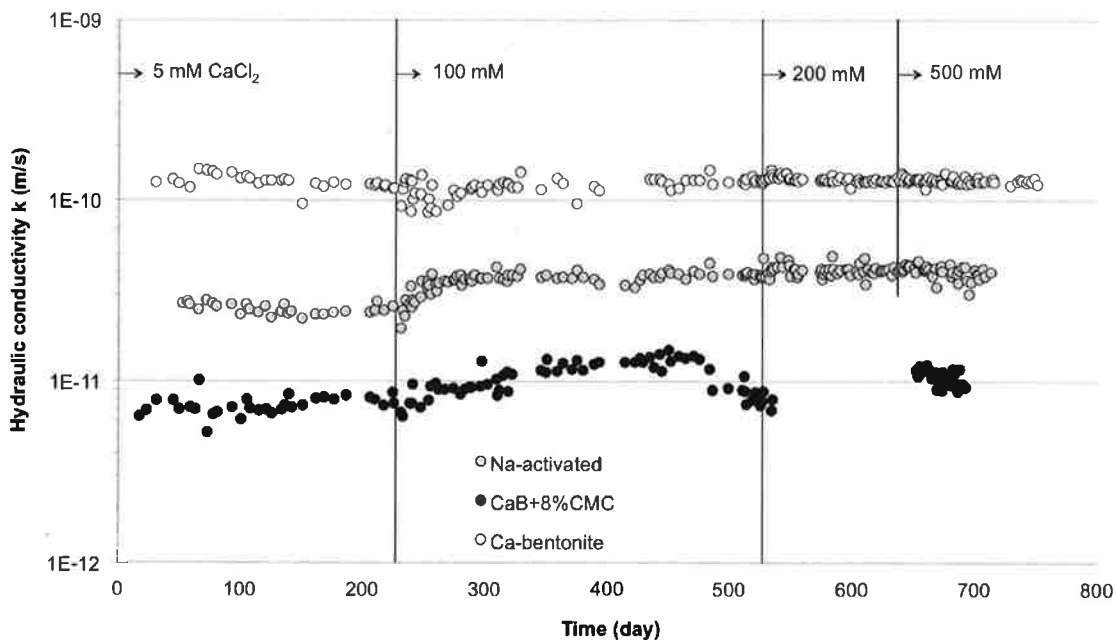


Figure 1. Hydraulic conductivity to various $CaCl_2$ solutions (5 mM, 100 mM, 200 mM, 500 mM) of the untreated calcium bentonite (Ca-bent), of the Ca-bent sodium activated (Na-act) and of the calcium bentonite treated with the HYPER clay technology using 8% CMC by dry weight (HYPER clay 8%).

5 CONCLUSION

The purpose of this research was to investigate the effect of sodium activation and polymer addition to calcium bentonites, in order to improve the hydraulic conductivity of these materials to highly concentrated calcium chloride solutions. Hydraulic conductivity tests were conducted for this purpose on untreated calcium bentonite clay, this same clay sodium activated and the calcium clay treated with polymers following the HYPER clay technology. The hydraulic conductivity of the untreated calcium clay was the highest due to an already collapsed double layer thickness. The hydraulic conductivity of the HYPER clay was the lowest. The low hydraulic conductivity of the HYPER clay is likely due to it maintaining a swollen state even in the long term also in presence of electrolyte solutions due to the irreversible adsorption of the polymer onto the clay. Further research is in progress (in order to reach the chemical equilibrium) to confirm these results for higher concentrations of the permeant solution (such as 200 mM and 500 mM $CaCl_2$).

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