

## WATER RETENTION OF TWO NATURAL COMPACTED BENTONITES

M. V. VILLAR\*

CIEMAT (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas), Avd. Complutense 22, 28040 Madrid, Spain

**Abstract**—This work presents the water retention curves obtained for two natural bentonites compacted at different dry densities. The density of the bentonite was kept constant during the determination, for which specific methodologies were developed. The materials tested are the FEBEX and the MX-80 bentonites, in the first of which divalent cations (Ca and Mg) predominate in the exchange complex; MX-80 is mainly sodic. The water retention capacity of the FEBEX bentonite is greater, although the difference between both bentonites becomes smaller towards low suctions. The effect of dry density on the water retention curve is very small or imperceptible for suctions >10 MPa, and below this value the lower the density of the bentonite, the greater its water content. The basal spacing of the samples equilibrated at different suctions has been measured and found to be in the order of those measured by other authors in powder samples equilibrated to the same suctions. The study was performed in the framework of projects concerning the engineered bentonite barrier of high-level radioactive waste repositories.

**Key Words**—Basal Spacing, Compacted Bentonite, Exchangeable Cations, Radioactive Waste Repositories, Smectite, Water Retention.

### INTRODUCTION

This work has been performed in the context of projects related to the study of the bentonite engineered barrier in high-level radioactive waste (HLW) repositories. Deep geological disposal is considered to be a realistic solution for the definitive disposal of HLW, its safety being based on the existence of a series of superimposed natural and artificial barriers. Among the latter are the sealing materials placed around the canister. Bentonite has been chosen as sealing material in most disposal concepts because of its low permeability, high swelling capacity and retention properties, among other features (Pusch, 1994).

The bentonite will probably be placed in the repository as compacted blocks around the waste containers. As this barrier will be manufactured with the clay at its hygroscopic water content, the bentonite will initially be unsaturated, *i.e.* air and water will coexist in the pores of the barrier. This confers on the bentonite a very high suction that promotes and conditions the saturation of the bentonite, which will take water from the surrounding geological medium. The saturation process will take place very gradually due to the low permeability of the bentonite. During the saturation of the barrier, as the clay becomes hydrated, expansion occurs. The swelling capacity of the bentonite will allow the filling of voids and gaps in the system – such as the voids between the bentonite blocks or between the blocks and the host rock – closing

preferential pathways for the migration of fluids. As a result, the density of the barrier will decrease in these areas, compared to the manufacturing density of the blocks. For instance, in the FEBEX *in situ* test performed at the Grimsel test site (Switzerland), which reproduces the Spanish disposal concept, the manufacturing density of the blocks was 1.7 g/cm<sup>3</sup>, and the final overall dry density of the barrier was 1.6 g/cm<sup>3</sup> (ENRESA, 2000). In addition, due to the expansiveness of bentonite and as the barrier will be confined in the host rock, the external areas of the barrier that are first hydrated will swell, compressing the internal parts not yet hydrated and causing their dry density to increase. In this way a density gradient is established in the system, with smaller densities in the areas affected by water, where the bentonite will have expanded, and greater in the innermost areas – not yet affected by water – which are ‘pushed’ by neighboring zones. Upon dismantling of the FEBEX in an *in situ* test, which ran for 5 y, the dry densities of the bentonite measured along the barrier were in the range from 1.4 to 1.7 g/cm<sup>3</sup> (Villar *et al.* 2005a).

In addition to the hydro-mechanical processes described, the barrier will be subjected to a thermal gradient caused by the heat generated by the radioactive decay of the wastes, which – in the Spanish disposal concept – is foreseen to give rise to a maximum temperature of 100°C at the surface of the canisters (ENRESA, 1995).

To gain confidence in the safety of the isolation system it is necessary to understand the various thermal, hydraulic, mechanical and geochemical processes taking place and their interactions in order to be able to develop models capable of predicting the long-term behavior of the near field of a repository. When modeling this

\* E-mail address of corresponding author:

mv.villar@ciemat.es

DOI: 10.1346/CCMN.2007.0550307

behavior, the saturation kinetics of the bentonite barrier is one of the features that draws more attention, because the predictions can be checked in large-scale tests performed in underground laboratories, increasing confidence in understanding the system. To analyze and model the hydration of the barrier, the key properties to know are the permeability of the bentonite and its water retention capacity. The latter is the object of this work.

The water retention capacity of a material is usually evaluated by determining its water retention curve, which relates suction and water content for a given temperature along a suction span as broad as possible. This is equivalent to the water adsorption isotherm, which is usually expressed as the relation between water content and relative vapor pressure, the relative vapor pressure being inversely related to suction according to Kelvin's Law. For the determination of the water retention curve of expansive materials compacted at high density, two main aspects have to be taken into account: the high suction of the bentonite and the volume changes occurring when the water content of the bentonite varies. Previous investigations have shown that the retention curve, for the same initial conditions of the material, differs significantly depending on the volume restriction, or confining stress, imposed on the sample during the determination (Yahia-Aissa, 1999, 2001; Al-Mukhtar *et al.*, 1999; Romero and Vaunat, 2000; Ng and Pang, 2000; Villar, 2002; Marcial, 2003; Lloret *et al.*, 2004). Water content for a given suction is greater if the sample is free to swell than if its volume change is constrained, especially for the lower suctions. The bentonite barrier will be overall confined; although, as has been explained above, a certain swelling will be allowed, especially in the external parts of the barrier, where the bentonite becomes wet earlier. For an appropriate characterization of the hydro-mechanical behavior of deformable clays, knowledge of the dependence of the water retention curve on dry density is necessary (Simms and Yanful, 2005) and the kind of retention curve chosen is a factor that significantly affects the predictions of the models on barrier behavior (ENRESA, 2000; Gens *et al.*, 2002). In addition, temperature, which will change and be high in the barrier, is another factor having an effect on the water retention capacity of bentonites (Villar and Lloret, 2004; Villar *et al.*, 2005b).

The materials tested in this work are two natural bentonites compacted to high densities: MX-80 and FEBEX. The first has a montmorillonite content of between 65 and 90% and Na is the predominant cation in its exchange complex. The FEBEX bentonite contains >90% montmorillonite with Ca and Mg as the main cations in the exchange complex, in which Na is also present. Both have been selected by different countries as reference materials for the sealing of HLW repositories. This paper presents the water retention curves

obtained at 20°C for the two bentonites compacted at initial conditions similar to those expected in the barrier with respect to dry density and water content and kept at constant volume during the determinations.

## MATERIAL

The FEBEX bentonite is from the Cortijo de Archidona deposit (Almería, Spain) and was selected by ENRESA (Spain) as suitable material for the backfilling and sealing of HLW repositories. A 300-t batch of bentonite was extracted from the quarry for the FEBEX Project (ENRESA 1998, 2000) and homogenized prior to packing. The processing at the factory consisted of disaggregation and gentle grinding, drying at 60°C and sieving at 5 mm. A comprehensive characterization of the FEBEX bentonite can be found in ENRESA (1998, 2000), Villar (2002), Fernández (2003) among others. The smectite content of the FEBEX bentonite is 92±3%. The smectitic phases of the FEBEX bentonite are a mixed-layer montmorillonite-illite with 10–15% of illite layers. The bentonite contains variable quantities of quartz (2±1%), plagioclase (2±1%), K-feldspar, calcite and opal-CT (cristobalite-trydimite, 2±1%). The <2 μm fraction of this bentonite is 67±3% of the total. The CEC varies from 96 to 102 meq/100 g, and the major exchangeable cations are: Ca (35–42 meq/100 g, depending on the determination method), Mg (31–32 meq/100 g), Na (24–27 meq/100 g) and K (2–3 meq/100 g). The liquid limit of the bentonite is 102±4%, the plastic limit 53±3% and the specific gravity is 2.70±0.04 g/cm<sup>3</sup>. The hygroscopic water content in equilibrium with laboratory atmosphere (relative humidity 50±10%, temperature 21±3°C) is 13.7±1.3%. The value obtained for the external specific surface area using the BET technique is 32±3 m<sup>2</sup>/g and the total specific surface area obtained using the Keeling hygroscopicity method is ~725 m<sup>2</sup>/g.

The MX-80 bentonite is extracted from Wyoming (USA), and has been selected in many HLW disposal concepts as backfilling and sealing material (Sweden, Finland, Germany, France). It is known worldwide and supplied in powder form. As it is a commercial material that has been exploited for decades, there is certain variability in the properties of the different batches that is reflected in the characterization performed by different authors (*e.g.* SKB reports, Madsen, 1998; Sauzéat *et al.*, 2001; Saiyouri *et al.*, 2004). The MX-80 bentonite consists mainly of montmorillonite (65–90%). It also contains quartz (4–15%), feldspars (2–9%), and smaller quantities of cristobalite, calcite, mica and pyrite. The <2 μm fraction of this bentonite comprises 76–90% of the total. The CEC is 75–82 meq/100 g, and the major exchangeable cations are: Na (61 meq/100 g), Ca (10 meq/100 g) and Mg (3 meq/100 g). The liquid limit of the bentonite as determined in CIEMAT laboratories is 526%, the plastic

limit is 46% and the specific gravity is 2.82 04 g/cm<sup>3</sup>. The hygroscopic water content at laboratory conditions (relative humidity 50±10%, temperature 21±3°C) is between 8 and 11%.

## METHODOLOGY

To determine the water retention curve of the compacted bentonite, two methodologies, the theoretical principle of each of which is different, have been followed. In one, the cell method, suction is imposed on the sample and the water content of the clay allowed to stabilize and then determined. In the other, the block/sensor method, the suction of samples compacted with various known water contents is measured by means of hygrometers. In both, the clay used is compacted to a high density which is kept constant during the determination.

### Cell method

To determine the water retention curve at constant volume, avoiding the swelling of the clay in wetting paths, special cells were designed (Villar, 2002; Villar and Lloret, 2004). The cells consist of a corrosion-resistant stainless steel cylindrical body of internal diameter 3.80 cm measuring 0.5 cm thick, with two perforated covers joined by bolts (Figure 1). Granulated clay is compacted directly inside the cell ring using static uniaxial compaction. The specimen is 1.20 cm long and its cross-sectional area is 11.34 cm<sup>2</sup>.

The cells are placed in desiccators with a sulfuric acid solution or with a NaCl solution. The suction is, therefore, imposed through the control of relative humidity (or relative vapor pressure), which is generated by the water activity of the solutions. The calculation of suction ( $s$ , MPa) on the basis of relative humidity (RH, %) is accomplished through Kelvin's equation.

$$s = -10^{-6} \frac{R \times T}{V_w} \ln \left( \frac{RH}{100} \right) \quad (1)$$

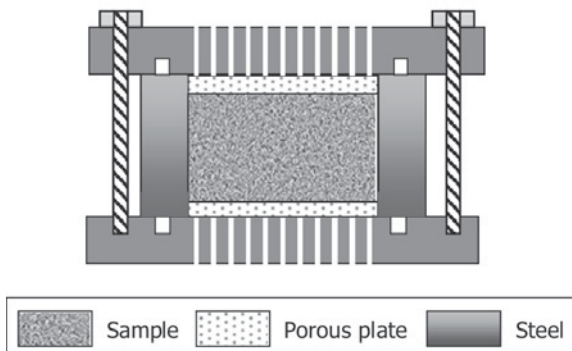


Figure 1. Schematic layout of the non-deformable cell for the determination of the retention curve.

where  $R$  is the universal gas constant (8.3143 J/mol K),  $T$  the absolute temperature and  $V_w$ , the molar volume of water ( $1.80 \times 10^{-5}$  m<sup>3</sup>/mol). The temperature was kept constant at 20°C during the tests.

The porous stones and the perforated covers of the cells allow the exchange of water in the vapor phase between the clay and the atmosphere of the desiccators. This process is very slow, not only because just the upper and lower parts of the surface of the sample act as an exchange surface, but also because the process is performed at constant volume. To speed up the water exchange process, vacuum is applied to the desiccators when they are first closed. Once the water content of the clay is stable (~2 to 4 months, depending on the dry density of the clay and the suction imposed), the solution in the desiccators is changed in order to apply a different suction. Obviously, the volume control can only be gained in wetting paths, as the clay shrinkage in drying paths cannot be avoided.

At the end of the tests, the final gravimetric water content ( $w$ ) of the specimens, defined as the ratio between the weight of water and the weight of dry solid, expressed as a percentage, is measured by oven drying at 110°C over 24 h, which is the temperature established in most standards of geotechnical and agricultural practice and was considered a convenient reference value. Several authors have reported that not all the hydration water of smectites disappears upon heating at this temperature, and values as high as 300°C have been suggested to determine accurately the amount of hydration water in smectites (Cuadros *et al.*, 1994). Heating at a temperature between 150 and 200°C has been proposed to eliminate all the interlayer water of the FEBEX bentonite (Fernández, 2003). The same author found no significant differences between the water losses of this bentonite after 24 and 48 h of heating.

Some of the samples were subjected to a single value of suction (single-step tests) and underwent X-ray diffraction (XRD) after water content stabilization in order to determine the basal spacing of the smectite. For that, they were preserved in paraffined foil immediately after extraction from the cell, and within <1 h, a sufficiently plane surface was X-rayed at laboratory temperature after removing the foil and without any further treatment. A Philips X'Pert-MPD diffractometer was used, employing CuK $\alpha$  radiation, a 0.1000 mm entrance slit and a scanning rate of 0.02°2 $\theta$ /s from 0.2 to 30°2 $\theta$ .

### Sensor/block method

The drawback of the method presented above is the duration of the test, because the time to reach equilibrium at each suction is very long. To overcome this disadvantage, another method to determine the retention curve at constant volume and at laboratory temperature has been fine-tuned (Svensk Kärnbränslehantering AB, 2002; Villar *et al.*, 2005b). It consists of the compaction of a

bentonite block with the clay previously mixed with the desired quantity of deionized water and the measurement of its relative humidity by means of a hygrometer. Deionized water was chosen in order to establish a clear reference condition. A previous investigation with the MX-80 clay using the same methodology showed that it was not possible to distinguish the influence of the salinity of the interstitial water on the value of the suction measured for salinities of up to 1.2% (Villar, 2005).

The wetted clay is kept for 2 days in a plastic bag to allow homogenization of the moisture, and afterwards, blocks are uniaxially compacted at the desired density. The compaction technique does not allow manufacture of blocks of a high degree of saturation (>80%). Neither does it allow compaction of blocks with less than hygroscopic water content, as they lack cohesion and crumble easily. Consequently, no results can be obtained for the lowest degrees of saturation. The nominal dimensions of the blocks are 10 cm × 4 cm × 3 cm.

Each block is allowed to stabilize for at least 2 days, wrapped in paraffined foil and, afterwards, a hole is drilled in it to allow a hygrometer to be installed inside (Figure 2). The transmitters used are ROTRONIC HYGROMETER<sup>®</sup> CK90, that include a humidity sensor (I-400) which changes its electrical characteristics with extremely small variations in humidity (capacitive-type relative humidity sensor). They also include a temperature sensing system (Pt 100). The accuracy of the humidity sensor at 23°C is ±1.5% over the range 0–100% RH. The clay block-sensor assembly is kept inside a closed plastic bag during the measurement to avoid moisture changes. The relative humidity and temperature values are checked periodically until stabilization, which usually takes place very quickly, although, as a rule, the values measured after 24 h have been used. To convert the values of relative humidity to suction values, Kelvin's law is used (equation 1).

Once the measurement phase is accomplished, the sensor is extracted from the block, and the latter is

measured, weighed and placed in an oven at 110°C to check its final dry density and water content.

