PREPRINT VERSION

Molecular dynamics data for modelling the microstructural behaviour of compacted sodium bentonites

Vicente Navarro ^{a*}, Ángel Yustres ^a, Andreas Jenni ^b, Gema De la Morena ^a, Laura Asensio ^a, Rubén López-Vizcaíno ^a, Virginia Cabrera ^a, Paul Wersin ^b, Urs Mäder ^b, Eveliina Muuri ^c, Mika Niskanen ^c, Bukunmi Akinwunmi ^d, Janne T. Hirvi ^d, Tapani A. Pakkanen ^d

^a Geoenvironmental Group, University of Castilla-La Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain

^b University of Bern, Institute of Geological Sciences, Rock-Water Interaction Group, Baltzerstrasse 3, 3012 Bern, Switzerland

^c Posiva Oy, Olkiluoto, FI-27160 Eurajoki, Finland

^d Department of Chemistry, University of Eastern Finland, P.O. Box 111, FI-80101 Joensuu, Finland

* Corresponding author. Email address: vicente.navarro@uclm.es; University of Castilla-La Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain. Tel. +34 926295300 ext. 3264:

Published version here

<https://doi.org/10.1016/j.clay.2020.105932>

Abstract

The water content of a bentonite at low saturation (equal to high suction) defines the void ratio of the nano-scale porosity located in the clay interlayers and close to the clay grain surfaces. However, the measured suction curves should not be extrapolated straightforwardly to lower suction values, because, in that case, the presence of water in larger pores between aggregates can be non-negligible. This work analyses the use of data obtained from molecular dynamics models to assess the validity of such extrapolations, and defines the variables needed to compare the results from molecular dynamics and suction experiments. The encouraging agreement contributed to the confidence in the proposed procedure, which enabled a new strategy that uses molecular dynamics data to model the macroscopic behaviour of compacted sodium bentonites.

Keywords

Sodium bentonite; continuum modelling; molecular dynamics; microstructural deformability

1. Introduction

The low permeability, retention properties and swelling capacity of compacted bentonites make them a material of great interest for the construction of engineered barriers in deep geological repositories of high-level radioactive waste (Pusch, 1994). Given the bimodal distribution of their pore size distribution (Romero et al., 1999; Lloret et al., 2003; Delage et al., 2006), many authors used double porosity approaches to describe their thermo-hydro-chemo-mechanical behaviour (Musso et al., 2013; Sánchez et al., 2016; Yustres et al., 2017; among others). Such approaches considered two overlapping continua, micro- and macrostructure. Both terms are understood in this paper as equivalent continuous media used to characterise the macroscopic behaviour of bentonite, not as definitions with textural meaning. The microstructure allows to simulate the effect that the processes occurring in the space inside the aggregates of clay particles have on the system behaviour, while the macrostructure is used to describe the effect of the pores among those aggregates (Gens and Alonso, 1992). The global strain increment of the system $d\boldsymbol{\varepsilon}$ (the engineering or Voigt notation is used for the strain tensor, and vectors are represented in bold) is generally decomposed using an additive structure:

$$d\boldsymbol{\varepsilon} = d\boldsymbol{\varepsilon}_m + d\boldsymbol{\varepsilon}_M + d\boldsymbol{\varepsilon}_{M-m} \quad (1)$$

where $d\boldsymbol{\varepsilon}_m$ is the strain increment induced by processes linked to the microstructure only, $d\boldsymbol{\varepsilon}_M$ is the analogous magnitude linked to the macrostructure, and $d\boldsymbol{\varepsilon}_{M-m}$ defines the strain increment caused by the macrostructure as a consequence of the rearrangement of the microstructure. Although the constitutive modelling of the stress-strain behaviour of bentonites is under development, there is a broad experience in the application of the Barcelona Basic Model (Alonso et al., 1990) to compute $d\boldsymbol{\varepsilon}_M$ (Alonso and Hoffmann, 2007; Chen and Ledesma, 2009; Gens et al., 2009), and in the use of the

modelling framework provided by the BExM (Gens and Alonso, 1992; