Impact of wet-dry cycles on the swell pressure of a polymer modified bentonite and theoretical interpretation of experimental results.

Effet des cycles de mouillage-séchage sur la pression de gonflement d'une bentonite traitée avec des polymères et interprétation théorique des résultats expérimentaux.

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ABSTRACT: Geosynthetic clay liners (GCLs) are widely used as hydraulic barrier to isolate waste disposal facilities thanks to their low permeability to water. In the field, the efficiency of GCLs can be altered by cation exchange and highly concentrated solutions during contact with aggressive liquids and by desiccation caused by temperature changes. As a consequence, wet and dry cycles lead to loss of swelling ability and cracking of the bentonite with possible loss of hydraulic efficiency and contamination of the surrounding ground. Swell pressure tests were performed to inspect the effect of wet and dry cycles with seawater on the swelling ability of untreated bentonite and a polymer modified bentonite, HYPER clay. Experimental results of untreated bentonite were back analyzed with a theoretical model to estimate the equilibrium concentration. Test results showed that HYPER clay presented improved behaviour in terms of swelling ability through the cycles.

RÉSUMÉ : Les revêtements d'argile et de géosynthétique (geosynthetic clay liners, GCLs) sont largement utilisés comme barrière hydraulique pour isoler les sites d'enfouissement sanitaire grâce à sa faible conductivité hydraulique. Dans le terrain, l'efficience des GCLs peut être altérée par l'échange de cations suite contact avec des liquides agressifs concentrés et aussi par la dessiccation provoquée par des changements de température. En conséquence, les cycles de mouillage–séchage provoquent une perte de la capacité de gonflement de la bentonite, et entrainent la formation de fissures avec une perte d' efficience hydraulique et une augmentation du risque de contamination. Des tests de pression de gonflement ont été effectués pour étudier les effets des cycles de mouillage-séchage en présence d'eau de mer sur la capacité de gonflement de la bentonite naturel et une bentonite traitée avec des polymères, l'HYPER clay. Les résultats expérimentaux obtenus avec la bentonite non traitée ont été analysés avec un modèle théorique qui a permis d'évaluer la concentration à l'équilibre. Les résultats des tests ont montré que la bentonite traitée (HYPER clay) montre une meilleure performance en termes de capacité de gonflement au cours de cycles de mouillage-séchage.

KEYWORDS: bentonite, polymer, wet-dry cycles, seawater, swell pressure.

1 INTRODUCTION.

Geosynthetic clay liners (GCLs) are widely employed to isolate waste disposal facilities in order to avoid release of leachate or gasses to the surrounding environment. GCLs are factory-manufactured hydraulic barriers containing a thin layer of bentonite sandwiched between two geotextiles, or glued to a geomembrane. GCLs provides low permeability to water, good swelling ability and limited thickness. In the recent years, a great number of theoretical and experimental studies has been produced on different types of bentonite and solutions in order to evaluate the mechanical behaviour and the swelling pressure of bentonites under different boundary conditions (Shackelford et al. 2000; Bouazza 2002; Dominijanni 2005; Jo et al. 2005; Dominijanni and Manassero 2012a,b; Dominijanni et al. 2013; Liu 2013; Hosney and Rowe 2014). In particular, Dominijanni et al. (2013) introduced in their theoretical model the parameter $\bar{c}_{sk,0}$, which represents the reference concentration of the charge of solid particles. Through this parameter they described how the swelling pressure (u_{sw}) can be expressed by the following equation when the pore solution contains a single salt constituted by monovalent ions (e.g. NaCl):

$$u_{sw} = 2RTc_s\left[\sqrt{\left(\frac{\bar{c}_{sk,0}}{2ec_s}\right)^2 + 1} - 1\right] \quad (1)$$

where c_s is the ion concentration of the external bulk solution, e is the bentonite void ratio, R is the universal gas constant, T is the absolute temperature of the external bulk solution. According to the equation, the swelling pressure increases decreasing void ratio and c_s and increasing $\bar{c}_{sk,0}$. The value of $\bar{c}_{sk,0}$ is proportional to the effective specific surface of the solid particles and is expected to decrease in case of aggregate microstructure, in which the montmorillonite lamellae forms tactoids.

In the field, GCLs might be exposed to cycles of wet and dry seasons, for example rainfalls or groundwater migration alternated by warm periods (Lin and Benson, 2000; Mazzieri and Pasqualini 2008; Rowe et al. 2011; Take et al. 2014; De Camillis et al. 2016a,b; Mazzieri et al. 2016). Contact with electrolyte solution in combination with desiccation lead to the compression of the diffuse double layer (DDL) of the bentonite and crack formation. The compression of the DDL impairs the swelling capacity of the bentonite, increasing the hydraulic conductivity. As a result, cracks formed during desiccation may not heal properly after rewetting with an electrolyte solution.

Modified bentonites have been developed in order to improve the hydraulic performance of barrier liners in aggressive environments (Mazzieri and Pasqualini 2006; Katsumi et al. 2008; Di Emidio 2010; Scalia et al. 2013; Bohnhoff and Shackelford 2014). Previous research has established the improved swelling, hydraulic and chemico-osmotic performance of bentonite treated with HYPER clay technology (Di Emidio 2010; Di Emidio et al. 2014; Di Emidio et al. 2015). HYPER clay is a polymer modified bentonite prepared by combining bentonite with sodium carboxymethyl cellulose (CMC). The DDL is then maintained open thanks to the intercalation of the CMC in the clay platelets and its irreversible adsorption even in presence of factors that generally accomplish the collapse of the interlayer.

This research seeks to investigate the swelling ability and crack formation of HYPER clay and untreated clay, by means of swell pressure tests, through wet and dry cycles in seawater. Moreover, the theoretical model developed by Dominijanni et al. (2013) was used to estimate the final concentration at the end of the tests and to set the basis for a possible prediction of the bentonite behaviour during wet and dry cycles.

2 MATERIALS

Sodium-activated bentonite untreated clay (UC) was used in this study and treated according to the HYPER clay procedure (as proposed by Di Emidio, 2010). The HYPER clay treatment consists of adding powder bentonite to a polymeric solution prepared by dissolving the anionic polymer sodium carboxymethyl cellulose (Na-CMC) in water. Then, this paste is first oven dried at 105℃ for 16 h, to irreversibly adsorb the polymer, and then ground first manually and then mechanically. In this research HYPER clay (HC) was produced with 8% of Na-CMC by dry mass of clay.

Sodium chloride (NaCl) solutions with increasing ionic strength (IS), ranging from 0.001 M to 2 M were used for a reference series to back analyse the results with the theoretical model. The chemical properties of the solutions used in this study are presented in Table 1. In addition, wet and dry cycles were simulated using deionised water (DW) during the first wet cycle and natural seawater in the consecutive cycles.

Table 1. Solutions characterization. IS: Ionic Strength; EC: Electrical conductivity

	Initial IS [M]	*Initial EC [mS/cm]*	*Final IS [M]*	*Final EC [mS/cm]*
NaCl	0.001	0.16	0.03	3.27
	0.6	55.5	0.74	59.5
	2	150	2.15	155
Seawater	0.764	48.8	NA	NA

3 METHODS

The swell pressure set up (Di Emidio, 2010) consisted of a stainless steel ring of 7.1 cm diameter accommodated in a standard one-dimensional oedometer cell. The cell was located in a frame provided with a load cell connected to a computer. The load cell was kept fixed, in order to maintain constant height during the test. Powder air-dried bentonite was evenly spread by assuming a density of 4.5 kg/m^2 and the final hydrated specimen had a porosity n = 0.718. After sample assembling, the oedometer was inundated with the testing solution.

Reference swell pressure tests were performed on UC with increasing ionic strength. Tests were concluded when constant swell pressure was achieved and the final electrical conductivity (EC) values were recorded.

A sample of UC (UC_DW+SW) and HC (HC_DW+SW) were subjected to wet and dry cycles and tested by means of swell pressure test. The samples were first hydrated for 14 days, then oven dried at 40℃ (until the water content was below 25%) and then hydrated again.

