# Porosity Changes due to Hydration of Compacted Bentonite

María Victoria Villar, Roberto Gómez-Espina, Rocío Campos, Icíar Barrios, and Luis Gutiérrez

**Abstract.** As a contribution to the understanding of bentonite hydration, the porosity of two different compacted bentonites with different degrees of saturation was analysed by mercury intrusion porosimetry and X-ray diffraction. The percentage of macropores, as well as the macropore mode, decreased with dry density both in wet and dry samples. Wet samples showed a predominance of microporosity. The basal spacing increased with water content. The porosity distribution for a given water content was not the same for samples hydrated before compaction than for samples saturated under constant volume. In the latter case it clearly evolved over time, the interlayer distance becoming higher.

**Keywords:** bentonite, hydration, porosity, interlayer, MIP.

## 1 Introduction

Deep geological repository concepts for high-level nuclear waste disposal often include a bentonite barrier around the waste containers. The bentonite is used with its hygroscopic water content, what means that initially the barrier is unsaturated. It will interact with the groundwater and eventually become saturated. The understanding of the hydration mechanism of compacted bentonite is key to assess the performance of engineered barriers, the time needed for their full saturation, their

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mechanical behaviour and their geochemical response. This work is a contribution to this understanding from a microstructural point of view.

Bentonites are mainly composed of clay minerals of the smectite type, which are made up of structural units known as laminae or layers that are piled one on top of the other, forming primary particles. The positions between these units are usually occupied by exchange cations and water may enter between them, causing the crystalline network to expand in the direction of *c*-axis. For this reason, this dimension of smectite –the basal spacing– is not fixed, but varies depending on the size of the molecule located between the units and on its hydration state.

The organisation of the laminae, particles and aggregates in any clay material gives rise to different types of porosity (Stepkowska 1990), as shown schematically in fig. 1:

- Interlaminar or interfoliar porosity, to which only polar molecules have access and whose spacing is usually up to 2 nm.
- Intra-aggregate porosity, inside the primary particles and between adjacent laminae piles. This is also known as microporosity, and includes pores having diameters of less than 0.002 µm.
- Inter-aggregate porosity (greater than 0.002 µm), which in turn may be classified as macroporosity or mesoporosity, depending on whether the diameter is above or below 0.05 µm.

There is experimental evidence that the microstructure of bentonite evolves during hydration (Villar & Lloret 2001). Thus, the proportion of external water (contained in macro and mesopores) in smectites decreases with increasing material density and decreasing water content (Pusch et al. 1990). Consequently, in highly compacted bentonite there is a predominance of interlayer water. Smectites typically show a stepwise hydration behaviour of the interlayer corresponding to the intercalation of discrete sheets of water molecules which are responsible for the crystalline swelling. It is considered that smectites display basal spacings of about 1.0, 1.25, 1.55 and 1.85 nm for the homogeneous 0, 1, 2 and 3 water layers hydration states, respectively (Cases et al., 1992; 1997).

Mercury intrusion porosimetry (MIP) has been used for long to study the microstructure of clays and its changes along mechanical and hydraulic paths (see Romero & Simms 2008 for a review). However, the adequacy of the PSD as measured by MIP is often questioned (Simms & Yanful 2004), in particular with respect to the representativity of the samples used (due to their size and way of preparation), the possible disruption of microstructure caused by the injection pressure, and the accessibility issues. The latter include the upper and lower pore entrance limits associated to the technique, and the bottle neck effect, which implies a difference between the pore entrance diameter and the actual diameter. In clay materials, and particularly compacted smectites in which the microporosity (pores of diameter smaller than 2 nm) may constitute most of the total porosity, the percentage of pores not intruded by mercury due to their small size can become predominant. Other techniques should then be applied to explore this range of porosity, such as the adsorption of gases. Additionally, X-ray and neutron diffraction can be used to measure the interlayer spacings (through the *d*(001) reflection), what also helps describing the microporosity.

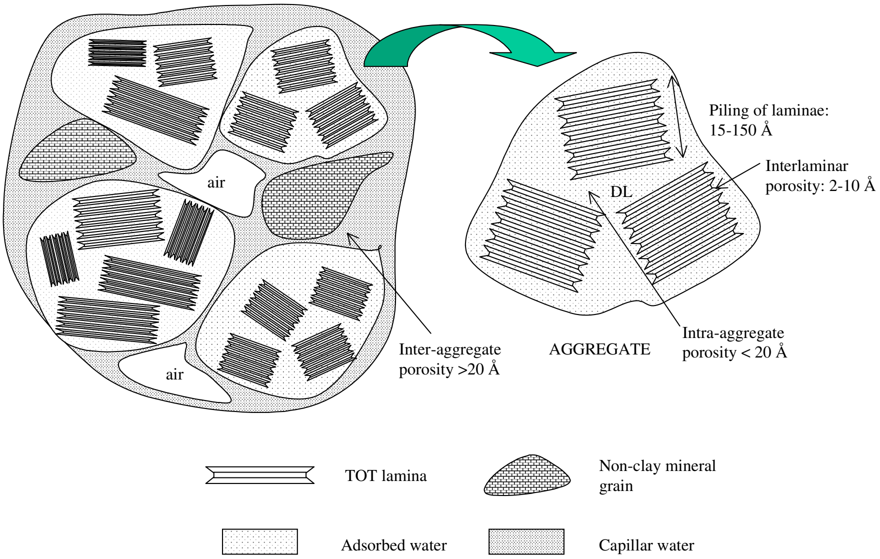

**Fig. 1.** Schematic diagram of the organisation of a clay material: types of porosity and water (Villar 2002).

## 2 Materials and Methods

The tests were performed with two untreated bentonites, the FEBEX and the MX-80.

The FEBEX bentonite was extracted from Almería (SE Spain). The montmorillonite content was above 90% (92±3 %) and it also contained variable quantities of quartz (2±1 %), plagioclase (2±1 %), K-felspar, calcite and opal-CT (cristobalite-trydimite, 2±1 %). The cation exchange capacity was 102±4 meq/100g, the main exchangeable cations being calcium, magnesium and sodium. The density of solid particles was 2.70 Mg/m$^3$ (ENRESA 2006).

The MX-80 bentonite was extracted from Wyoming (USA). The MX-80 batch used in this investigation was composed mainly of montmorillonite (83%) and it also contained quartz (4%), feldspars (7%), cristobalite (6%) and smaller quantities of calcite, gypsum, dolomite, halite and pyrite. The CEC was 65 meq/100g, and the major exchangeable cations were sodium, calcium and magnesium. The density of solid particles was 2.82 Mg/m$^3$.

All the results presented in this paper were obtained in compacted samples, although they were prepared in two different ways. In the first way the sample water content was fixed before compaction, whereas in the second one the sample water content changed after compaction, but in both cases under constant volume conditions:

- The bentonite was either mixed with deionised water to obtain a nominal water content of 30% (wet samples) or dried in a low relative humidity (4%) environment until reaching an equilibrium water content of 6% (FEBEX) and 2% (MX-80) (dry samples). Subsequently the bentonite, both wet and dry, was compacted to dry densities between 1.0 and 2.1 Mg/m$^3$ and the specimens were let stabilise for different periods of time wrapped in paraffined foil under no confinement at 20°C. At least two samples were compacted with the same dry density, water content and stabilisation time. The samples obtained through compaction of the bentonite with a water content of 30% are referred to in the rest of the paper as "wet samples", whereas those obtained through compaction of the desiccated bentonite are referred to as "dry samples".
- Other samples were manufactured by uniaxial compaction of the clay with its hygroscopic water content to dry densities between 1.1 and 1.8 Mg/m$^3$. They were flooded at room temperature with deionised water in oedometers, keeping their volume constant by adding the appropriate loads when tendency to swell was observed. Under a constant vertical load the vertical strain stabilised after about 4 days, but the tests were prolonged for much longer, up to durations of between 8 and 160 days. The samples reached full saturation at the end of the tests.

The pore size distribution of both kinds of samples was determined by mercury intrusion porosimetry (MIP). Samples smaller than 3 cm$^3$ were cut and lyophilised to eliminate the water in the pores. The porosimeter used was a Micromeritics AutoPore Series IV 9500, allowing the exploration of pore diameter sizes between 0.006 and 600 μm.

For the determination of the basal spacings of the smectite a sufficiently flat surface of the samples was X-rayed at room temperature without any previous treatment. An anticatode of Cu (CuK$_\alpha$) radiation was used with a Philips model X'Pert-MPD diffractometer at 40 mA, 45 kV operating condition.

## 3 Results

The mercury intrusion method allows access only to the macroporosity (pores smaller than 600 μm) and to part of the mesopores (pores of diameter larger than 0.006 μm). An estimation of the percentage of pores actually intruded can be made by comparing the actual void ratio of the samples (computed from their dry density and density of solid particles) and the apparent void ratio calculated from mercury intrusion. Thus, the pore size distribution curves obtained by MIP were corrected to take into account the percentage of pores not intruded (fig. 2). The percentage of pores intruded decreased with dry density and was higher for the dry samples than for the wet ones.

