Wet and dry ageing of polymer treated clays using seawater: swell potential and hydraulic conductivity

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ABSTRACT: The efficiency of Geosynthetic Clay Liners may decrease if they are exposed to aggressive solutions. The performance of the barrier can be further altered if the contact with aggressive solutions is accompanied by wet-dry cycling. Modified clays have been introduced in barrier applications to improve their chemical resistance to aggressive permeants. This study deals with the comparison of a newly-developed polymer treated bentonite clay, HYPER clay, and the untreated bentonite clay. Oedometer free swell tests and hydraulic conductivity tests were conducted to assess how wet-dry cycling affects the swell and the permeability of geosynthetic clay liners hydrated with deionized water and seawater. Wet-dry cycling in deionized water had little effect on the swelling of the untreated bentonite. In contrast, its swelling decreased dramatically after two wetting cycles with seawater. The hydraulic conductivity of the untreated specimens permeated with the salt solution increased considerably after the first rewetting with seawater. The hydraulic conductivity increased because cracks, formed during desiccation, did not fully heal after rehydration with seawater. The treated specimen showed lower hydraulic conductivity and a larger swelling ability compared to the non-amended clay. In contrast to the untreated clay, these beneficial effects were maintained even after wet-dry cycles with the salt solution.

Keywords: polymer, bentonite, wet-dry cycles, hydraulic conductivity, swelling, ion exchange

1 INTRODUCTION

Clay liners are used as cover or bottom lining of waste containment facilities to avoid infiltration of water to the waste and the release of leachate. The main types of clay liners are Compacted Clay Liners (CCLs) and Geosynthetic Clay Liners (GCLs). GCLs are factory-manufactured hydraulic barriers containing a thin layer of bentonite sandwiched between geotextiles or glued to a geomembrane. Bentonite clay is widely used in clay liners because of its low hydraulic conductivity to water and high swelling ability. The geosynthetic layers can be glued, bonded with an adhesive, needlepunched, or stitch-bonded to the bentonite. The main advantages of GCLs, compared to CCL, are the limited thickness, easy installation and, in particular, the good compliance with differential settlements of underlying soil or waste (Bouazza, 2001).

GCLs are often in contact with liquids other than water. Direct exposure to salt solutions can impair the self-healing capacity of bentonite clay and increase its permeability (Lin and Benson, 2000; Egloffstein, 2001; Bouazza et al., 2007). Considering this, the effect of cation concentration and valence of the permeant fluid on the bentonite must be assessed. An increase in valence results in higher permeability (Shackelford et al, 2000) that has also been associated with high concentrations of monovalent cations. Katsumi et al. (2008) confirmed that when multivalent cations are present, the expansion capacity of the crystal layers in the bentonite is restricted.

Calcium bentonite is the most used despite the fact that sodium bentonite is known to present better swelling ability and lower hydraulic conductivity. To improve its properties, calcium bentonite is often activated by sodium ions. However, electrolyte fluids are likely to exchange the sodium ions with calcium, altering the swelling properties of the bentonite. According to Egloffstein (2001) ion-exchange usually happens over a period of one to several years, until it is completed.

Seawater (SW) is an electrolyte fluid with high content of monovalent and multivalent cations that can inhibit the osmotic swelling and increase the hydraulic conductivity of bentonite (Egloffstein, 2001). Wet-dry cycles combined with ion-exchange can lead to further damages of the bentonites. The bentonite self-healing capacity can be affected by crack formations during the dry phase (Lin and Benson, 2000) and lead to a permeability increase on soil bentonite backfills (Malusis et al., 2011). Bouazza et al. (2007) detected a decrease in swelling capacity of the bentonite as the number of wet-dry cycles increased.

To avoid barrier deterioration, modified bentonites have been studied to enhance their resistance in aggressive environment . Several laboratory studies are validating new amended clays (Mazzieri et al., 2008; Katsumi et al., 2008; Di Emidio, 2010 a&b, Razakamanantsoa et al., 2012; Di Emidio et al, 2013; Malusis and McKeehan, 2013; Malusis and Di Emidio, 2014).

The purpose of this research is to investigate, through oedometer and hydraulic conductivity tests, how the swelling and permeability characteristics of a modified bentonite with anionic polymer, HYPER clay, and regular sodium bentonite can be affected by wet-dry cycles and contact with seawater.

2 MATERIALS

The principle of HYPER clay is to combine sodium bentonite with an anionic polymer – Carboxymethil Cellulose, Na-CMC. The treatment method consists in mixing the base clay with a polymeric solution 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 (Di Emidio, 2010 a&b). In this research 2% and 8% of polymer, by dry weight of clay, were used. The material is characterized by 7.5 kg/m^2 of dry mass per unit area (as used in Lin and Benson, 2000) and 0.718 porosity.

