Macroscopic effects of the hydration mechanisms in smectites; applications to engineered and geological barriers for radioactive waste disposal

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This Lecture is dedicated to the memory of our colleague and friend Prof. Tom Schanz, who prematurely passed away in December 2017, and to his significant contributions in the fields of unsaturated soil mechanics and of the behaviour of compacted bentonites.

ABSTRACT: Clay materials have a paramount role in the deep geological disposal of radioactive waste concepts adopted in some countries, either because the selected host rocks are clays or claystones, or because engineered barriers and plugs made up of bentonite materials are used to optimize sealing. After commenting the retention properties and microstructure of both materials, it is shown that, in both cases, the hydration mechanisms of smectites and its dependence on suction changes, allow to explain some aspects of the microstructure changes that govern the macroscopic response of bentonite materials and clay rocks, in terms of swelling and sealing properties.

1 INTRODUCTION

Clays play an important role in the geological confinement of highly activity radioactive waste disposal at great depth (e.g. Delage et al., 2010), particularly in countries where the option of using clays or claystone as host rocks is considered. This is the case in Belgium with the Boom clay, Switzerland with the Opalinus Clay, and France with the Callovo-Oxfordian (COx) claystone. Engineered barriers and plugs that are made up of bentonite are also used in most concepts, both as engineered barriers placed between the waste canisters and the host rock, and as plugs to seal some cavities and galleries, particularly once the waste disposal system has been filled and the operational phase finished.

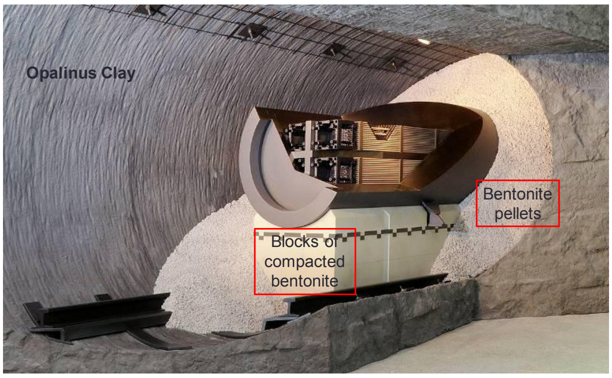


Figure 1. Swiss concept of high activity radioactive waste at great depth in the Opalinus clay, in which canisters are placed on compacted bentonites, and surrounded by pellets (Nagra).

An illustration is given in Figure 1, in which the Swiss concept developed by Nagra, the Swiss agency for the management of radioactive wastes, is presented. One can see that the waste canisters are placed on a support made up of compacted bentonite blocks designed to support the canister load, whereas pellets of bentonites are placed all around, between the canister and the wall of the gallery excavated in the Opalinus Clay.

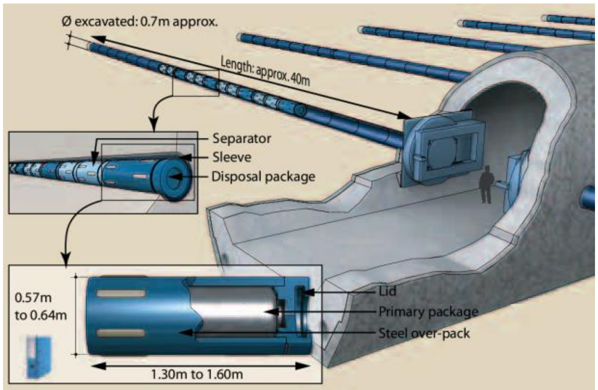


Figure 2. French concept, in which canisters are placed in sleeved galleries to allow for some reversibility in the disposal during 300 years (Andra).

Alternatively, the French concept developed by Andra, the French agency, does not use any engineered barrier, with the canisters inserted into around 40 m long horizontal galleries of smaller diameter (0.7 m) in which metallic sleeves have been previously placed (Figure 2). This concept allows for a reversible system, with the possibility to retrieve the canisters during the first 300 years of the disposal, in case a better alternative solution of waste management or treatment has been found in the meantime. Note also, in the figure, the presence of inert separators placed between exothermic canisters to limit the temperature elevation to a maximum of 100°C in the COx claystone.

The water tightness of the sealing systems made up of bentonite is achieved through the hydration of the smectite minerals contained in the bentonite, that occur in conditions of limited volume expansion. Smectite minerals also play an important role in the claystones considered in France (COx) and Switzerland (Opalinus Clay) as host rocks, that indeed exhibit significant swelling properties that are also beneficial for disposal issues.

2 THE WATER RETENTION PROPERTIES OF ENGINEERED AND GEOLOGICAL BARRIERS

2.1 *Engineered barriers*

To better understand and model the water retention and transfer properties that govern the hydration of compacted bentonites, their water retention properties have been investigated for a long time by using typical techniques of testing unsaturated soils. Given that suction in compacted bentonites can be as high as several tens or hundreds of MPa, the vapour control technique (Delage at al., 1998) is particularly adapted.

Another typical feature of engineered barriers is that swelling is not fully allowed in galleries due to volume constraints, which led to the investigation of the water retention properties of compacted swelling bentonites under constant volume conditions. The technique to do so by using the vapour control technique and rigid cells allowing for vapour water exchanges was initially developed by Yahia-Aissa (1997) and Yahia-Aissa et al. (2001), and adopted and used afterwards by many authors, including Villar et al. (2005), Lloret et al. (2003) and Devineau et al. (2006).

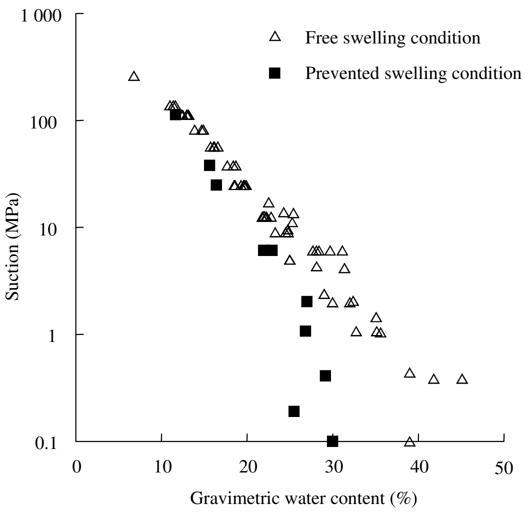


Figure 3. Water retention properties along the wetting path of FoCa 7 compacted bentonite under free and constant volume conditions (Yahia-Aissa et al., 2001).

Typical retention properties of compacted bentonites under free and constant volume change conditions are presented in Figure 3 in the case of FoCa7 bentonite, with hydration starting along the wetting path from an initial suction of 113 MPa. The difference between the retention curve under free swelling conditions and that with no volume changes allowed is clear, with comparable water adsorption at high suction (100 MPa), a little less adsorbed water below 50 MPa and significantly less below 10 MPa. Further comments about this trend will be given later. Similar results have been obtained, among others, by Loiseau et al. (2002) and Cui et al. (2008) on Kunigel V1 bentonite from Japan, by Lloret et al. (2003) on a bentonite from Cortijo de Arjidona and by Delage et al. (2006) and Wang et al. (2013) on MX80.

2.2 *The Callovo-Oxfordian claystone*

The water retention properties of claystones are also worth investigating because the evaporation due to the ventilation of the galleries during the operational phase affects the gallery walls, with a partially saturated zone developing along several centimetres close to the walls (Delage, 2014). Also, claystone specimens brought to the laboratory are not fully saturated due to the combined effects of air coring, core storage, transport and specimen trimming before lab testing. In this context, detailed investigations of the water retention properties of the COx claystone (Wan et al., 2013, Menaceur et al., 2016) and of the Opalinus Clay (Ferrari et al., 2014) have been conducted.

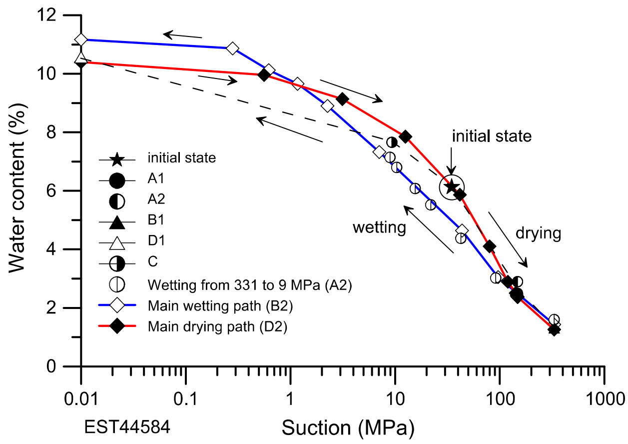


Figure 4. Water retention properties of the Callovo-Oxfordian claystone (Menaceur et al., 2016).

