Polymer treated clays subjected to wet-dry cycling with seawater

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ABSTRACT

Free swell in oedometers and hydraulic conductivity tests were conducted to assess how wet-dry cycling affects swell and the hydraulic conductivity of geosynthetic clay liners (GCLs). Similar tests were performed on clays treated with 2% and 8% of polymers to compare their efficiency after wet and dry cycles using deionized water and seawater. Swelling of the untreated clay decreased sharply after two wetting cycles with salt solution and cracks were noticed since the second dry. The amended clays showed good swelling capacity after three cycles, presenting fine cracks only during the third dry. The hydraulic conductivity of the untreated specimens, once permeated with seawater, increased dramatically in respect of the treated bentonite. The permeability increased because cracks formed during desiccation did not fully heal after rehydration.

Keywords: bentonite, polymer, hydraulic conductivity, swelling.

1 INTRODUCTION

Compacted Clay Liners (CCLs) and Geosynthetic Clay Liners (GCLs) are often used for waste containment facilities due to the ability of the clay to perform as a barrier that restricts the passage of solutes. Therefore, clay liners are used as cover or base lining components to avoid infiltration to the waste and the release of leachate.

GCLs are factory-manufactured hydraulic barriers containing a thin layer of bentonite sandwiched between geotextiles or glued to a geomembrane. Sodium bentonite clay is widely used in GCLs because of its low hydraulic conductivity to water and high swelling ability. The geosynthetic layers can be glued, bonded with an adhesive, needle-punched, or stitch-bonded with 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, 2002).

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, 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.

The efficiency of the barrier is related to the osmotic adsorption of water molecules between montmorillonite platelets, which is the primary mineral within sodium bentonite. Sodium bentonite is known to present better swelling ability and lower hydraulic conductivity than calcium bentonite. However, sodium bentonite is sensitive in environments where multivalent cations are present (Scalia et al. 2013). In fact, electrolyte fluids are likely to exchange the sodium ions into calcium leading an increase of the hydraulic conductivity and the osmotic swelling does not occur. Cation exchange occurs slowly, depending on the rate of diffusion of the cations. 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, increasing the hydraulic conductivity of bentonite (Egloffstein, 2001). Komine et al. (2009), investigated the effect of artificial seawater on the swelling characteristics of compacted clay of radioactive waste repository. The authors reported a slight susceptibility of calcium bentonite to seawater, while sodium bentonite was more affected, especially when low vertical stress levels were applied.

Clay liners may be influenced by repeated cycles with temperature changes, which may lead to desiccation of the bentonite and associated cracking. Crack formations result in reduction of the liner thickness, allowing potentially preferential flow paths with increase in permeability as a consequence (Hewitt and Philip, 1999). Desiccation of the clay liner in composite lining system is reported in several case histories. Basnett and Brungard (1992) reported it in a compacted clay liner in a composite landfill lining system. The authors noticed that the clay on the bottom of the landfill was in good condition because the condensed water, formed overnight, rehydrated the clay during the day. This did not happen on slopes as the liquid did not accumulate. Another research, carried out by Hewitt and Philip (1999), studied cracks formation during a landfill extension in the UK. The landfill comprised 1m thick compacted clay liner overlain by HDPE liner. Three months after construction, control of the liner revealed that the clay forming the perimeter presented significant cracking due to temperature cycles. James et al. (1997) exhumed a GCL consisting of sodium bentonite to study why a GCL cover was leaking. It was found that cation exchange have occurred causing flocculation of the bentonite and shrinkage. As a consequence of this process, cracks were observed on the GCLs. The authors suggest avoiding sources of calcium nearby GCLs that may be prone to Na for Ca ions exchange.

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; Meer and Benson, 2007) 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 in $CaCl_2$ increased.

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

The authors in a preliminary study (De Camillis et al. 2014) found that the treatment of sodium bentonite with anionic polymer, HYPER clay, compared to regular sodium bentonite, improved the swelling ability and the hydraulic conductivity over two consecutive wet-dry cycles in seawater. That study is followed by the present paper which has the aim to evaluate the effects of the more wet-dry cycles in seawater.

2 MATERIALS

The adding value of HYPER clay technology was investigated in this research. The amended bentonite was compared with untreated sodium bentonite (NaB).

The principle of HYPER clay is to combine sodium bentonite with an anionic polymer (Carboxymethyl Cellulose, Na-CMC). The treatment method consists of mixing the base clay with a polymeric solution with a mechanical stirrer for 30 minutes to increase the surface area available for polymer adsorption. 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 (HC+2% and HC+8% respectively). A replicate of HYPER clay 8% (HC+8% BIS) was made for the swell test. The material is characterized by 7.5 kg/m^2 of dry mass per unit area, as used in Lin and Benson (2000). Other characteristics of tested soils are listed in Table 1.