Table 1. Characteristics of tested soils (NaB= untreated sodium bentonite; HC+2%= HYPER clay with 2% of polymer; HC+8%= HYPER clay with 8% of polymer

Characteristics	NaB	HC+2%	HC+8%
Swell index (ml/2g)	19	26	52
Specific gravity	2.66	2.53	2.25
Smectites – Mica (%)	91-0	91-0	91-0
Quartz – Opal (%)	4-0	4-0	4-0
Feldspars (%)	2	2	2

Deionized water (DI) was used during the first wet cycle for oedometer and hydraulic conductivity tests. The electrical conductivity of the DI is EC=0.002 mS/cm, the pH=7.57 and the redox potential is Eh=293 mV. In the second cycle the specimens were then hydrated with seawater (SW) collected in the North Sea (Ostend, Belgium). The salt solution has EC= 44.8 mS/cm, salinity= 28.6, pH= 7.42 and Eh= 183 mV. Some properties of the solution are listed in Table 2.

Table 2. Chemical properties of the electrolyte solutions

Solution	EC	Salinity	pH	Eh
	[mS/cm]	[-]	[-]	[-]
Deionized water	0.002	0.0	7.57	293
Seawater	44.8	28.6	7.42	183

3 METHODS

The various cycles followed in this research, for swell tests and hydraulic conductivity tests, are illustrated in Figure 1. More details are given in the next paragraphs.

WET1 DI 20 days* 30 days**	→	DRY 1 Oven 40°C	→	WET2 SW 20 days* 30 days**	→	DRY 2 Oven 40°C	→	WET3 SW 20 days* 30 days**	→	ongoing

* Swell test: until around 16 days.

** Hydraulic conductivity tests: until steady state, at least two PVF were reached and chemical equilibrium.

Figure 1. Various phases followed

3.1 *Swell tests*

Free swell tests in oedometer cells were performed to analyze the swelling ability and self-healing capacity on untreated sodium bentonite, HYPER clay 2% and HYPER clay 8%.

Tests were performed with DI and SW in accordance with Method A of ASTM D 4546, without loading the specimens after the primary swell. The specimens were placed in 7cm diameter oedometer cells and inundated with the hydrating liquids, DI and SW. The specimens were allowed to swell vertically under a seating pressure of 1kPa applied by the weight of the top porous stone and load plate. Readings were recorded by a displacement transducer during hydration.

According to Lin and Benson (2000), the termination criteria was around 400 hours (16 days) of hydration. Even if sometimes equilibrium was still not established, it was detected that the rate of swelling decreased substantially after 400 h (Lin and Benson 2000). This termination criteria also fulfilled the standard NF P 84-705 (AFNOR, 2008). When at least 90% of the infinite swell had been reached (Guyonnet et al., 2005; Guyonnet et al., 2009; and Rosin-Paumier et al., 2010), in case swell occurred, the tests were terminated.

Test specimens were dried at 40°C into the oven inside the oedometer cells for about 20 days. At the end of every dry step, the cells were placed back in the oedometer apparatus and hydrated again.

The sequence started with the first wetting. The cells were inundated with deionized water, to establish the baseline swelling. Afterwards, the hydrating cycles were conducted using seawater.

3.2 *Hydraulic conductivity tests*

Hydraulic conductivity tests were conducted on untreated sodium bentonite, HYPER clay 2% and HYPER clay 8%. Specimens were permeated with deionized water, during the first wet cycle, and then with seawater in the subsequent cycles. The purpose was to simulate desiccation during dry seasons and rehydration during rainy seasons (Melchior, 1997) in presence of seawater. Tests were carried out in rigid wall permeameters. Due to sidewall leakage, the specimen HYPER clay 8% was moved to a flexible wall permeameter (with an effective stress of 15 kPa and the second wet cycle is still on going. Termination criteria were considered to evaluate interactions between barrier soils and permeant solutions (Shackelford et al., 2000). The dry phase could begin when the following termination criteria were fulfilled (ASTM D 5084; Ruhl and Daniel, 1997; Jo et al., 2005; Lee and Shackelford, 2005; Malusis and McKeehan, 2013): steady hydraulic conductivity was achieved, at least two pore volumes of flow (PVF) have passed through the specimen and chemical equilibrium was reached. Chemical equilibrium was defined based on the EC ratio criterion in ASTM D 6766 (1.0±0.1) and this guarantees that the chemical reactions between the permeant liquid and the bentonite are complete (Jo et al., 2005). At about ¼ PV of outflow, specimens were collected and analyzed to measure EC, pH, salinity and Eh.