4 RESULTS

4 .1 *Swell pressure*

The swell pressure values (u_{sw}) of untreated bentonite are plotted versus the initial and final ionic strength in Figure 1. There is a linear relationship between EC and concentration of NaCl solutions, listed in Table 1. Using this linear relationship, the EC measured at the end of the swell pressure test as used to calculate the equilibrium concentration and the final ionic strength of the hydrating solutions. This procedure was necessary as the bentonite was not subjected to removal of soluble salts prior of being tested.

The difference between initial and final electrical conductivity decreased increasing IS. Therefore, using 0.001 M ions that were released from the bentonite into the solution increased considerably the final concentration of the hydrating liquid (up to 0.03 M). Whereas, the difference became negligible when approaching to 2 M.

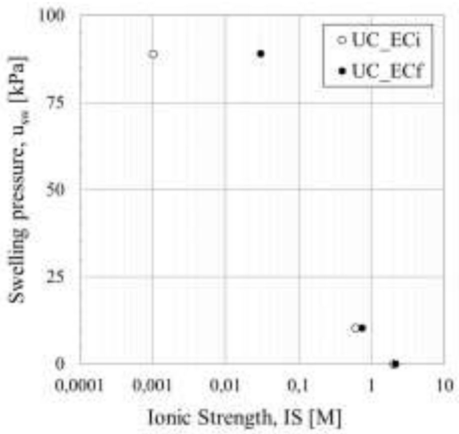

Figure 1. Swell pressure results of untreated bentonite versus initial (EC_i) and final (EC_f) ionic strength.

As expected, the swell pressure was reduced increasing NaCl concentration. When hydrated with 2 M NaCl, the UC did not swell and the swelling pressure recorded was taken equal to zero. The 2 M NaCl concentration might be considered as threshold concentration at the considered void ratio after which the osmotic swelling might not occur anymore and the bentonite undergo only the crystalline swelling. This trend is in accordance with the Gouy-Chapman diffuse double layer theory. The DDL is prone to decrease its thickness increasing valence and concentration of the ions in the interlayer surface (McBride, 1994). As a consequence, the swelling ability is inhibited when the cations are high concentrated in the solution due to the thin double layer surrounding clay particles and an aggregate structure of the bentonite.

4 .2 *Wet and dry cycles*

A sample of Na-activated bentonite and HYPER clay were subjected to three wet and dry cycles and the swell pressure was measured during the hydration cycles (Figure 2). Note that the samples were hydrated with deionized water in the first cycle and seawater was used in the consecutive cycles.

The swell pressure was measured based on the area of the samples at the end of the wetting cycles. However, the height and diameter of UC were not constant throughout the sample, as it can be observed in Figure 3. For this reason, the average diameter was considered for the calculation of the area.

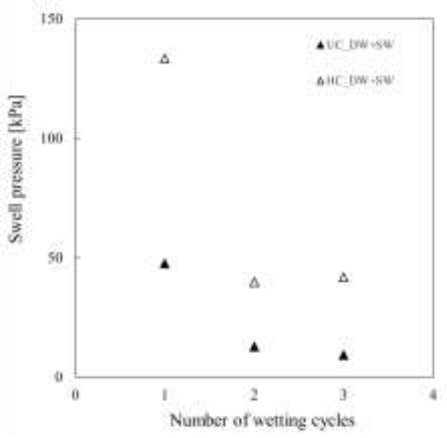

Figure 2. Swell pressure at the end of the wetting cycles

As expected, the swell pressure decreased increasing number of cycles. Untreated bentonite swelled up to 46.03 kPa during the first cycle in DW. After being desiccated, it was hydrated with seawater and the u_{sw} sharply decreased to 16.21 kPa and 12.34 kPa during the second and third cycle respectively. An interesting finding is that UC_DW+SW likely presented still osmotic swelling after three cycles. This can be observed by the swell pressure which was not zero until the third cycle. In order to be able to measure the osmotic swelling, enough space was left in the oedometer cell to let the sample undergo crystalline swelling first and then record the pressure applied by the osmotic swelling. On the other hand, HYPER clay swelled up to 133 kPa during the first cycle and the recorded swell pressure during the second cycle was 40 kPa. Therefore, the polymer modified bentonite presented better behaviour even after wet and dry cycles with seawater compared to untreated bentonite.