Deionized water (DI) was used during the first wet cycle for oedometer and hydraulic conductivity tests. The electrical conductivity of the DI has EC=0.002 mS/cm, the pH=7.57 and the redox potential is Eh=293 mV. 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 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
Smectites-Mica (%)	91-0	91-0	91-0
Quartz-Opal (%)	4-0	4-0	4-0
Feldspars (%)	2	2	2

Table 2: Chemical properties of the electrolyte solutions

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

3 METHODS

3.1 Swell tests

The swelling ability and the self-healing capacity were analysed through free swell tests on untreated sodium bentonite, HYPER clay 2% and HYPER clay 8%. The specimens were placed in oedometer cells with 7 cm of diameter and loaded with a topcup by 1 kPa. Readings were recorded every hour by a displacement transducer connected to a computer during hydration.

The termination criteria was around 20 days of hydration. Constant height was always reached, with the exception of the first cycle with deionised water.

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 in presence of seawater. Tests were carried out in rigid wall permeameters with 7.1 cm of diameter. A porosity of 0.718 was fixed for all the specimens. Since sidewall leakage occurred during the second wet cycle, HYPER clay 8% was moved to a flexible wall permeameter. An effective stress of 15 kPa was applied to simulate the in situ condition. (Bouazza, 2002; Mazzieri and Pasqualini, 2008; Scalia and Benson, 2011).

Termination criteria were followed to evaluate interactions between barrier soils and permeant solutions (Shackelford et al, 2000). Tests were stopped when steady hydraulic conductivity was achieved (ASTM D 5084), 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). At about ¼ PV of outflow, specimens were collected and analysed 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 sample 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

Specimens of untreated sodium bentonite, HYPER clay 2% and HYPER clay 8% were subjected to wet-dry cycles. Figure 1 shows the vertical swell versus time during three wet-dry cycles. The wet phase are draw with markers, while the dashed lines represent initial and final height of dehydration phases.

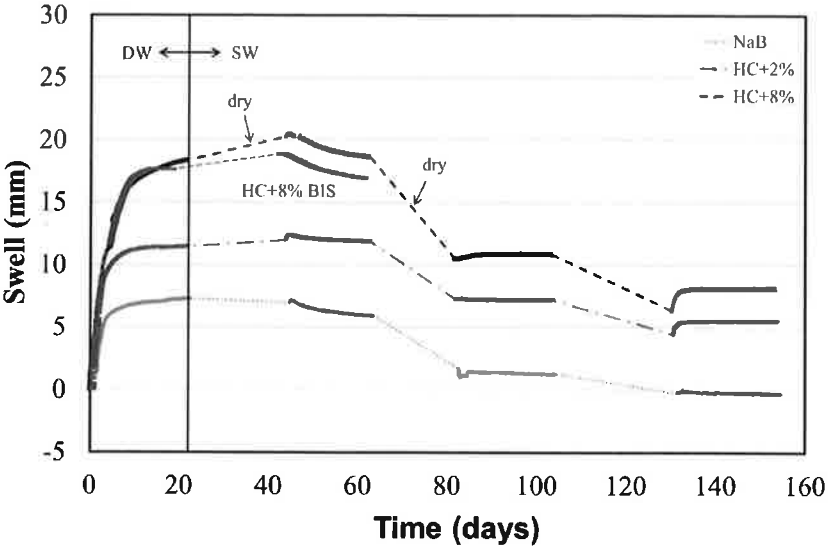

Figure 1. Temporal behaviour of swell tests at various wet-dry cycles

The first wet cycle was performed with deionized water in order to have a base reference. As the specimens were submerged in DI, HYPER clay 8% swelled the most, whereas the untreated bentonite swelled the least. HYPER clay 8% was so swellable that it did not reach equilibrium, even after 20 days. Moreover, it lost some soil from the bottom of the oedometer ring and a replicate was made, HC+8% BIS shown in the graph. The behavior of both specimens was found to be very similar, indicating that the effect of the loss of soil was negligible. The increase of the swell with increasing polymer dosage (up to 8%) is consistent with Di Emidio et al. (2013). The author showed, through XRD analysis, that the interlayer space increased with increasing polymer dosage, which corresponds to an increase of the swell pressure between platelets. This behaviour 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 placed in the oven for 20 days. At the end of the first dry step, the treated clays presented an increase in height, probably because water was retained and it allowed to swell more. An overall beneficial effect was noticed for treated bentonite with anionic polymer when submerged with deionised water. The next cycles were performed using seawater. The swell decreased during the second wet cycle but, thanks to the considerable swelling of the first cycle, HYPER clays still presented a height larger compared with that of the respect untreated bentonite.

Figure 2 shows an example of the water content decrease over time during the second and the third dry cycles. All the specimens reached a constant mass loss after around 20 days but the water content of each of them was rather different. HYPER clay 8% was still showing the best behaviour because it adsorbed the largest amount of water, up to 350%, and ended with 30.2%. At the same time, untreated bentonite reached a very low water content, 9.36% and HYPER clay 2% presented 24% of water content. HYPER clays retained more water and the specimens showed no visible cracks indicating a higher resistance to salt solution.

The untreated bentonite showed visible cracks already during the first days of dehydration. Furthermore, test specimens shrank volumetrically and treated bentonites formed a monolithic disk, as shown in Figure 3 that shows the specimens at the end of the second and third dry cycles.

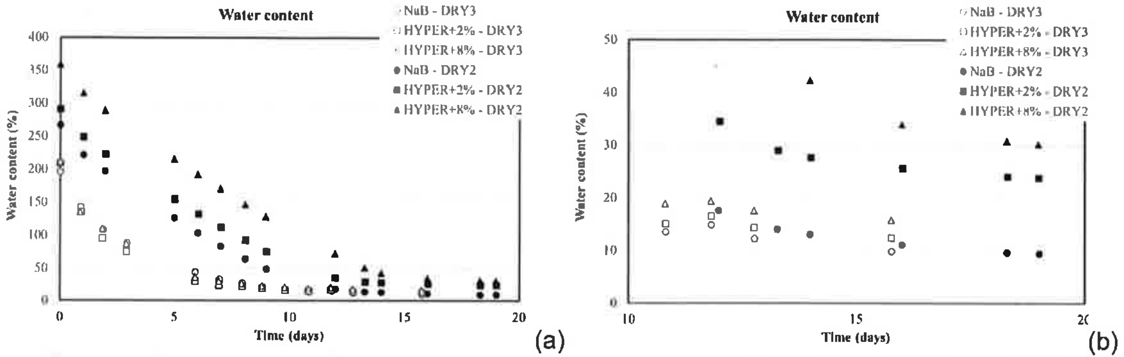

Figure 2. Water content related to the second and third dry cycles (a) and close-up of the water content related to the last days of the second and third dry cycles (b)

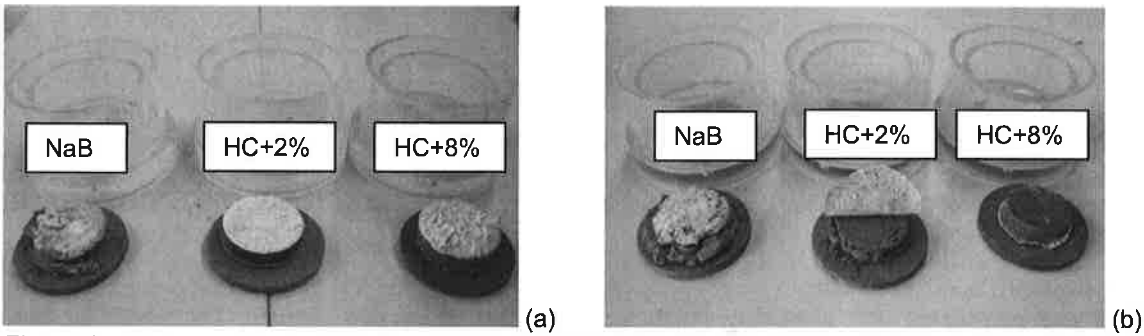

Figure 3. Test specimens after the second (a) and third (b) dry cycles. CELL3 = NaB; CELL2 = HYPER+2%; CELL4 = HYPER+8%

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 the expense of its height. In contrast, HYPER clay 8% increased slightly in vertical and lateral direction. HYPER clay 2% showed an intermediate behaviour, at the beginning it maintained its height but later on it started to swell also in the horizontal direction. Furthermore, HYPER clay 8% until the fourth wet cycle presented a height comparable to the one of NaB at its maximum swelling with deionised water. As reported by Lin and Benson (2000), an 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, as it was the case with sodium bentonite. The better behaviour of treated bentonites suggests the permanence of the polymer in the interlayer region after addition.

The water content of the third dry cycle is also reported in Figure 2. As expected, the adsorbed amount of water decreased with increasing number of wet-dry cycles and the constant weight was reached earlier than 20 days. A difference in final water content was still found. Untreated sodium bentonite reached 10% of water content, HYPER+2% ended with 12.4% and HYPER+8% with 15.7% of water content. During this cycle, crack formation were noticed also on treated bentonite, but they were very fine and they did not yield to the collapse of the specimen structures, as shown in Figure 3 (b).

To conclude, the swelling capacity increased with increasing polymer dosage. The sodium untreated bentonite collapsed after three wet-dry cycles, while HYPER clays were still maintained a consistent height until the fourth wet cycle.

4.2 Hydraulic conductivity tests

Hydraulic conductivity tests were carried out on untreated sodium bentonite, HYPER clay 2% and HYPER clay 8%. The specimens were permeated first with deionized water and after the first dry cycle with seawater. Figure 4 illustrates the results of hydraulic conductivity tests of these specimens subjected to wet-dry cycles. During the first cycle with DI, all the specimens showed low hydraulic conductivity, without large difference between them. The effect of polymer addition started to be more evident in the following cycle. In fact, HYPER clay 2% increased its hydraulic conductivity by two order of magnitude, while untreated sodium bentonite more than three, when hydrated with SW. HYPER clay 8% presented the best behavior in contact with seawater, this test is still running because chemical equilibrium is not yet reached, due to the low permeability. The permeation ended when chemical equilibrium was reached and 25 pore volumes of flow passed through NaB and 9 pore volumes of flow through HYPER clay 2%.

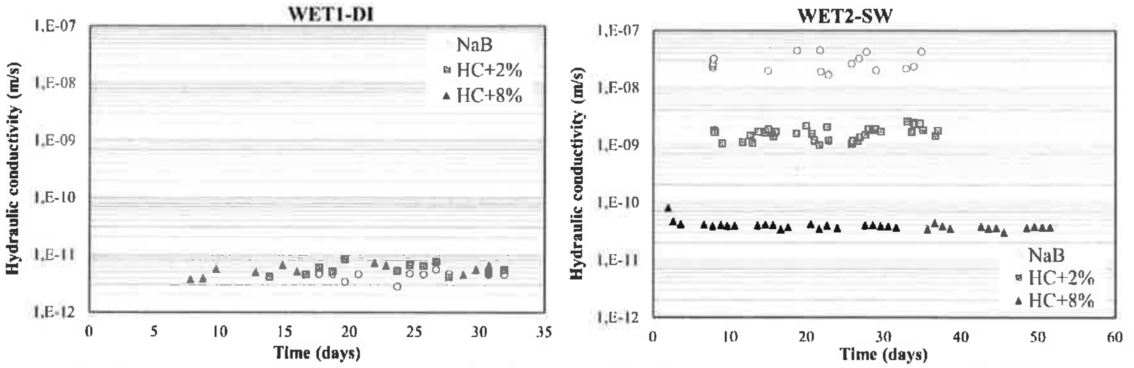

Figure 4. Hydraulic conductivity to deionized water (WET1-DI) and seawater (WET2-SW) of NaB, HC+2% and HC+8%.

The expected damage of sodium bentonite is due to several reasons. Once back to the permeameter, NaB was permeated with seawater, which represents an aggressive solution. The bentonite self-healed the fissures, formed during the first dry, but at this point cation exchange occurred, increasing the permeability. The behavior of bentonite is dominated by the thickness of the diffuse double layer (DDL). The DDL is in fact influenced by the concentration and the valence of the cations present in the electrolyte solution (Egloffstein, 2001). Therefore, increasing these parameters the thickness of the DDL decrease and the extension and tortuosity of the flow paths between clay particles decreases. On the other hand, HYPER clays showed lower hydraulic conductivities respect untreated sodium bentonite. This is due to their thick diffuse double layer 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 helps to keep it thick adsorbing lots of immobile water molecules and ions. Therefore, the pore space is restricted and the flow pathways will be long and tortuous, decreasing the permeability of the soil.

5 CONCLUSIONS

The efficiency of GCLs can be influenced by wet-dry cycles, especially if salt solutions are involved. The process that strongly affects the behavior is a combination of cation exchange and crack formation. Cation exchange leads to reduction in swelling and self-healing capacity. On the other hand, crack formation induces an increase of the permeability of the bentonite because the liquid can easily flow through the fissures before they are healed. For this reason the aggressive solution is more in contact with clay particles near the cracks and they are prone to cation exchange. These phenomena lead to worsening of GCLs performance, which are not able to contain leachate or liquid other than water. The aim of this study was to simulate closely the actual condition of GCLs in the field. Even if polymer addition improves bentonite behaviour, strong electrolyte solutions may lead to loss of efficiency. This effect is due to the compression of the diffuse double layer that will reduce the swelling ability and increase the hydraulic conductivity of the bentonite.

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HYPER clay treatment showed beneficial effects on the swelling and hydraulic behaviour of the bentonite exposed to seawater. The swelling ability of HYPER clays was significantly higher in respect to the untreated sodium bentonite. Moreover, crack formation was found after the second cycle on sodium bentonite, for this reason its swelling was greatly affected from desiccation. Hydraulic conductivity tests also provided good results for HYPER clays, the permeabilities were maintained low after the dry cycle 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 through hydraulic conductivity tests.

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 soil cover layer is always recommended to reduce desiccation to the minimum.

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