Dehydration was performed in a 40°C oven for about 20 days, or until steady state was reached. During the first dry cycle NaB and HC + 2%, reached quickly the steady state due to higher exposure of the specimen to the heat. This type of exposure was confined in the following cycles to represent better the gradual dehydration expected in situ.

4 RESULTS

4.1 *Swell tests*

The effects of swelling behavior are shown in Figure 2. The vertical swell versus time during various cycles is reported. The wet steps are plotted with markers, while the dashed lines represent initial and final height of dehydration. From the graph it is clear that HYPER clay 8% swelled the most, whereas the untreated bentonite swelled the least. Moreover, while sodium bentonite and HYPER clay +2% reached equilibrium, HYPER clay +8% was still adsorbing water and increasing in height. Since HYPER clay +8% was too swellable, it lost some soil from the bottom of the oedometer ring and a replicate was made, HC+8% BIS in the graph. The behavior of both specimens was found to be very similar, indicating that the loss of soil did not affect considerably the results. The increase of the swell with increasing polymer dosage (up to 8%) is consistent with Di Emidio (2010). The author showed that the interplatelet space increased with increasing polymer dosage, which corresponds to an increase of the swell pressure between platelets. This behavior can be due to the additional polymer charge intercalated between platelets, which results in adsorption of a large number of cations and water molecules during wetting.

The specimens were then dried for 20 days. The graph shows an increase of heights for HYPER clay, probably because water was retained. On the contrary, untreated bentonite decreased its height.

Starting from the second wet cycle, specimens were submerged in seawater. The swell dropped after the second cycle. For HYPER clay 8% specimen the height increased during the first dry cycle until 20.35 mm and then dropped to 18.66 mm when seawater was used.

HYPER clay 2% showed a similar behavior. It swelled up to 11.45 mm during the first cycle, increased its height during the dry cycle, and at the end of the second wet 11.87 mm of swell was achieved. The final height was similar to that of the first cycle, thanks to the swelling during dehydration. The untreated bentonite swelled approximately 7.2 mm in the first cycle and then dropped to 5.9 mm in the second one.

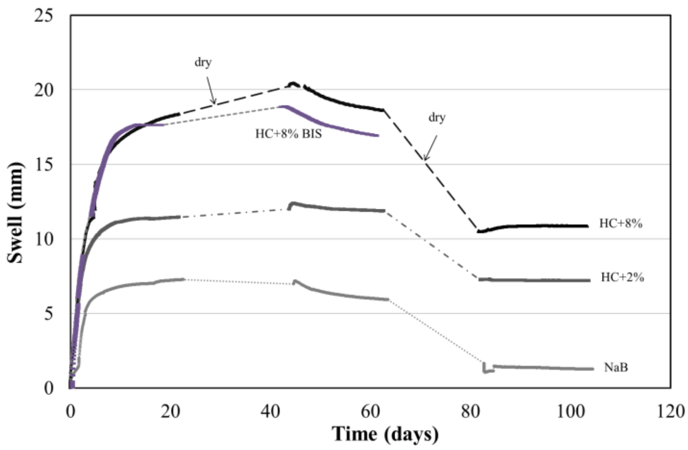

Figure 2. Temporal behavior of swell tests at various wet-dry cycles

Figure 3 shows the water content percentage over time during the second dry cycle. It is possible to notice the different behavior of the specimens. During the wetting phase, HYPER clay 8% adsorbed the largest amount of water, up to 350%, considerably higher than 266% of untreated bentonite.

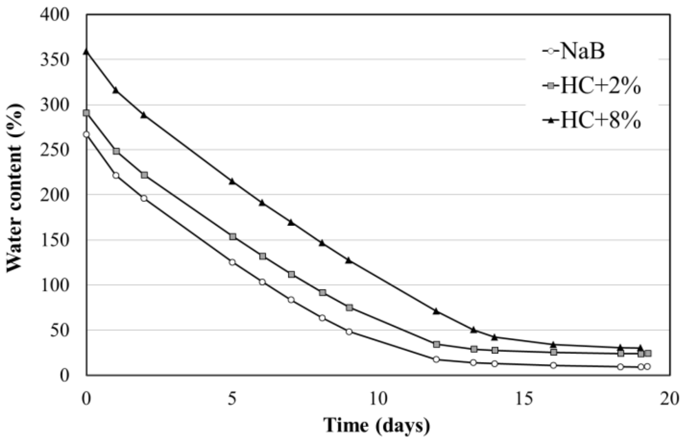

Figure 3. Water content related to the second dry cycle

The second dry cycle ended after 20 days as no additional weight loss was observed. At this points NaB presented a water content of 9.36%, HYPER clay 2% water content was 24.01% and HYPER clay 8% ended with 30.20% of water content. Although no further reduction of mass was observed, HYPER clay 8% retained more water and it showed no visible cracks.