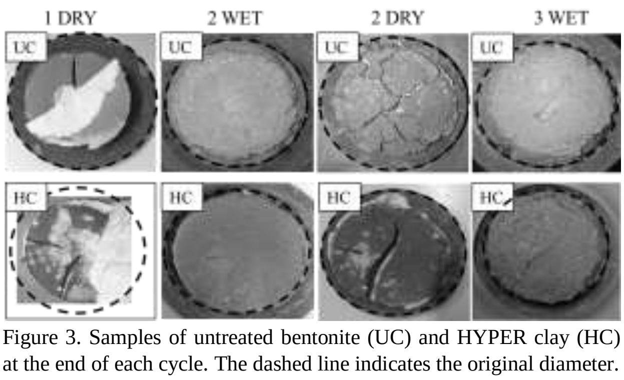

Figure 3. Samples of untreated bentonite (UC) and HYPER clay (HC) at the end of each cycle. The dashed line indicates the original diameter.

Both samples shrunk during the first drying cycle, as it is possible to notice in Figure 3. Therefore, upon rewetting with SW the samples first needed to swell in radial direction, leading to a lower vertical swell compared to the first cycle. The initial diameter of 7.1 cm was never fully recovered and therefore the void ratio changed. Additionally, cracks formed during desiccation of UC were healed during the second wetting and partially healed during the third wetting cycle with seawater. Nevertheless, Figure 3 shows that the swelling of UC_DW+2SW was not isotropic, the diameter of the sample was not constant and some kind of conous shape was observed upon rewetting. On the other hand, HYPER clay hydrated in a more uniform way (as a cylinder) and presented less cracks, as also observed by De Camillis et al. (2016b).

However, the main cause of the decrease in swell pressure which is connected also to the phenomena described above, was the contact with seawater. The high concentration of monovalent cations (mainly Na^+) and the presence of several divalent cations (Ca^{2+} and Mg^{2+}) in seawater might have compressed the DDL which contributed to the decrease in swell pressure. This result complies with the research of Di Emidio (2010) who showed a decreasing swell pressure with increasing concentration and valence of the ions. In addition, the swell pressure is linked to the healing capacity. Therefore, as the swell pressure is reduced, the cracks formed during desiccation might not be completely healed once the sample is rewetted. However, HYPER clay presented higher swell pressure and better self-healing capacity compared to untreated clay. These results also agree with the research from De Camillis et al. (2016a,b) where the lower hydraulic conductivity of HYPER clay, through wet and dry cycles with seawater, is associated to its improved swelling ability. The better performance of HYPER clay might be linked to the adsorption and intercalation of the anionic polymer into the clay which helps to keep the interlayer open even during wet and dry cycles.

4 .3 *Back analysis of experimental results*

The theoretical model developed by Dominijanni et al. (2013) based on Donnan's equilibrium equations was used to back analyse experimental data.

The swell pressure of untreated bentonite versus the ionic strength was evaluated. In addition, the behaviour of the same bentonite subjected to wet and dry cycles with seawater was back analyzed through the theoretical curve found previously.

The best fitting of the theoretical curve with the experimental data was obtained by using a $c_{sk,0}$ equal to 0.205 M. The theoretical curve, together with the experimental results, is reported in Figure 4.

The experimental results of UC were in good agreement with the theoretical simulation for NaCl solution. Experimental data from UC_DW+SW were interpolated to the theoretical curve found for UC (Figure 4) to estimate the final ionic strength at the end of the test through the cycles. The final ionic strength and swell pressures of UC_DW+SW are provided in Table 2.

Table 2. Wet and dry final ionic strength (IS) and swell pressure (u_{sw}) of untreated bentonite (UC).

Cycles	*Solution*	*u_{sw} UC [kPa]*	*Final IS [M]*
1	DW	46	0.078
2	SW	16.2	0.24
3	SW	12.3	0.32

The first observation to emerge was that the swell pressure of UC_DW+SW during the first cycle in deionized water was lower than the swell pressure of UC to 0.03 M ionic strength. In addition, the swell pressure of UC_DW+SW during the second and third wetting cycle in seawater (EC = 48.8 mS/cm) was lower than the swell pressure of UC to 0.74 M (EC = 59.5 mS/cm) used to simulate the seawater (ECi = 55.5 mS/cm).