Figure 4 shows the water retention curve of the COx claystone, with various paths determined starting from an initial point, as received in the laboratory prior to testing, defined by a suction of 34 MPa and an initial water content of 6.2%, corresponding to a degree of saturation of 79%. Note that these characteristics denote rather poor conservation conditions, given that optimised coring and conservation procedures now allow degree of saturation higher than 90%, with suctions less than 20 MPa. The wetting path under vapour hydration from the initial point results in a water content of 10.2% at zero suction and 100% degree of saturation, corresponding to a significant swelling of 6%, as shown in Figure 5(c) that shows the volume changes with respect to suction changes.

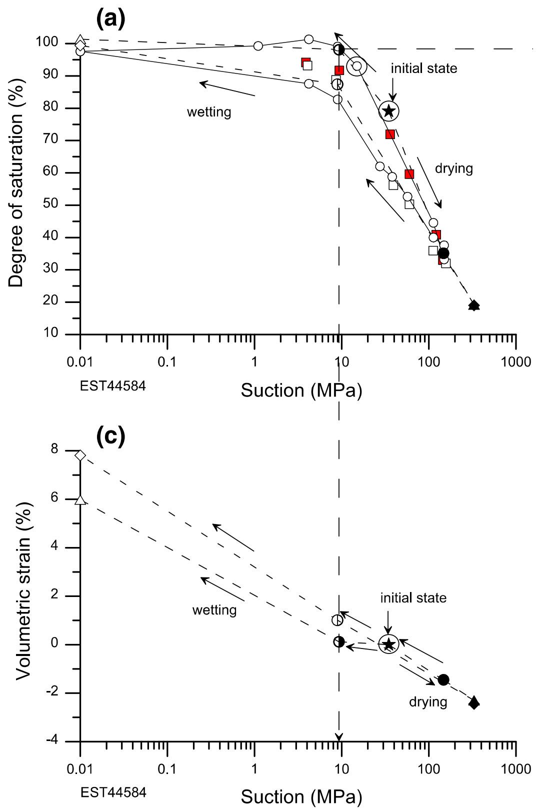


Figure 5. Changes in degree of saturation and volume with respect to suction, COx claystone (Menaceur et al., 2016).

Further observation of Figure 5(a) shows that full saturation is reached at a rather high value of suction of 10 MPa, whereas little swelling is observed when decreasing suction from 34 to 10 MPa (Figure 5(c)). Most of the swelling then occurs under a saturated state between 10 and 0 MPa.

Figure 4 also shows that drying the specimen at a maximum suction of 331 MPa brought the water content down to 1.3%, with 2.5% shrinking.

3 MICROSTRUCTURE OBSERVATIONS

3.1 *Scanning electron microscope*

It is well known that compacted clays have an aggregate microstructure, as derived from mercury intrusion porosimetry investigations carried out by Ahmed et al. (1974) and further completed by scanning electron microscope by Delage et al. (1996). This remains true in compacted bentonite, even at high density, as initially shown by Cui et al. 2002 (see Figure 6), with a clear evidence of inter-aggregate pores of several micrometres diameter.

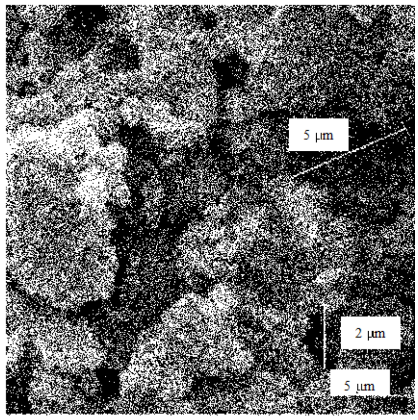


Figure 6. Scanning electron microscope view of a compacted Kunigel bentonite (Cui et al., 2002).

The microstructure of claystones is significantly different, given their natural origin, the depth at which they have been extracted (490 m in the Bure Underground Research Laboratory for the COx claystone) and the diagenesis effects that occurred over a time period as long as 158 My. This can be observed in the photo of Figure 7 (Menaceur, 2014) which shows a hydrated specimen of the COx claystone.

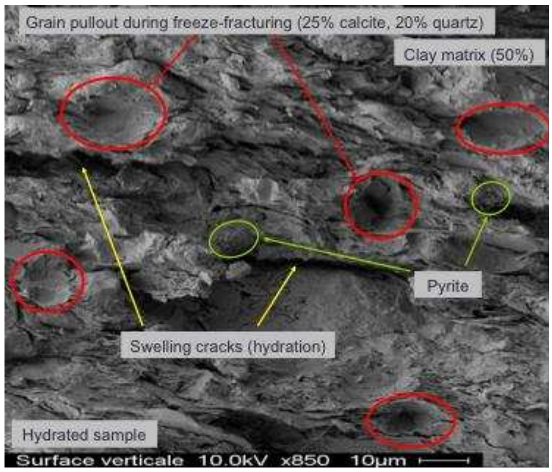


Figure 7. SEM observation of a hydrated specimen of the COx claystone (Menaceur, 2014).

The photo has been taken on a freeze-dried specimen that has been fractured in a frozen state so as to provide a nice observation plane. It shows that the clay matrix, which constitutes around 50% of the COx claystone. The remaining shapes of grains that have been pulled out during freeze fracturing are observable. They correspond to detritic grains of carbonate (20%) and quartz (22%), that are embedded in the clay matrix with no contacts between them. Two small aggregations of framboidal pyrites are also observed (pyrites oxidises when in contact with the air and this may have some effects in cracks).

An interesting feature is the observation of cracks that result from hydration and swelling. This confirms previous indirect observations (Mohajerani et al., 2011, Wan et al., 2013) evidencing in claystones the coupling between swelling and damage. It also confirms the statement by Wan et al. (2013) that swelling occurs through the extension of saturated cracks, as observed when considering Figure 5(a) and 5(c) when considering the wetting path from the initial sate at suction below 10 MPa. In the COx claystone, swelling is because of the smectite fraction contained in the illite-smectite inter-layer clay minerals that constitute the clay matrix.

Comparing the photos of compacted bentonite (Figure 6) and claystone (Figure 7) also confirms that swelling mechanisms are completely different in both cases, given that the inter-aggregates pores of the compacted bentonite have first to be filled prior to exhibiting swelling. Another conclusion that can be drawn from the photos is that the average thickness of the platelets is between 0.1 to 0.5 µm, corresponding to a number between 100 to 500 elementary layers of 0.96 nm thick, a number typical of smectites (Mitchell and Soga, 2005).

3.2 *Mercury intrusion porosimetry (MIP)*

Figure 8 (Delage et al. 2006) shows the curves of pore size distribution (PSD) of two compacted freeze-dried MX80 specimens at comparable (low) dry densities (ρ_d = 1.32 – 1.33 Mg/m^3) and void ratios (e = 0.998 – 1.006) but with two different water contents w = 12.5 – 28.5%, respectively).

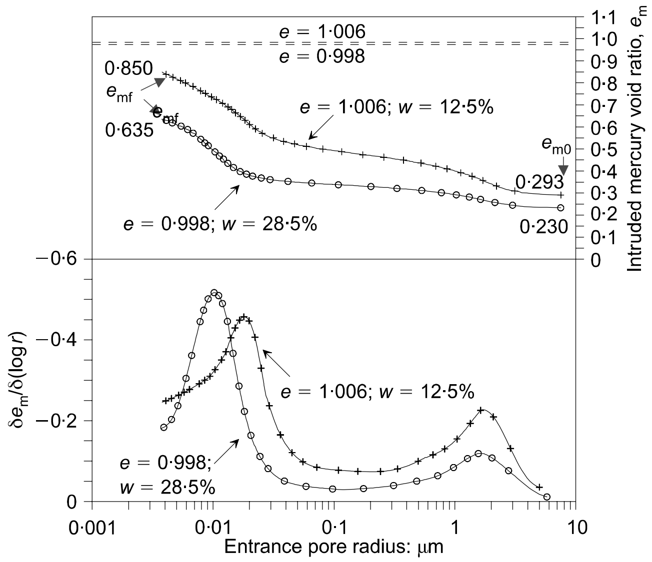


Figure 8. Pore size distribution curve of compacted MX80 specimens at two water contents and same void ratio (Delage et al., 2006).

The PSD curves exhibit bimodal shapes typical of aggregate an microstructure (see Figure 6), with a population of small intra-aggregates pores (mean diameter of 20 nm at w = 12.5% and 10 nm at w = 28.5%), whereas the average diameter of inter-aggregates pores is around 1.5 µm, a value comparable with what can be observed in Figure 6.

The curves also show that some large pore (radius r > 7.5 µm) and small pores (r < 3.5 nm) could not be detected by MIP. Interestingly, the infra-porosity (r < 3.5 nm) is larger at larger water content. As commented in Delage et al. (2006), this is because of the large amount of water molecules adsorbed along the smectite faces at such a high water content, in intra-platelets pores that are too small to be detected by MIP.