For the untreated bentonite cracks were already visible after about 10 days of dehydration. Furthermore, test specimens shrank volumetrically and treated bentonites formed a monolithic hard disk, as shown in Figure 4 that represents the specimens at the end of the second dry cycle.

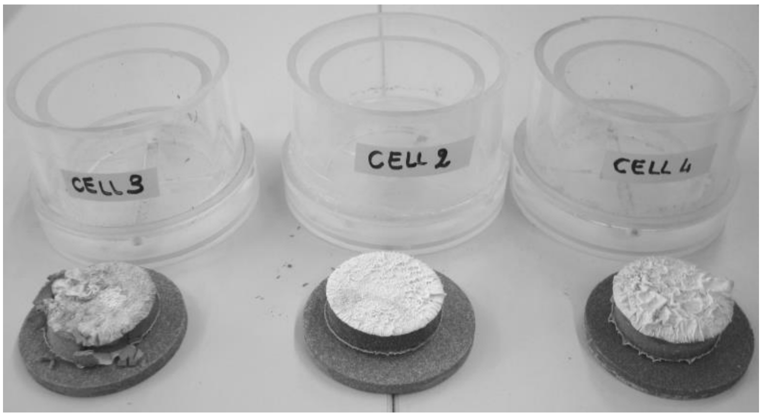

Figure 4. Test specimens after the second dry cycle. CELL3 = NaB; CELL2 = HC+2%; CELL4 = HC+8%

Once back to the oedometer apparatus, the untreated sodium bentonite was quickly wetted by the solution because of desiccation cracking. This led to a crumbling of the material on the bottom porous stone. Sodium bentonite healed cracks at expense of its height. In contrast, HYPER clay 8% increased slightly in vertical and lateral directions. HYPER clay 2% showed an intermediate behavior, at the beginning it maintained its height but later on, it started to swell also in the horizontal direction. As reported by Lin and Benson (2000), initial exposure to deionized water delays ion exchange, but only temporarily. Then, as the salt solution penetrates the bentonite, cation exchange will occur and calcium will be replaced for sodium. This effect may be accelerated when cracks are present, like happened with sodium bentonite. The better behavior of treated bentonites suggests the permanence of the polymer in the interlayer region after addition. To conclude, an overall overlook to the cycles performed (Figure 2) helps to better understand the results. The swelling capacity increased with increasing polymer dosage. The HYPER clays have shown larger swell in seawater respect to the untreated bentonite. The sodium untreated bentonite collapsed after three wet-dry cycles. The collapse compared to the reference swelling in DI and the swelling in SW is much larger in untreated bentonite than in HYPER clay. As shown in Figure 2, the final height of the HYPER clays (after two wet-dry cycles in seawater) was equal or higher (10,85 mm for HC+8%) compared to the initial swell of untreated bentonite in deionized water (7,2 mm).

4.2 Hydraulic conductivity tests

The results of hydraulic conductivity tests subjected to wetting and drying are illustrated in Figure 5. The effects of polymer treatment start to be more evident in the second cycle. During the first wet cycle, all the specimens have shown low hydraulic conductivities. Once hydrated with seawater, it is possible to notice that the untreated bentonite increased its hydraulic conductivity by three orders of magnitude, fluctuating around $3{,}3 \times 10^{-8}$ m/s. HYPER clay 2% also showed some increase in hydraulic conductivity to sea water but the permeability remains one order of magnitude lower compared to untreated bentonite (around $1{,}6 \times 10^{-9}$ m/s). HYPER clay 8% retained the lowest hydraulic conductivity, $4{,}2 \times 10^{-11}$, showing the best behavior regarding watertightness. HC+2% and HC+8% improved the sealing capacity of the bentonite in sea water, after a dry-wet cycle.

Tests duration was 28 pore volumes of flow for NaB, 8 pore volumes of flow for HYPER clay 2% and 0,35 PVF for HYPER clay 8% after 21 days (HC+8% is still ongoing). When termination criteria and chemical equilibrium were fulfilled tests were stopped.