However, a positive correlation was found between the data of UC_DW+SW and the theoretical curve concerning the ionic strength. Indeed, looking at the last two points in the chart of UC_DW+SW, the lower swell pressure of the third cycle was associated to a higher concentration of the solution. This effect can be linked to a build-up in ionic strength of the wetting solution due to the water, and salts, retained in the sample at the end of each wetting cycle (Bouazza et al., 2007).

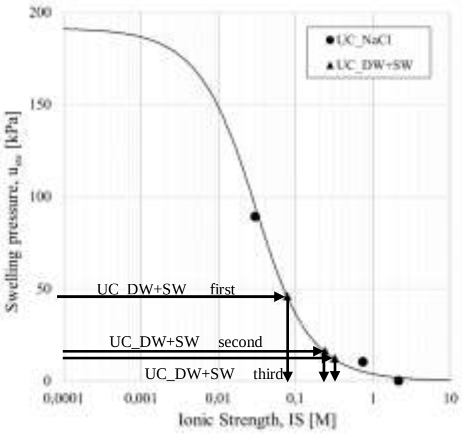

Figure 4. Theoretical interpretation of the swell pressure of sodium-activated bentonite.

The beneficial effect of prehydration can be seen comparing UC_NaCl and UC_DW+SW. Although the desiccation phases, the sample subjected to wet and dry cycles presented higher u_{sw} compared to the reference sample at comparable IS. A possible explanation can be related to the retained water in the bentonite structure which might delay the detrimental effect of wet and dry cycles (Lin and Benson, 2000; Mazzieri and Pasqualini, 2008; De Camillis et al., 2016). Prehydration with deionized water yields to a more resistant bentonite to aggressive solutions than non-prehydrated bentonite.

5 CONCLUSIONS

The impact of wet and dry cycles on the swelling ability of a polymer modified bentonite, HYPER clay, and untreated sodium activated bentonite was investigated by means of swell pressure tests. In addition, the theoretical model proposed by Dominijanni et al. (2013) was used to interpret experimental data of wet and dry cycles on Na-activated bentonite.

The swelling ability of HYPER clay was higher compared to that of untreated bentonite through wet and dry cycles. Moreover, HYPER clay presented less crack and a more homogeneous rehydration than sodium activated bentonite.

The theoretical curve was drawn based on the swell pressure of untreated bentonite to increasing ionic strength. The swell pressures through wet and dry cycles were back analyzed to estimate the equilibrium concentrations.

The results of this investigation showed that generally the ion concentration in the pore water increased increasing number of wetting cycles. However, care must be taken as several factors are involved in the mechanisms, such as salt concentration, effect of prehydration, and void ratio.

The study is limited by the lack of information on ion concentration at the end of each wetting cycle. Therefore, more research using controlled trials is required to better compare wether experimental results fit the theoretical curve.

6 ACKNOWLEDGEMENT

The authors would like to thank An-Sofie Lierman for her fundamental collaboration to the research work. Funding for this study was provided in part by the CWO (Commissie Wetenschappelijk Onderzoek) by Ghent University, Belgium.

7 REFERENCES

Bohnhoff G.L. and Shackelford C.D. 2014. Hydraulic conductivity of chemically modified bentonites for containment barriers. *7th Int. Congress on Env. Geotechnics,* Melbourne, 440–447.

Bouazza A. 2002. Geosynthetic clay liners. *Geotex. Geomem.*20(1).

Bouazza A., Jefferis S. and Vangpaisal T. 2007. Investigation of t he effects and degree of calcium exchange on the Atterberg li mits and swelling of geosynthetic clay liners when subjected t o wet and dry cycles. *Geotex. Geomem* 25 (3), 170-185.

De Camillis M., Di Emidio G., Bezuijen A. and Verastegui-Flores R.D. 2016a. Hydraulic conductivity and swelling ability of a polymer modified bentonite subjected to wet–dry cycles in se awater. *Geotextiles and Geomembranes*, 44(5), 739–747.