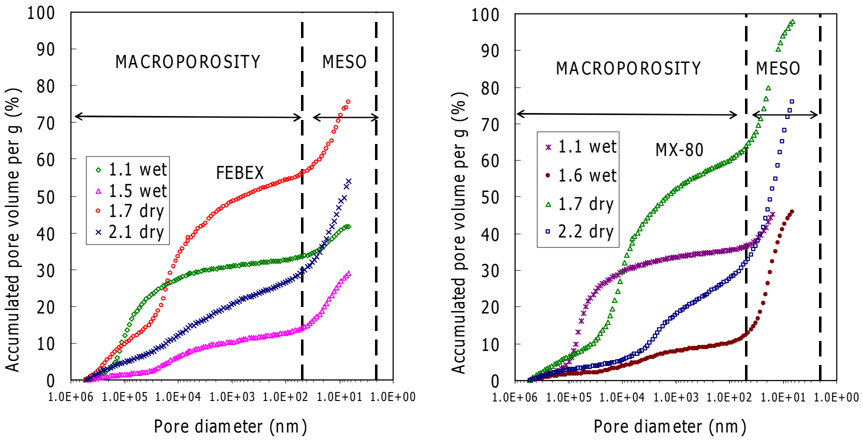

**Fig. 2.** Mercury intrusion curves of samples of FEBEX and MX-80 bentonites compacted at different dry densities (in Mg/m$^3$) and water contents and stabilised under no confinement for 150-230 days.

The percentage of pores not intruded by mercury included not only those whose sizes were below or above the technique limit, but also those whose entrance pore size was below the lower entrance limit of the equipment or those isolated, even if the pores themselves were larger. Nevertheless, assuming that the percentage of pores not intruded in a clay corresponds entirely to the micropore size, an estimation of the percentage of micropores can be inferred from the percentage of pores intruded. This was done for all the samples and the percentage of each pore size recalculated (fig. 3). The micropores were clearly predominant in the wet samples (30% water content). There was a clear trend both in the wet and the dry samples for the percentage of micropores and mesopores to increase as the dry density was higher, while the macropore percentage tended to decrease. Under no confinement, the maturation time did not seem to affect these pore size distributions. The comparison between both bentonites showed a higher percentage of micropores in the FEBEX than in the MX-80 bentonite.

Under no confinement, the macropore size mode of the two bentonites decreased as the dry density increased, both in the dry and the wet state (fig. 4). In fact, the macropore size was the less represented for the highest density (2.1 Mg/m$^3$). In the dry state the pore mode of the mesopores decreased also with dry density. The macropore size mode tended to be smaller for the MX-80 bentonite. However, in samples saturated under confinement (oedometer tests), the macro and mesopore size mode was the same irrespective of the dry density and even of the bentonite, with average values of 25.9±9.2 μm and 16±3 nm, respectively (the effect of maturation time was not investigated).

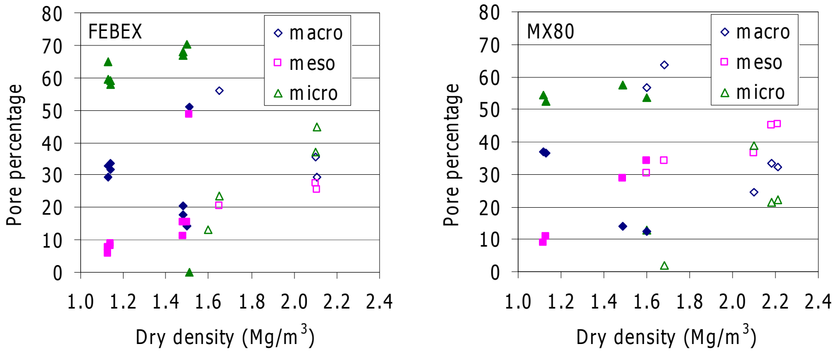

**Fig. 3.** Pore size distribution in bentonite samples compacted at different dry densities and stabilized for different periods of time under no confinement. Filled symbols: wet samples, open symbols: dry samples.

In each specimen stabilized under no confinement two X-ray measurements were performed on two perpendicular surfaces. Fig. 5 shows the average values for each pair of specimens (3 to 5 measurements). There was not a clear evolution of basal spacing over time either in the wet or in the dry samples, so in the figure the basal spacings shown correspond to different maturation times between 0 and 130 days. For all the densities and times of stabilisation, the average value of the *d*(001) reflection for the 30% water content samples indicated the predominance of the 2-layer hydrate state and the transition to the 3-layer hydrate state, with values slightly lower for the MX-80 bentonite. In the low water content samples the basal spacing corresponded to a 1-layer hydrate, although in the case of the FEBEX bentonite there must have been still a significant proportion of particles with a 2-layer hydrate. The effect of dry density on the basal spacing was not clear.

The basal spacings measured at the end of the oedometer tests are shown in fig. 6 as a function of the duration of the tests. For similar dry densities different basal spacings were measured at the end of the tests depending on their duration. Overall, longer tests gave place to higher final basal spacings, despite the fact that the final water content and swelling pressure values were quite independent on the duration of the tests. The dispersion of the results could be due to the slight differences in dry density, since the samples were grouped in dry density intervals of 0.1 $\mathrm{Mg/m^3}$. Except for the shortest durations (especially if the density was high), the basal spacings corresponded to the 3-layer hydrate.

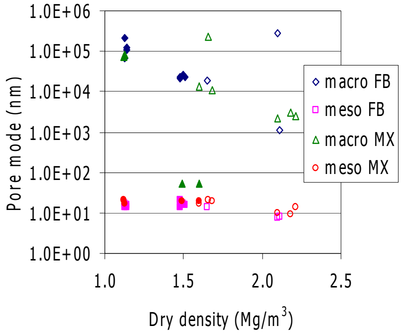

**Fig. 4.** Pore mode of macropores and mesopores of FEBEX (FB) and MX-80 (MX) compacted with different water contents and stabilised under no confinement (filled symbols: wet samples, open symbols: dry samples).

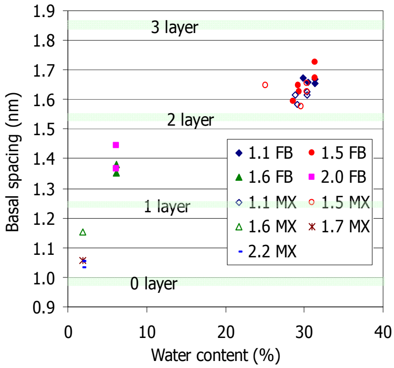

**Fig. 5.** Basal spacings of samples of FEBEX (FB) and MX-80 (MX) compacted at different dry densities (indicated in Mg/m$^3$) measured at different times after compaction.

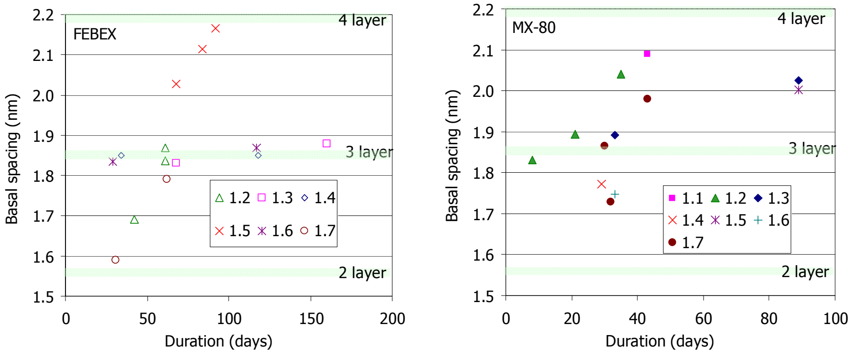

**Fig. 6.** Basal spacings measured at the end of the oedometer tests (dry densities in Mg/m$^3$).

## 4 Conclusions

Both the pore size distribution and the basal spacings of bentonite depended on the water content and the way of hydration. Samples hydrated prior to compaction showed a decrease of the percentage of macropores and their mode with dry density, while microporosity was higher in wet samples than in dry samples. The basal spacing increased with water content. The maturation time had no noticeable effect on the pore size distribution or basal spacing. However, in samples saturated at isochoric conditions, the interlayer distance increased with time, even for the highest dry densities. This points to a redistribution of the water inside the clay microstructure over time with no impact on swelling pressure. In fact, samples with the same water content and dry density had higher basal spacings if they were saturated under constant volume than if they were hydrated before compaction.

**Acknowledgements.** The preparation and analyses of samples was carried out by Ramón Campos, Juan Aroz, Ana González and Francisco Javier Romero. Part of the research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement no249681, the PEBS project.

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