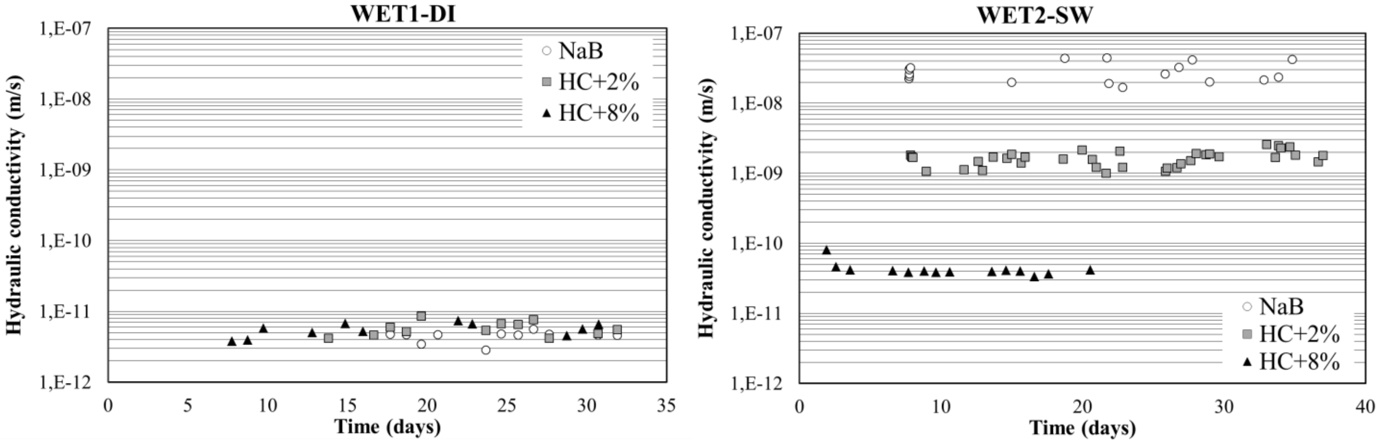

Figure 5. Hydraulic conductivity to deionized water (left hand plot, wet 1, first cycle) and seawater (right hand plot, wet 2, second cycle) of NaB, HC+2% and HC+8%

HYPER clay showed low hydraulic conductivity. This is due to their thick diffuse double layer (DDL) maintained open in the long-term due to the irreversible adsorption of the polymer into the clay (Di Emidio, 2010b). The polymer intercalation in the interlayer maintains the DDL thick adsorbing lots of immobile water molecules and ions. Therefore, the pore space available to the flow is restricted and the flow pathways are long and tortuous, decreasing the permeability of the soil.

5 CONCLUSIONS

Wet-dry cycles in seawater can strongly affect the behavior of GCLs because two important processes are involved: cation exchange and cracks formation. A reduction in swelling and loss of self-healing capacity are caused from cation exchange. Therefore, if cation exchange is accompanied by cracks formation, the bentonite structure is further damaged, the hydraulic conductivity of the bentonite increases and the overall GCL performance is negatively affected. The aim of this study was to simulate closely the actual condition of GCLs in the field. Even if polymer adding improves bentonite behavior, strong electrolyte solutions may lead to loss of efficiency. This effect is due to the compression of the diffuse double layer that reduces the swelling ability and increases the hydraulic conductivity of the bentonite.

HYPER clay treatment showed beneficial effects on the swelling and hydraulic behavior of the bentonite exposed to seawater. The swelling ability of treated bentonite was larger than that of the untreated bentonite even after wet-dry cycling. Sodium bentonite swelling was affected by desiccation cracking after the second cycle, which influenced the swelling capacity of the specimen in the next wet cycle. The HYPER clays have shown larger swelling in seawater with respect to the untreated bentonite. The final height of the HYPER clays, after two wet-dry cycles in seawater, was equal or higher (10,85 mm for HC+8%)compared to the height of untreated bentonite (7,2 mm) after the first cycle in deionized water. Hydraulic conductivity tests also provided good results for HYPER clays, the permeability of the amended clays was maintained lower after the dry cycle ($4,2 \times 10^{-9}$ m/s for HC+2% and $1,6 \times 10^{-9}$ m/s for HC+8%), with respect to the untreated sodium bentonite ($3,3 \times 10^{-8}$ m/s), thanks to the thick diffuse double layer, maintained in the long-term.

Further research will investigate the development of cracks formation and the self-healing capacity of HYPER clay after several wet-dry cycles.

The practical implication of this study is that HYPER clay may be used instead of untreated bentonite in aggressive environment as it is more resistant to salt attack during wet-dry cycling. However, a protective soil cover layer is always recommended.

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