## RESULTS

### *FEBEX bentonite*

The FEBEX bentonite was tested when compacted to different dry densities, applying the two methods described above. The dry densities chosen are in the order of those expected in the HLW Spanish disposal concept, from the manufacturing density of the blocks to the final values observed upon dismantling of the FEBEX *in situ* test run for 5 y under representative conditions (ENRESA, 2000; Villar *et al.*, 2005a). The initial water content was, in all cases, hygroscopic, since this will be the case when the blocks are manufactured.

The results obtained for samples compacted to nominal dry density of 1.70 g/cm<sup>3</sup> are shown in Figure 3. Using the cells, a wetting path was followed from the suction corresponding to the hygroscopic water content of the bentonite (110 MPa) to a suction of 1 MPa. The results shown in Figure 3 under the label 'wetting path' are in fact the averages of the results obtained in the wetting paths followed in two cells. Also, blocks were compacted to this dry density from bentonite that had previously been mixed with different quantities of deionized water. In each of these blocks the relative humidity was measured with hygrometers and this converted to suction. The individual points obtained in this way are also plotted in Figure 3 and referred to as 'block/sensor' points. A good agreement between the results obtained with the two methods is observed, except for the highest suctions, for which the suctions measured with the block/sensor method for a given water content are lower than those obtained in the cells.

The same measurements were performed in samples compacted to nominal dry density of 1.60 g/cm<sup>3</sup>, and the results obtained are plotted in Figure 4. Besides, three

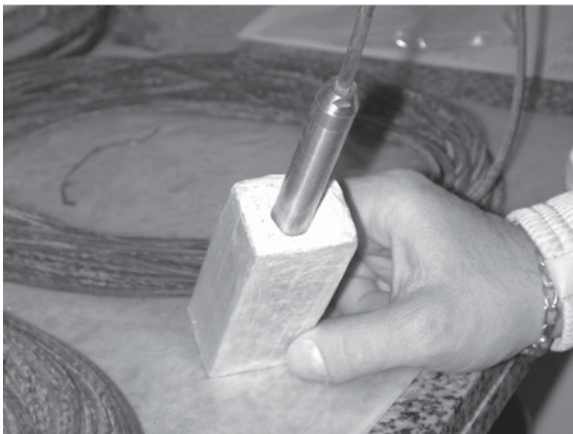


Figure 2. Compacted block of bentonite with a hole drilled for the insertion of the RH sensor.

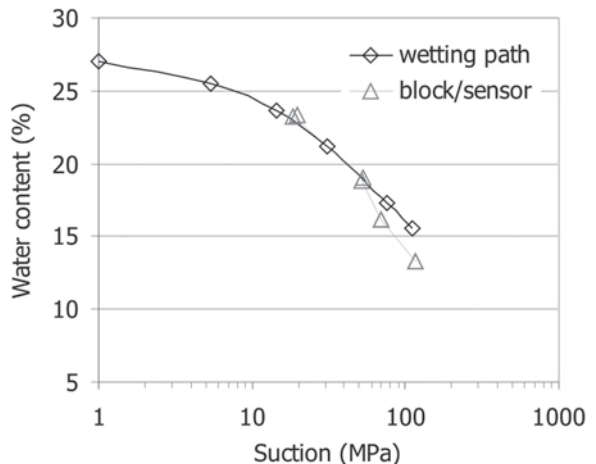


Figure 3. Water-retention curve obtained with different methods for the FEBEX bentonite compacted at dry density of 1.7 g/cm<sup>3</sup>.

samples were compacted in cells and kept inside desiccators at a given relative humidity, without following a wetting path (single-step tests). The results obtained in this case are indicated as ‘points’ in Figure 4. The results obtained with the two methods agree well except for suctions below 10 MPa, for which the suctions measured with the hygrometers for a given water content are greater than expected according to the results obtained in cells. This may be due to the fact that the densities are close but not the same: as expected, the samples with the lower density, those tested with the block/sensor method, the average dry density of which was in fact 1.53 g/cm<sup>3</sup>, tend to retain more water for the lower suctions (Villar, 2002; Villar and Lloret, 2004). The lower density of these samples is caused by the difficulty of compacting bentonite to high densities when its water content is elevated, because the pressures that have to be applied are huge.

The results obtained for samples compacted to a nominal dry density of 1.50 g/cm<sup>3</sup> are shown in Figure 5. In this case the results of the wetting path have been obtained in just one cell. An important discrepancy between the results obtained in cells (‘wetting path’ and ‘points’) and those obtained through the block/sensor method is observed for suctions below 10 MPa. In this case there were no significant differences among the actual dry densities of the samples, and this cannot be invoked as the reason for the divergence observed.

Figure 6 shows the results obtained in cells for the three dry densities tested. For suctions above 10 MPa no major differences in the retention curves as a function of dry density can be discerned, although the highest-density samples (1.7 g/cm<sup>3</sup>) reached slightly higher water contents than the others for the same suctions, whereas the lowest-density samples (1.5 g/cm<sup>3</sup>) reached the lowest water contents. However, the trend changes for suctions below this value (10 MPa) and thus, for a

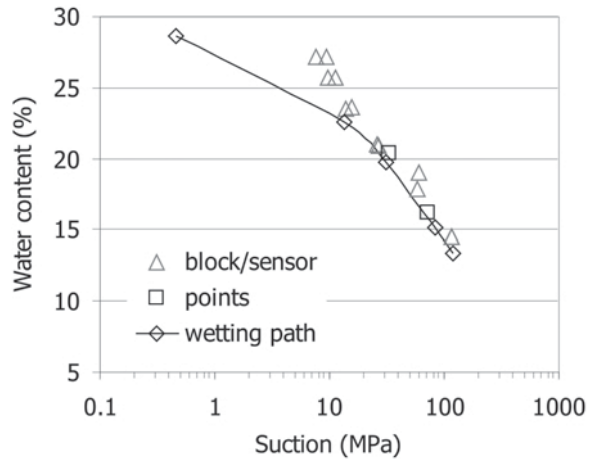


Figure 5. Water-retention curve obtained with different methods for the FEBEX bentonite compacted at dry density of 1.5 g/cm<sup>3</sup>.

given suction, the samples of dry density 1.7 g/cm<sup>3</sup> show the lowest water contents.

As has been explained above, the samples labeled as ‘points’ in Figures 4 and 5 were stabilized under just a single relative humidity (*i.e.* suction). Once the water content stabilization was reached at this target suction, these samples were extracted from the cells and their upper surface was immediately subjected to XRD to measure the basal spacing of the smectite. The results obtained are summarized in Table 1 in which the initial and final water content (*w*) and dry density ( $\rho_d$ ) of the samples are indicated. The XRD patterns obtained are plotted in Figures 7 and 8. For the two densities there is a decrease of intensity as suction increases. The intensities obtained for the lower density are also noticeably lower.

*MX-80 bentonite*

The dry densities used for testing the MX-80 bentonite are similar to those used in several *in situ*

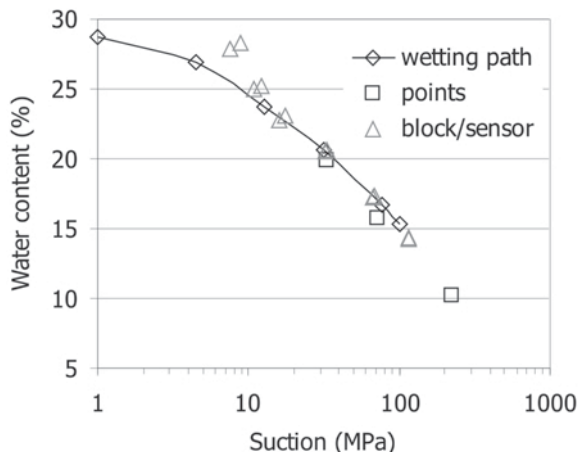


Figure 4. Water-retention curve obtained with different methods for the FEBEX bentonite compacted at dry density of 1.6 g/cm<sup>3</sup>.