De Camillis M., Di Emidio G., Bezuijen A., Verastegui-Flores R. D., Van Stappen J. and Cnudde V. 2016b. Effect of wet-dry c ycles on polymer treated bentonite in seawater: swelling abilit y, hydraulic conductivity and crack analysis. *App. Clay Sci.*

Di Emidio G. 2010. Hydraulic and Chemico-osmotic Performance of Polymer Treated Clays. *PhD Thesis*, Ghent University.

Di Emidio G., De Camillis M., Bezuijen A. and Verastegui Flores R. D. 2014. Beneficial Impact of Polymer Treatment of Ca-b entonites on Long- Term Hydraulic Conductivity. *10th Internat ional Conference on Geosynthetics,* Berlin.

Di Emidio G., Mazzieri F., Verastegui-Flores R.D., Van Impe W. a nd Bezuijen A. 2015. Polymer-treated bentonite clay for chem ical-resistant geosynthetic clay liners. *Geosynthetic International* 22 (1), 125-137.

Dominijanni A. 2005. Osmotic properties of clay soils, *PhD thesis*, Politecnico di Torino.

Dominijanni, A. and Manassero, M. 2012a. Modelling the swelling and osmotic properties of clay soils. Part I: The phenomenol ogical approach. *Int. J. of Engineering Science* 51, 32-50.

Dominijanni, A. and Manassero, M. 2012b. Modelling the swellin g and osmotic properties of clay soils. Part II: The physical a pproach. *Int. J. of Engineering Science* 51, 51-73.

Dominijanni A., Manassero M., Puma S. 2013. Coupled chemical-hydraulic-mechanical behaviour of bentonites. *Géotechnique* 63 (3), 191-205.

Hosney M.S. and Rowe R.K. 2014. Performance of GCL after 10 Years in service in the Arctic. *Journal of Geotechnical and Geoenvironmental Engineering* 12 (6).

Jo H.Y., Benson C.H., Shackelford C.D., Lee J.M., and Edil T.B. 2005. Long-term hydraulic conductivity of a geosynthetic clay liner permeated with inorganic salt solutions. *Journal of Geot echnical and Geoenvironmental Engineering* 131 (4), 405-417.

Katsumi T., Ishimori H., Onikata M., Fukagawa R. 2008. Long-ter m barrier performance of modified bentonite materials against sodium and calcium permeant solutions. *Geotextiles and Geom embranes* 26 (1), 14-30.

Lin L.C. and Benson C.H. 2000. Effect of wet-dry cycling on sw elling and hydraulic conductivity of GCLs. *Journal of Geotech nical and Geoenvironmental Engineering* 126 (1), 40-49.

Liu L. 2013. Prediction of swelling pressures of different types of bentonite in dilute solutions. *Colloids and Surfaces A: Physic ochemical and Engineering Aspects* 434, 303–318.

Mazzieri F. and Pasqualini E. 2006. Evaluating the permeability of an organically modified bentonite to natural seawater. *5th IC EG Environmental Geotechnics*, London, 749756.

Mazzieri F. and Pasqualini E. 2008. Effect of Dry/Wet Cycles and Cation Exchange on the Permeability of a Dense Prehydrated GCL. *Eurogeo4*, Edinburgh.

Mazzieri F., Di Emidio G. and Pasqualini E. 2016. Effect of wet-and-dry ageing in seawater on the swelling properties and hyd raulic conductivity of two amended bentonites. *Appl. Clay Sci*

McBride M.B. 1994. Environmental Chemistry of Soils. Oxford U niversity Press, New York.

Rowe R.K., Bostwick L.E. and Take W.A. 2011. Effect of GCL p roperties on shrinkage when subjected to wet-dry cycles. *J. G eotec. Geoen. Eng.* 137 (11), 1019-1027.

Rowe R.K., Bostwick L.E. and Take W.A. 2011. Effect of GCL P roperties on Shrinkage When Subjected to Wet-Dry Cycles. *J. Geotec. Geoen. Eng.* 137(11), 1019–1027.

Shackelford C.D., Benson C.H., Katsumi T., Edil T.B. and Lin, L. 2000. Evaluating the hydraulic conductivity of GCLs permeat ed with non-standard liquids. *Geotextiles and Geomembranes* 18, 133-161.