Figure 9 presents the PSD curve of a freeze-dried specimen of the COx claystone, with a well-defined pore population around an average diameter of 32 nm, to be linked to the morphology of the clay matrix observed in Figure 7. Here also, reporting the total porosity (n = 0.173) indicates that some infra porosity, non-intruded by mercury, is observed.

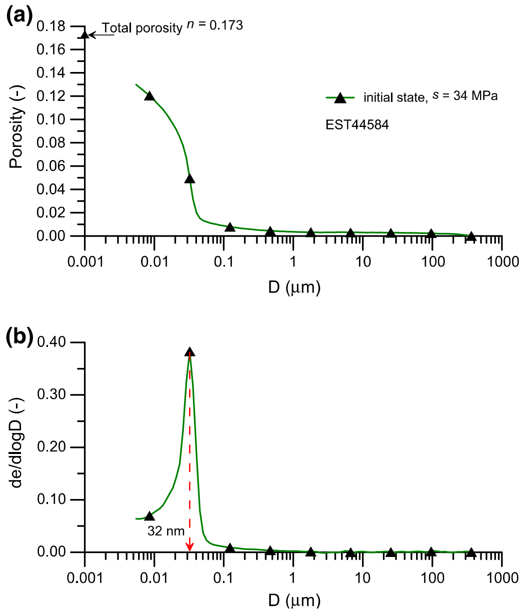


Figure 9. Pore size distribution curve of a Callovo-Oxfordian claystone specimen (Delage et al. 2014).

Based on a simplified microstructure model of the COx claystone (Yven et al., 2007), Menaceur et al. (2016) considered that this value provided an estimation of the average thickness of the mixed-layer illite-smectite platelets that constitute the clay matrix. Note also that no large pore population is observed. These microstructure features are now interpreted considering the mechanisms of hydration of smectites.

4 THE ROLE OF SMECTITES

4.1 *Hydration mechanisms in smectites*

In geotechnical engineering, the most frequently used theory to describe and model the microscopic phenomena at the origin of swelling is the diffuse double layer (DDL) theory (see among others, Bolt, 1956, Sridharan and Jayadeva, 1984, Tripathy et al., 2004, Mitchell and Soga, 2005). This theory accounts for the effects that the concentration and valence of the exchangeable cations of the pore water have on the electrical repulsion between two elementary 9.6 Å thick (0.96 nm) layers of smectite. This electrical repulsion is counter-balanced by the van der Waals attractive forces, with repulsion dominant at low salt concentration and cation valence (e.g. Na^+), and attraction dominant with large salt concentration and cation valence (e.g. Ca^{++}). A pioneering contribution relating these nano-scale phenomena to macroscopic swelling was provided by Bolt (1956), under the hypothesis of having individual smectite layers interacting together. However, further investigation using scanning or transmission electron microscopes showed that individual smectite layers didn't exist in natural soils, but that they were aggregated into stacks of various thicknesses, according to the salt concentration and cations valence.

The hydration of smectites has been first investigated in suspensions of pure smectites by using X-ray diffractometer. It has been shown for a long time (Mooney et al., 1952, Méring and Glaeser, 1954, Norrish, 1954), from estimating the basal spacing of hydrated smectites at various suctions, that water molecules adsorbed at the surface of smectite elementary layers in a discrete fashion, with a layer of one molecule at high suction (1W hydration), followed by two (2W hydration), then three and finally four. The basal spacing starts from 9.6 Å and goes to 12.6 Å with one layer of water molecules, 15.6 Å with two layers and 18.6 Å for three layers.

This feature, confirmed by many further investigations (including Ben Rhaïem et al., 1985, Bérend et al., 1995, Cases et al., 1997, Ferrage et al., 2005, Ferrage et al., 2007) has also been extended to compacted specimens of MX80 bentonite by Saiyouri et al. (2000, 2004) based on small angle X-ray diffractometry.