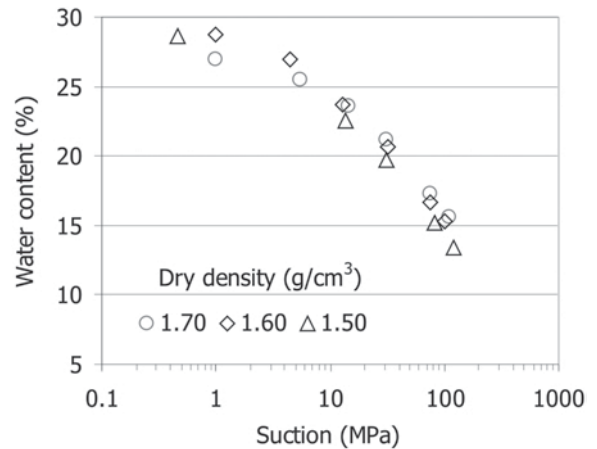


Figure 6. Retention curves obtained in cells (wetting paths) for the FEBEX bentonite compacted to different dry densities.

Table 1. Results of the single-step tests in cells performed on the FEBEX bentonite.

Initial $\rho_d$ ( $\text{g}/\text{cm}^3$ )	1.60	1.60	1.60	1.50	1.50
Initial $w$ (%)	14.1	14.1	14.3	14.1	14.3
Suction (MPa)	223.2	71.2	33.0	71.2	33.0
RH (%)	20.4	60.3	79.1	60.3	79.1
Stabilization time (days)	58	61	112	61	112
Final $w$ (%)	10.2	15.8	19.9	16.2	20.3
Basal spacing ( $\text{\AA}$ )	14.49	15.03	15.53	15.02	15.16

tests performed at the Äspö Hard Rock Laboratory according to the Swedish disposal concept (Svensk Kärnbränslehantering AB, 2002).

The MX-80 bentonite was tested compacted to a dry density of  $1.60 \text{ g}/\text{cm}^3$  using the two methods described above. The results are plotted in Figure 9. The results obtained in cells are those labeled as ‘wetting path’ and ‘points’. In the first case the data correspond to a sample compacted with its hygroscopic water content (8%) that was subjected to a wetting path from suction 120 MPa to 1 MPa inside a cell. The experimental results labeled as ‘points’ were obtained in cells subjected to different relative humidities (single-step tests). In this case the initial water content of the bentonite was also hygroscopic (9 or 10.5%). The points labeled as ‘block/sensor’ were obtained by measuring the relative humidity (suction) of samples compacted with different water contents.

Eight points were obtained with the single-step cell method in samples compacted with its hygroscopic water content to a dry density of  $1.30 \text{ g}/\text{cm}^3$ . They are plotted in Figure 10 together with the points obtained for a dry density of  $1.60 \text{ g}/\text{cm}^3$  with the same methodology. The difference between both densities is not appreciable for suctions  $>10$  MPa. However, for lower suctions, the higher water retention capacity of the low-density samples becomes clear.

The samples in Figure 10 were stabilized under just a single relative humidity (*i.e.* suction). Once the water content stabilized at this target suction, these samples

were extracted from the cells and their upper surface was immediately subjected to XRD to measure the basal spacing of the smectite. The results obtained are summarized in Table 2 for the dry density  $1.60 \text{ g}/\text{cm}^3$  and in Table 3 for the dry density  $1.30 \text{ g}/\text{cm}^3$ , in which the initial and final water content ( $w$ ) and dry density ( $\rho_d$ ) of the samples are indicated. The XRD patterns obtained are plotted in Figures 11 and 12. For the two densities there is a trend for the intensity to be less as suction is greater. The intensities recorded in samples of dry density  $1.3 \text{ g}/\text{cm}^3$  for a given suction are in all cases less than the intensities recorded for samples of greater density subjected to the same suction.

## DISCUSSION

Two methods have been used to determine the retention capacity of two natural bentonites compacted to high densities: the ‘cell method’, based on the imposition of a known relative humidity up to stabilization of the water content, and the ‘block/sensor method’ based on the measurement of the relative humidity of a sample of known water content. The second is easier and quicker to apply. The results obtained with both are coherent, except for the lower suctions ( $<10$  MPa), for which the water content obtained with the ‘block/sensor method’ is sometimes greater (up to 4%) for a given suction. If we compare ours with the more conventional ‘cell method’ results, we see that, for a given water content, the hygrometer measures lower relative humid-

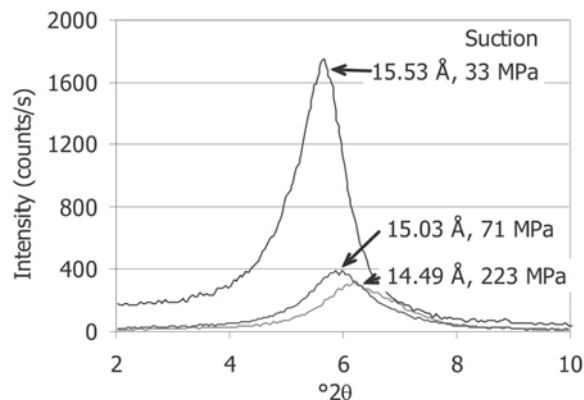


Figure 7. XRD patterns of the FEBEX bentonite compacted at dry density of  $1.6 \text{ g}/\text{cm}^3$  after stabilization at different suctions.  $\text{CuK}\alpha$  radiation.

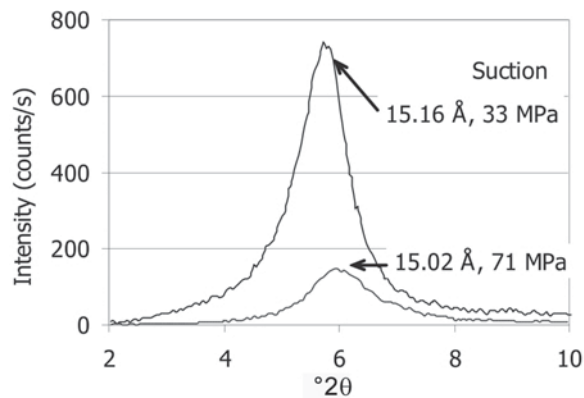


Figure 8. XRD patterns of the FEBEX bentonite compacted at dry density of  $1.5 \text{ g}/\text{cm}^3$  after stabilization at different suctions.  $\text{CuK}\alpha$  radiation.

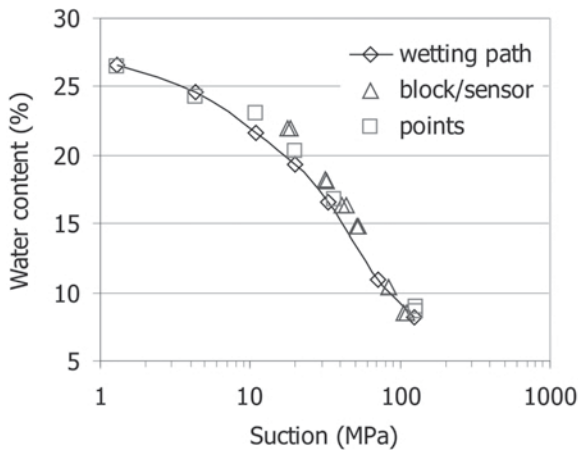


Figure 9. Water-retention curve obtained with different methods for the MX-80 bentonite compacted at dry density of 1.6 g/cm<sup>3</sup>.

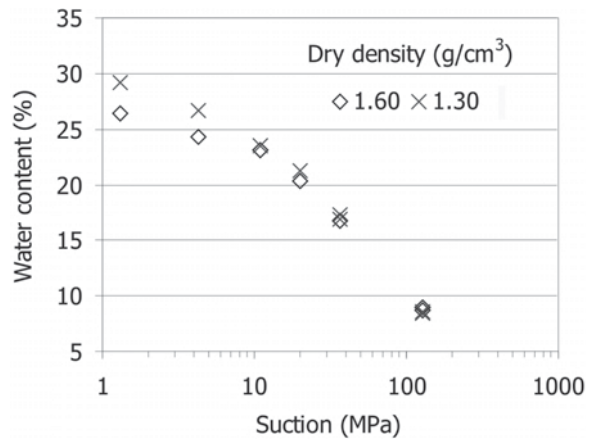


Figure 10. Water-retention curve obtained with the single-step cell method for the MX-80 bentonite compacted at different dry densities.

ities (higher suctions) when the water content of the bentonite is high. This could be due to a lack of stabilization of suction after compaction, as was pointed out by Marcial (2003): in bentonite compacted with high water content there is a subsequent redistribution of porosity that can take several days after compaction (up to 90), the proportion of micropores increasing with time. This would imply a change in suction that we would not have been able to measure because the stabilization time in our tests was just 2 days after compaction.

The effect of dry density on the water retention capacity has also been checked. For the two bentonites, and in terms of water content, the effect of dry density is imperceptible or very small for suctions >10 MPa. For higher suctions, the water must be predominantly in the microstructure, and because the density changes affect mainly the macrostructure, they are not reflected on the retention curve. For lower suctions, *i.e.* for high RH and when the specimen is approaching saturation, the lower the dry density of the bentonite the greater the water content for a given suction. This is the expected behavior, as the porosity of samples of low density, and consequently the pore volume available for water uptake, is greater. The same was observed by Villar (2002), Lloret *et al.* (2004) and Villar *et al.* (2005b). It must also be recalled that the retention capacity of compacted bentonite, especially for the low suctions, is very much affected by the external stress state, and it is less when the swelling of the bentonite is hindered.

Marcial (2003) analyzed this difference by determining the water retention curves of the MX-80 bentonite in powder and compacted to a dry density of 1.70 g/cm<sup>3</sup> and kept confined during the test. For the high suctions, both retention curves are quite similar, but below ~10 MPa they clearly diverge, because the powder continues to take water as suction decreases, while the water content of the confined sample barely increases with further suction reduction. For the FEBEX bentonite, the difference between the water retention capacity of compacted samples allowed to swell freely and kept under constant volume has also been checked (Villar, 2002; Villar and Lloret, 2004). In this case, the difference between both curves also becomes obvious for suctions of <10 MPa.

Figure 13 shows the retention curves obtained for different dry densities with the block/sensor method. Some of the data plotted were presented above and others (those for the MX-80 bentonite compacted at 1.5 and 1.7 g/cm<sup>3</sup>) have been taken from Villar (2005). The results are plotted in terms of degree of saturation in order to appreciate the difference between densities. The figure shows that for each suction value, the amount of water taken by the FEBEX bentonite is greater than that taken by the MX-80 bentonite compacted at the same dry density. The disparity attenuates as the degree of saturation (*i.e.* water content) of the bentonites increases, *i.e.* as suction decreases. The retention curves obtained with the ‘cell method’ following a wetting path for the FEBEX and the MX-80 bentonites compacted at

Table 2. Results of the single-step tests in cells performed with MX-80 bentonite compacted at  $\rho_d$  1.60 g/cm<sup>3</sup>.

Initial <i>w</i> (%)	10.5	10.5	10.5	8.7	9.2	9.2	9.2
Suction (MPa)	127.2	127.2	36.3	19.9	10.9	4.3	1.3
RH (%)	40.5	40.5	77.3	86.8	92.5	97.0	99.1
Stabilization time (days)	98	98	181	92	64	81	76
Final <i>w</i> (%)	8.6	9.0	16.8	20.3	23.0	24.2	26.5
Basal spacing (Å)	12.70	12.77		15.52	15.54	15.80	15.99

Table 3. Results of the single-step tests in cells performed with MX-80 bentonite compacted at  $\rho_d$  1.30 g/cm<sup>3</sup>.

Initial <i>w</i> (%)	10.5	10.5	10.5	10.5	8.7	9.2	9.2	9.2
Suction (MPa)	127.2	127.2	36.3	36.3	19.9	10.9	4.3	1.3
RH (%)	40.5	40.5	77.3	77.3	86.8	92.5	97.0	99.1
Stabilization time (days)	98	98	92	92	92	64	81	76
Final <i>w</i> (%)	8.6	8.4	17.3	16.9	21.3	23.5	26.7	29.1
Basal spacing (Å)	13.05	12.83	15.53	15.18	15.54	15.43	15.50	15.55

dry density of 1.60 g/cm<sup>3</sup> are compared in Figure 14. Again, the retention capacity of the FEBEX bentonite is manifest, *i.e.* for a given suction, the water content of the FEBEX bentonite is greater than that of MX-bentonite. However, as in the case of the block/sensor method results, the difference between the two bentonites becomes smaller towards lower suctions.

It is usually accepted that the amount of water sorbed by smectites increases as the ionic potential of the exchangeable cation increases, as this is strongly correlated to the hydration energy of the cations, thus increasing in the order Na<Ca<Mg. For example, Hall and Astill (1989) determined the adsorption isotherms for water on SWy-1 montmorillonite homoionized in different cations, and found a clearly greater retention capacity for the Ca-form than for the Na-form for the relative pressure range from 0 to 0.7. Dontsova *et al.* (2004) studied the sorption of water by the clay fractions of two agricultural soils exchanged with different cations and concluded that the amount of water sorbed increased in the order Na<Ca<Mg. Caballero *et al.* (2004) determined the adsorption isotherms of the FEBEX bentonite exchanged with different proportions of Ca and Na, and found that the retention capacity of the Ca-FEBEX was greater than for the Na-FEBEX, although the difference decreased towards high RH, the retention capacity of the Na-exchanged form being slightly greater for the highest relative pressure ( $P/P_0 = 1$ ). Moreover, Saiyouri *et al.* (2004) hydrated samples of MX-80 and FoCa (which is mainly calcic) bentonites from a very strongly compacted

initial state, and the wetting curves showed that the MX-80 bentonite sorbed much more water than FoCa for suctions below 0.1 MPa (RH = 99.9%).

These published results indicate that for most of the relative pressure (or suction) range, the retention capacity of predominantly divalent (Ca and Mg) smectites is greater than that of sodic ones, consistent with what is observed in the current work. This trend inverts for very high RH. It must be pointed out that the examples taken from the literature correspond to powder samples or compacted samples allowed to swell freely during absorption (results of Saiyouri *et al.*, 2004), whereas in this work the samples were compacted and confined, swelling being hindered.

Figures 15 and 16 show the results of the single-step equilibration in cells in terms of the basal spacings and water contents measured after equilibrium at a given suction for the two bentonites. For the FEBEX bentonite, the water content decrease as suction increases is accompanied by a decrease in the basal spacing, although in the range of RH tested (from 21 to 79%), it remains between 14 and 16 Å, corresponding in all cases to a 2-layer hydrate. For the MX-80 bentonite, the basal spacings measured in the interval of water contents from 17 to 29%, which correspond to RH from 77 to 99%, range from 15.18 to 15.80 Å. This can be considered a narrow span indicating the existence of a 2-layer hydrate in the interlayer for the range of suctions tested. However, for a suction of 127 MPa, corresponding to a RH of 40%, the water content of the bentonite decreases to values

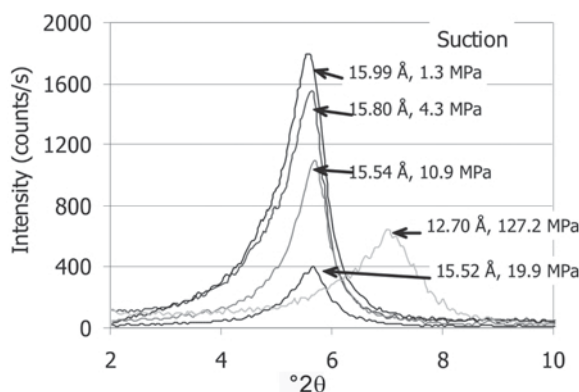


Figure 11. XRD patterns of the MX-80 bentonite compacted at dry density of 1.6 g/cm<sup>3</sup> after stabilization at different suctions. CuK $\alpha$  radiation.

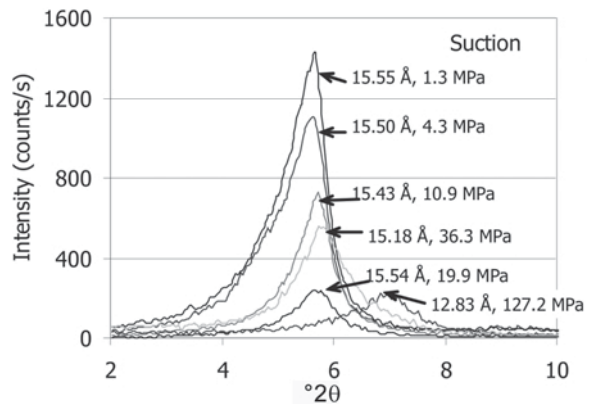


Figure 12. XRD patterns of the MX-80 bentonite compacted at dry density of 1.3 g/cm<sup>3</sup> after stabilization at different suctions. CuK $\alpha$  radiation.

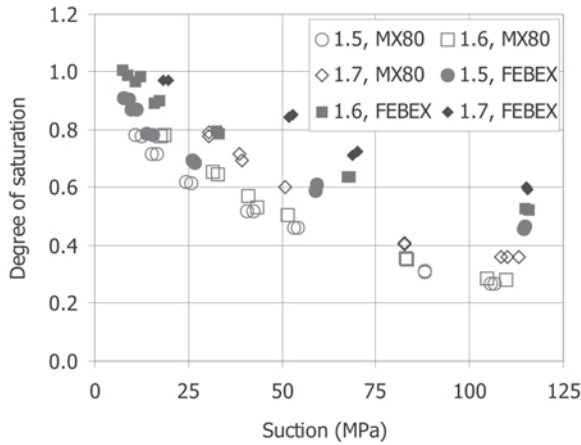


Figure 13. Retention curves of the compacted FEBEX and MX-80 bentonites obtained using the block/sensor method.

slightly below initial (from 11 to 8–9%), reflected in basal spacings of <math><13 \text{ \AA}</math> for the two clay densities, indicating the existence (or at least the predominance) of just a 1-layer hydrate in the interlayer. From the analysis of water-adsorption isotherms, Madsen (1998) considered that the first layer hydrate of the MX-80 bentonite powder is completed for a RH of ~50%.

Ca and Mg are the predominant cations in the exchange complex of the FEBEX bentonite, and with their high energy of hydration and octahedral coordination they are known to lead to a predominant 2-layer hydration state over an extensive range of relative humidity. Iwasaki and Watanabe (1988) showed that Ca-smectite forms its two water layer complex at 20% RH and, after that, increasing humidity increases the  $d$  spacing of the smectite only slightly, indicating that the water complex remains basically the same. Cases *et al.* (1997) state that an homogeneous 2-layer hydrate develops during adsorption in Ca-montmorillonite at

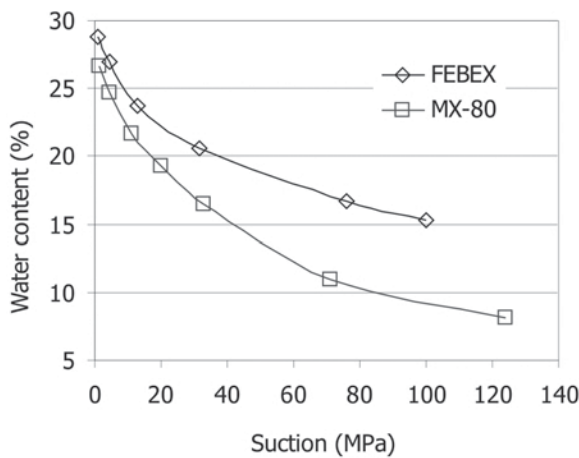


Figure 14. Retention curves obtained in cells following a wetting path for FEBEX and MX-80 bentonites compacted at dry density of  $1.60 \text{ g/cm}^3$ .

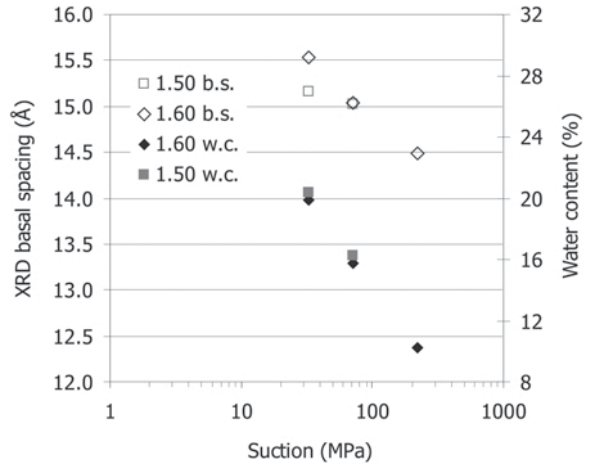


Figure 15. Results of the single-step equilibration tests in cells for the FEBEX bentonite (filled symbols: water content; open symbols: basal spacing).

$P/P_0 = 0.7$ , and in Mg-montmorillonite at  $P/P_0 = 0.4$ . Saiyouri *et al.* (2004) found the transition from the 2 to the 3-layer hydrate ( $15.6$  to  $18.6 \text{ \AA}$ ) for the FoCa bentonite (which is mainly calcic) at a RH of 97% (suction of 4 MPa), which is the same RH value found by Fernández (2003) for this transition in the granulated FEBEX bentonite.

The basal spacings measured in Ca or Mg homoionic montmorillonites by different authors are plotted in Figure 17 as a function of the relative humidity at which the samples were equilibrated. The values reported by Cases *et al.* (1997) were obtained in oriented samples of homoionized Wyoming montmorillonite, as well as those by Ferrage *et al.* (2005). It seems that below a RH of 35%, the basal spacing of these montmorillonites is  $<15 \text{ \AA}$ ; in the range from 35 to 60%, the spacings are maintained at  $\sim 15 \text{ \AA}$  and above this relative humidity, the basal spacings increase gradually, retaining values

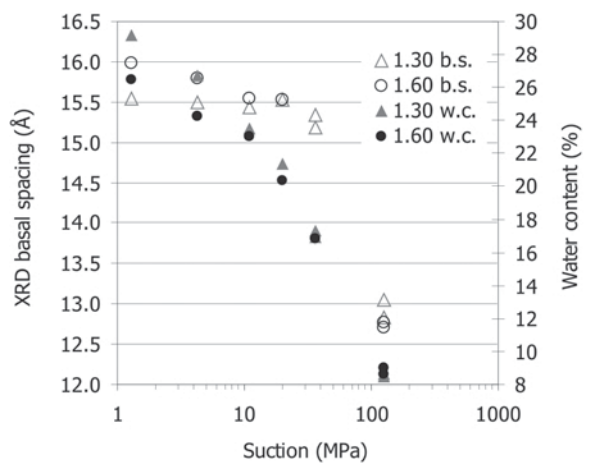


Figure 16. Results of the single-step equilibration tests in cells for the MX-80 bentonite (filled symbols: water content; open symbols: basal spacing).

which indicate the predominance of the 2-layer hydrate up to RH as high as 95%. Caballero *et al.* (2004) measured the  $d_{001}$  of FEBEX powder samples homoionized in Ca. For low vapor pressures ( $P/P_0$  between 0.05 and 0.08) they obtained values of 14 Å, and for relative pressures between 0.15 and 0.80 they measured a constant value of 15.5 Å that increased to 19 Å for  $P/P_0 = 1$ . However, Fernández (2003) found a continuous increase of the basal spacing of the natural granulated FEBEX bentonite from 14.2 to 15.8 Å when the  $P/P_0$  increased from 0.20 to 0.85.