4.2 *Application to compacted bentonites*

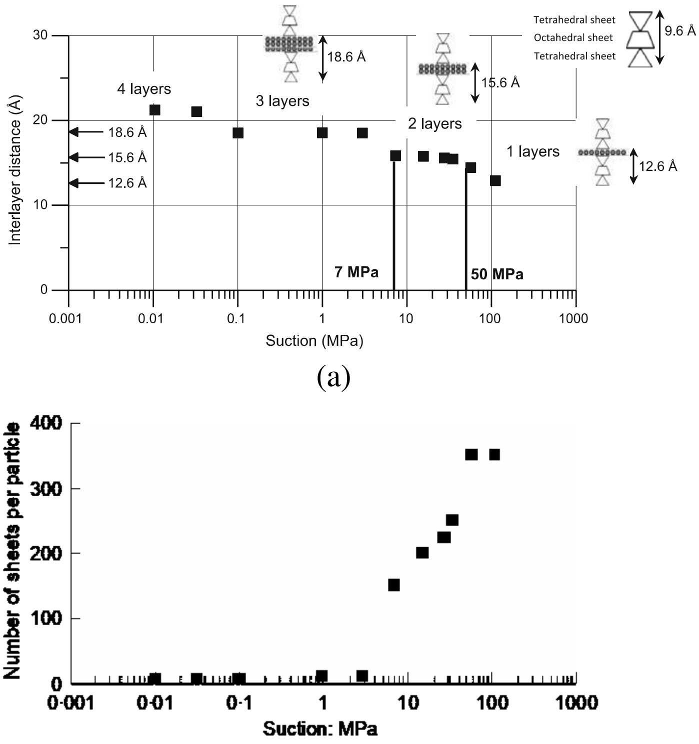
Saiyouri et al. (2004) also showed that the thickness of the stacks (i.e. the number of stuck layers within a smectite platelet) decreased during hydration with decreased suction, starting from various hundreds down to various tens of layers per platelet. Their data have been used by other authors dealing with compacted bentonites, including Delage et al. (2006), Delage (2007), Villar (2007), Villar et al. (2012) and Seiphoori et al. (2014).

Sayiouri et al. (2004)'s data are shown in Figure 10, together with the simultaneous decrease with increased suction in clay platelet thickness that they observed. One can observe that 1 W hydration prevails for suctions larger than 100 MPa, with 2 W hydration between 50 and 7 MPa, 3 W hydration between 7 and 0.1 MPa and 4 W hydration at low suction. Simultaneously, the platelet thickness decreases with around 350 layers in the 1 W hydration state above 50 MPa, coming in the down to around 150 at 7 MPa (2 W state) and falling at 10 below 3 MPa (3 W state).

These data first confirm the conclusion previously drawn with respect to the platelet thickness, with a number of layers per platelet estimated, from SEM observations, between 100 and 500.

The suction of the bentonite powders used to compact the MX80 specimens at 12.5% and 28.5% were respectively equal to 67 and 4 MPa, indicating that the hydration states of the specimens were 1 W and 3 W, respectively. The smaller infra-porosity observed in the drier compacted specimen in Figure 8 (w = 12.5%) can be related to the larger thickness of the platelets.

Figure 10 indicate that, at 67 MPa, platelets are made up of around 300 layers with a 0.126 nm inter-basal spacing, giving a platelet thickness of 37.8 nm, easily detectable by MIP.



(b)

Figure 10. Hydration mechanisms in MX80 bentonite, after Saiyouri et al. (2004): (a) changes in inter basal spacing with suction; (b) decrease in the number of smectite layer per platelets under decreased suction.

Actually, this value is quite compatible with that deduced from the average micro-pore radius of 21 nm observed in Figure 8. By adopting a brick model for the microstructure, the average thickness can be derived from the 42 nm diameter, giving a number of 333, in excellent agreement with the data of Figure 10. In the same way, given that the thickness layer increases to 0.186 nm in the wetter specimen (w = 28.5%), the average radius at 12 nm provides an average platelet thickness of 24 nm with an average number of 129 layers per platelet. Again, this number is in very good agreement with the data in Figure 10.

The fall in platelet thickness at 3 MPa is the main driving force of the exfoliation of aggregates, that progressively clogs the inter-aggregates pores observed in Figure 6, prior to the development of swelling pressure. This clogging is responsible for the one can conclude that the introduction of one water layer along the smectite layers unexpected decrease in permeability of compacted bentonites during hydration, evidenced in Cui et al. (2008), that is contrary to the well-known trend in unsaturated (non-swelling) soils.

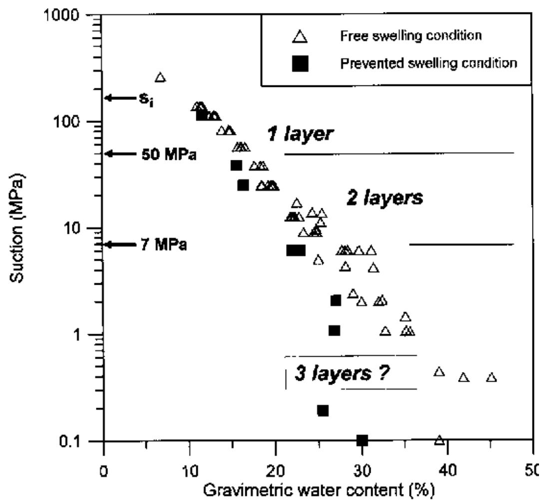


Figure 11. Re-interpretation of the water retention curve of Fo-Ca clay under free and constant volume change (Delage, 2007).

The data of Figure 3 can also be interpreted based on smectite hydration mechanisms of Figure 10, as proposed by Delage (2007) and shown in Figure 11. Both the free swell and constant volume wetting curves coincide in the 1 W hydration state above 50 MPa, and become significantly different below 7 MPa, where 3 and 4 W hydrations prevail, with also the reduction in thickness of the platelets. This aspect has been considered in more details by Devineau et al. (2006).

4.3 *Application to claystones*

Exfoliation is also the reason of the remarkable self-sealing properties of swelling claystones like the COx claystone, as evidenced by Zhang (2011), Davy et al. (2004), Menaceur et al. (2013), among others. In swelling claystones, the exfoliated smectite particles along the walls of the cracks that are put in direct contact with water when a permeability test is carried out by injecting water in a cracked or sheared specimen, clogs the cracks and reduce the crack permeability to that of the intact claystone itself. This sealing property is most favourable for the performance assessment of the radioactive waste disposal, more particularly with respect to the behaviour of the excavation damaged zone in the close field around the galleries.

The role of the smectite hydration mechanisms has been recently evidenced in swelling claystone by Menaceur et al. (2016), through a detailed investigation of the change in microstructure of the COx claystone along various paths of the water retention curve presented in Figure 4.

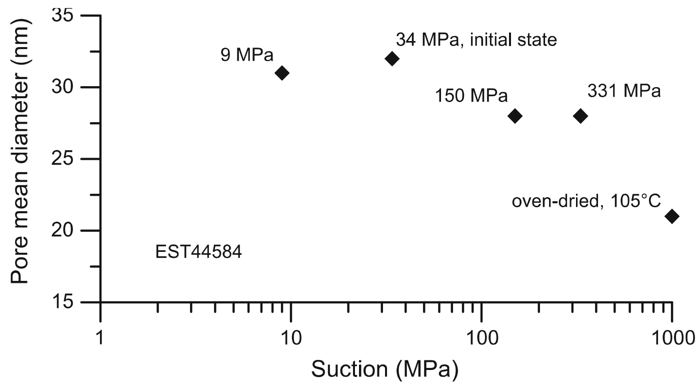


Figure 12. Changes in mean pore diameter of the COx claystone with respect to suction.

Figure 12 shows the changes in mean pore diameter with respect to suction of COx specimens at initial suction (34 MPa) and brought to 9 MPa along the wetting path, to 150 and 300 MPa along the drying path, and oven-dried (the PSD curve at initial state, defining an average pore diameter of 32 nm, is presented in Figure 9).

It is interesting to observe that the positions of the points of Figure 12 are comparable to that observed in Figure 10a, with a stepwise change in mean diameter with respect to suction, limited by comparable suction values. Based on the simplified brick model proposed by Yven et al. (2007), one can relate the average diameter of the pores to an estimation of the platelet thickness. Considering an inter-basal spacing of 0.96 nm in the mixed-layer illite-smectite minerals of the COx clay matrix, an average number of 21 – 22 layers per platelet can be deduced from the 21 nm mean diameter measured in the dry state.

Adopting the 50–70 % proportion of smectite minerals in the clay matrix (Yven et al., 2007), one can conclude that the introduction of one water layer along the smectite faces would result in the placement of between 11 and 15 layers of 0.3 nm thick layer of water molecules, resulting in an increase in platelet thickness between 3.3 and of 4.6 nm, from 21 to 24.3–25.6 nm. This is not far from the 28 nm value measured by MIP under suctions of 150 and 331 MPa. Adding another water layer would then provide a thickness between 27.6 and 30.2 nm, reasonably comparable to the 32-nm value measured by MIP under 34 and 9 MPa suctions.

This shows that, in the suction range considered (above 9 MPa) the volume changes of the COx claystone are mainly governed by the hydration mechanism of smectites, extending to swelling claystones the findings of Saiyouri et al. (2004) on compacted bentonites. Indeed, hydration forces appear to be strong enough to erase the effects of inter-particle bonding that prevail in the clay matrix of the claystone, mainly due to the carbonate fraction. This also explains why no significant increase in volume of the COx specimen was observed between the initial 34 MPa suction and 9 MPa (see Figure 4).

Figure 13 presents the PSD curves of the COx claystone at initial state (34 MPa) and at two points along the wetting path (suctions of 9 and 0 MPa). The stability of the microstructure between 34 and 9 MPa is confirmed by the excellent comparability of the PSD curves, and by the same values of infra-porosity. The data of Figure 13 shows that the 6% swelling observed between 9 and 0 MPa corresponding to an increase in porosity from 0.173 to 0.220 (Figure 5), occurred while keeping a comparable average micropore diameter, by both the development of a larger pore population made up of (saturated) cracks with a largest diameter of around 30 µm, and an increase in infra-porosity. This increase had already been observed in compacted bentonite (Calcigel) by Agus & Schanz (2005).

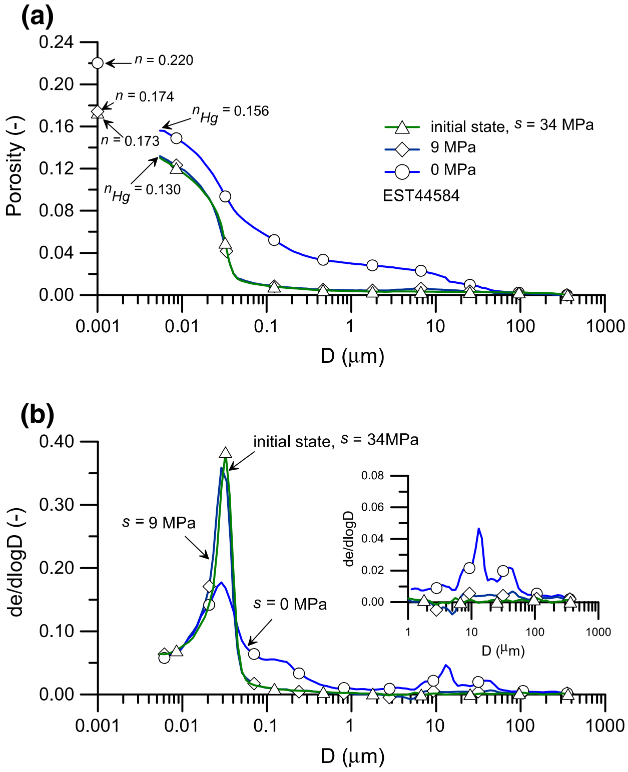


Figure 13. PSD curves of COx claystone along a wetting path.

4.4 *Discussion*

It has been shown that intra-layer smectite hydration mechanisms was the main driving force in the swelling/shrinkage behaviour of compacted bentonites and swelling claystones at suctions higher than 9 MPa. Other mechanisms are involved between 9 and 0 MPa, in link with the decomposition of the stacks and the reduction to around 10 of the number of layers per platelet (Figure 10). This decomposition results in much more disordered structures that involve larger pores and larger interaction distances between the platelets, through which osmotic phenomena and DDL effects may develop. This is also true for the cracks observed in Figure 7 in a hydrated specimen of the COx claystone. The use of the DDL theory to describe the macroscopic response of soils has been initiated by Bolt (1956), with also, among others, the significant contribution of Sridharan & Jayadeva (1982) and those of Prof. Tom Schanz's research group (e.g. Tripathy et al., 2004).

5 CONCLUSIONS

The hydration mechanisms intervening at the level of the elementary smectite layer were used to better interpret the macroscopic response of two different swelling materials involved in geological radioactive waste disposal at great depth, i.e. compacted bentonites and the Callovo-Oxfordian claystone, a possible host rock considered in France. Following the validation carried out by Sayiouri et al. (2000, 2004), on compacted bentonites, of well-known concepts developed on pure smectite suspensions for a long time, some common behaviour tends were observed on compacted bentonites and the COx claystone. At suctions larger than 7 – 9 MPa, the retention properties and macroscopic volume response of both materials are mainly governed by the discrete adsorption of layers of water molecules along the smectite faces (1, 2 and 3 W hydrations under decreased suction). At lower suctions, the changes in microstructure allow for the developments of larger spaces between clay platelets that have considerably reduced in thickness, and hydration and swelling involves other mechanisms involving osmotic effects and the developments of diffuse double layers. In claystone, this occurs through the development of localised cracks that develop in a saturated state. In compacted bentonite, it occurs through an exfoliation mechanism that progressively fills the aggregates and change the microstructure towards a so-called card house structure, similar to what has been observed in smectite suspensions. This phenomenon is also responsible, for the excellent self-sealing properties observed in claystones.

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