The basal spacing measurements in Wyoming Na-montmorillonite reported by several authors in the range of RH tested in this work are plotted in Figure 18. The spacings tend to increase with relative humidity and, for RH >70%, fall between 15.2 and 16 Å, *i.e.* they correspond to the range in which the 2-layer hydrate is predominant. Cases *et al.* (1992) measured basal spacings of 15.55 Å under RH of 90% ( $P/P_0 = 0.9$ ) in Wyoming Na-montmorillonite powder, and Bérend *et al.* (1995) measured, in oriented samples of the same material,  $d_{001}$  of 15.76 Å for RH of 98%. Ferrage *et al.* (2005), also using oriented slide mounts, measured  $d_{001}$  of 15.28 Å for Na-homoionized Wyoming montmorillonite under a RH of 80%. For RH below 60% they reported basal spacings corresponding to mono-hydrated smectites (*i.e.* between 12.3 and 12.7 Å). For a RH of 40%, similar basal spacings have been measured in this work in the samples compacted at dry density of 1.60 g/cm<sup>3</sup>, and slightly higher for the samples compacted at dry density of 1.30 g/cm<sup>3</sup> (~13 Å), indicating the initiation of the transition to the 2-layer hydrate. Devineau *et al.* (2006) report an evolution of the basal spacing measured for an MX-80 pellet of initial density 1.70 g/cm<sup>3</sup> equilibrated in free conditions (*i.e.* allowed

to swell) from 14 Å for a relative pressure of ~0.65 to 16 Å for a relative pressure of 0.97. For confined bentonite compacted at 1.7 g/cm<sup>3</sup> they measured in neutron diffraction patterns a 001 reflection of 15.2 Å for a RH of 81%.

Figures 17 and 18 show that, despite the fact that the specimens in this work were compacted and confined, the  $d_{001}$  values measured are of the order of those measured by other authors in powdered or oriented samples. However, as discussed above, for suctions of <10 MPa, the water content of the bentonite is affected by its stress state, being less in confined samples. This points to the predominance of interlayer water as the water content of the bentonite increases in confined conditions. The fact that the difference in water content for a given suction is not reflected in the basal spacings also indicates that the hydration of the exchangeable cations is not hindered by confinement (at least for the range of dry densities and RH tested). Moreover, Devineau *et al.* (2006) observed that confinement appears to modify the repartition of water molecules between inter-aggregate pores and interlayer spaces, favoring adsorption in the interlayer domain, thus leading to the early formation of a 3-layer hydrate when the bentonite is compacted at dry density of 1.7 g/cm<sup>3</sup>. The lower dry densities tested in this work could be the reason why this 3-layer formation has not been observed, but nevertheless, the basal spacings measured for the MX-80 bentonite compacted at dry density of 1.6 g/cm<sup>3</sup> and stabilized at high RH values are slightly greater than those measured for dry density of 1.3 g/cm<sup>3</sup>, although the water contents corresponding to the higher density are lower (Figure 16).

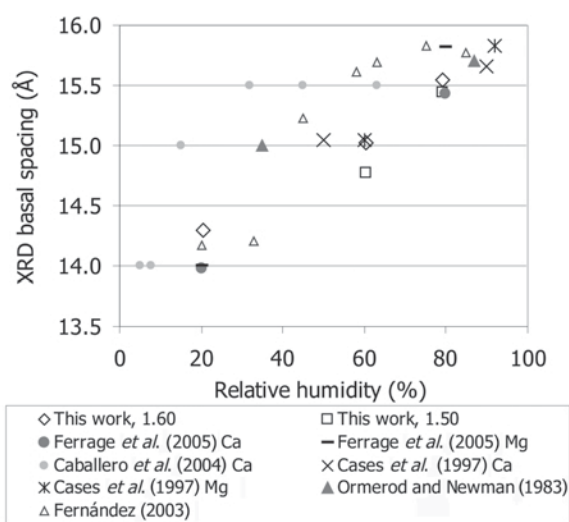


Figure 17. Basal spacings measured in Ca- and Mg-montmorillonites by different authors in the range of relative humidities studied in this work (dry density indicated in g/cm<sup>3</sup>).

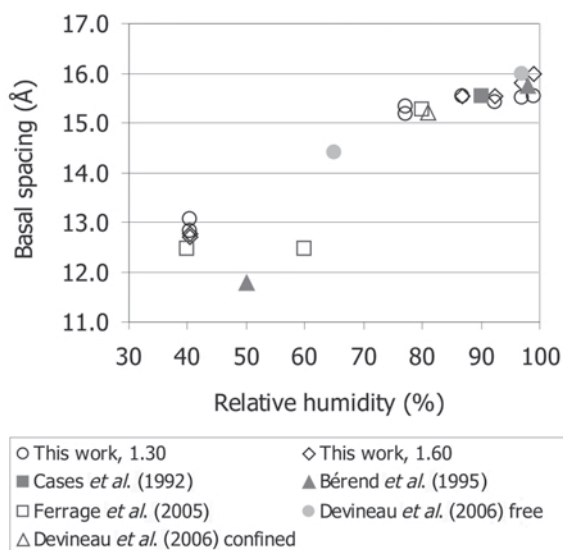


Figure 18. Basal spacings measured, by different authors, in Na-montmorillonites in the range of relative humidities studied in this work (dry density indicated in g/cm<sup>3</sup>).

## SUMMARY AND CONCLUSIONS

The aim of this work was the determination of the retention curves of two natural compacted bentonites, trying to reproduce, as far as was possible, the conditions of the engineered barrier of a HLW repository. For this reason the bentonites were used in their natural state (without previous drying or grinding), compacted at high density and kept at constant volume during the determination, as the volume changes of the bentonite barrier in the repository are restricted. Two methods were developed. In the cell method the compacted bentonite is kept in a rigid, perforated cell while it equilibrates in a controlled-RH atmosphere. In the sensor/block method the bentonite is mixed with water, the mixture is compacted, and the suction inside the block is measured with a hygrometer. The results obtained with both methods are largely consistent, the second being much quicker to obtain but unsuitable for the very low and very high suctions. Also, a disparity between both methods has been found for suctions of <10 MPa (RH of 93%) in the case of the FEBEX bentonite.

The application of the two methodologies has allowed the determination of the water retention curves at 20°C of the FEBEX bentonite compacted at dry density of 1.50, 1.60 and 1.70 g/cm<sup>3</sup> and of the MX-80 bentonite compacted at 1.30 and 1.60 g/cm<sup>3</sup>. The repercussion of the dry density on the water retention capacity is clear in both bentonites only for suctions of <10 MPa, the retention capacity decreasing with the increase of dry density.

Despite the fact that the materials used are natural bentonites, with impurities and different mineralogy and texture, their behavior is consistent with that of other, purer smectites with the same exchangeable cations. This confirms that the behavior of bentonites with respect to water adsorption (which in turn conditions many of their hydro-mechanical properties) is mainly controlled by the exchangeable cations.

The basal spacings of some samples have been measured after equilibration at different RH by XRD over a plane surface of the compacted specimen. The values obtained are in the order of those found by other authors for powdered smectites or compacted smectites allowed to swell during the water uptake, showing that, at least in the ranges of RH and dry density tested, the interlayer swelling is not hindered by external confinement, and also that when the bentonite is saturated under confined conditions, there is a predominance of inter-layer water.

## ACKNOWLEDGMENTS

The work on the FEBEX bentonite was co-funded by ENRESA (Spanish National Agency for Waste Management) and the European Commission (EC Contracts FI4W-CT95-006 and FIKW-CT-2000-00016). The research

agreement CIEMAT/ENRESA 00/271 financed the research related to the MX-80 bentonite. The laboratory work was performed by R. Campos and J. Aroz at CIEMAT (Madrid, Spain). The XRD tests were performed by L. Gutiérrez at CIEMAT.

## REFERENCES

- Al-Mukhtar, M., Qi, Y., Alcocer, J.-F. and Bergaya, F. (1999) Oedometric and water-retention behavior of highly compacted unsaturated smectites. *Canadian Geotechnical Journal*, **36**, 675–684.
- Bérend, I., Cases, J.-M., François, M., Uriot, J.-P., Michot, L., Masion, A. and Thomas, F. (1995) Mechanism of adsorption and desorption of water vapor by homoionic montmorillonites: 2. The Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>-exchanged forms. *Clays and Clay Minerals*, **43**, 324–336.
- Caballero, E., Jiménez de Cisneros, C. and Linares, J. (2004) Physicochemical properties of bentonite: effect of the exchangeable cations. PP. 40–47 in: *FEBEX II Project. THG laboratory experiments* (T. Missana, editor). Publicación Técnica ENRESA **09/2004**, Madrid.
- Cases, J.M., Bérend, I., Besson, G., François, M., Uriot, J.P., Thomas, F. and Poirier, J.E. (1992) Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite. 1. The sodium-exchanged form. *Langmuir*, **8**, 2730–2739.
- Cases, J.M., Bérend, I., Besson, G., François, M., Uriot, J.P., Michot, L. and Thomas, F. (1997) Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite. 3. The Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> exchanged forms. *Clays and Clay Minerals*, **45**, 8–22.
- Cuadros, J., Huertas, F., Delgado, A. and Linares, J. (1994) Determination of hydration (H<sub>2</sub>O) and structural (H<sub>2</sub>O<sup>+</sup>) water for chemical analysis of smectites. Application to Los Trancos smectites, Spain. *Clay Minerals*, **29**, 297–300.
- Devineau, K., Bihannic, I., Michot, L., Villiéras, F., Masrouri, F., Cuisinier, O., Fragneto, G. and Michau, N. (2006) In situ neutron diffraction analysis of the influence of geometric confinement on crystalline swelling of montmorillonite. *Applied Clay Science*, **31**, 76–84.
- Dontsova, K.M., Norton, L.D., Johnston, C.T. and Bigham, J. (2004) Influence of exchangeable cations on water adsorption by soil clays. *Soil Science Society of America Journal*, **68**, 1218–1227.
- ENRESA (1995) *Almacenamiento geológico profundo de residuos radiactivos de alta actividad (AGP). Diseños conceptuales genéricos*. Publicación Técnica ENRESA **11/95**, Madrid, 105 pp.
- ENRESA (1998) *FEBEX. Bentonite: origin, properties and fabrication of blocks*. Publicación Técnica ENRESA **4/98**, Madrid, 146 pp.
- ENRESA (2000) *FEBEX Project. Full-scale engineered barriers experiment for a deep geological repository for high level radioactive waste in crystalline host rock*. Final Report. Publicación Técnica ENRESA **1/2000**, Madrid, 354 pp.
- Fernández, A.M. (2003) Caracterización y modelización del agua intersticial en materiales arcillosos: Estudio de la bentonita de Cortijo de Archidona. PhD thesis, Universidad Autónoma de Madrid, Madrid, 505 pp.
- Ferrage, E., Lanson, B., Sakharov, B.A. and Drits, V.A. (2005) Investigation of smectite hydration properties by modeling experimental X-ray diffraction patterns: Part I. Montmorillonite hydration properties. *American Mineralogist*, **90**, 1358–1374.
- Gens, A., Guimaraes, L. do N., Garcia-Molina, A. and Alonso, E.E. (2002) Factors controlling rock-clay buffer interaction in a radioactive waste repository. *Engineering Geology*, **64**,

- 297–308.
- Hall, P.L. and Astill, D.M. (1989) Adsorption of water by homoionic exchange forms of Wyoming montmorillonite (SWy-1). *Clays and Clay Minerals*, **37**, 355–363.
- Iwasaki, T. and Watanabe, T. (1988) Distribution of Ca and Na ions in dioctahedral smectites and interstratified dioctahedral mica/smectites. *Clays and Clay Minerals*, **36**, 73–82.
- Lloret, A., Romero, E. and Villar, M.V. (2004) *FEBEX II Project. Final report on thermo-hydro-mechanical laboratory tests*. Publicación Técnica ENRESA **10/04**, Madrid, 180 pp.
- Madsen, F.T. (1998) Clay mineralogical investigations related to nuclear waste disposal. *Clay Minerals*, **33**, 109–129.
- Marcial, D. (2003) Comportement hydromécanique et microstructural des matériaux de barrière ouvragée. PhD thesis, École Nationale des Ponts et Chaussées, Paris, 316 pp.
- Ng, C.W.W. and Pang, Y.W. (2000) Influence of stress state on soil-water characteristics and slope stability. *Journal of Geotechnical and Geoenvironmental Engineering*, **126**, 157–166.
- Ormerod, E.C. and Newman, A.C.D. (1983) Water sorption on Ca-saturated clays: II. Internal and external surfaces of montmorillonite. *Clay Minerals*, **18**, 289–299.
- Pusch, R. (1994) *Waste Disposal in Rock*. Developments in Geotechnical Engineering, **76**. Elsevier, Amsterdam, 490 pp.
- Romero, E. and Vaunat, J. (2000) Retention curves of deformable clays. Pp. 91–106 in: *Experimental Evidences and Theoretical Approaches in Unsaturated Soils* (A. Tarantino and C. Mancuso, editors). Balkema, Rotterdam, The Netherlands.
- Saiyouri, N., Tessier, D. and Hicher, P.Y. (2004) Experimental study of swelling in unsaturated compacted clays. *Clay Minerals*, **39**, 469–479.
- Sauzéat, E., Guillaume, D., Neaman, A., Dubessy, J., François, M., Pfeiffert, C., Pelletier, M., Ruck, R., Barrès, O., Yvon, J., Villiéras, F. and Cathelineau, M. (2001) *Caractérisation fine de l'argile brute MX-80: caractérisation minéralogique, cristallographique et texturale de l'argile MX-80*. ANDRA C RP IENG 01-001, France, 94 pp.
- Simms, P.H. and Yanful, E.K. (2005) A pore-network model for hydromechanical coupling in unsaturated compacted clayey soils. *Canadian Geotechnical Journal*, **42**, 499–514.
- Svensk Kärnbränslehantering AB (2002) *Äspö Hard Rock Laboratory. Annual Report 2001*. SKB Technical Report **TR-02-10**, Stockholm, 184 pp.
- Villar, M.V. (2002) *Thermo-hydro-mechanical characterisation of a bentonite from Cabo de Gata. A study applied to the use of bentonite as sealing material in high level radioactive waste repositories*. Publicación Técnica ENRESA **01/2002**, Madrid, 258 pp.
- Villar, M.V. (2005) *MX-80 bentonite. Thermo-hydro-mechanical characterisation performed at CIEMAT in the context of the Prototype Project*. Informes Técnicos CIEMAT **1053**, Madrid, 45 pp.
- Villar, M.V. and Lloret, A. (2004) Influence of temperature on the hydro-mechanical behaviour of a compacted bentonite. *Applied Clay Science*, **26**, 337–350.
- Villar, M.V., García-Siñeriz, J.L., Bárcena, I. and Lloret, A. (2005a) State of the bentonite barrier after five years operation of an in situ test simulating a high level radioactive waste repository. *Engineering Geology*, **80**, 175–198.
- Villar, M.V., Martín, P.L. and Lloret, A. (2005b) Determination of water retention curves of two bentonites at high temperature. Pp. 77–82 in: *Advanced Experimental Unsaturated Soil Mechanics. Experus 2005* (A. Tarantino, E. Romero and Y.J. Cui, editors). A.A. Balkema Publishers, London.
- Yahia-Aissa, M. (1999) Comportement hydromécanique d'une argile gonflante fortement compactée. PhD thesis, École Nationale des Ponts et Chaussées, CERMES, Paris.
- Yahia-Aissa, M., Delage, P. and Cui, Y.J. (2001) Suction-water content relationship in swelling clays. Pp. 65–68 in: *Clay Science for Engineering* (K. Adachi and M. Fukue, editors). Balkema, Rotterdam.

(Received 19 September 2006; revised 19 January 2007; Ms. 1219)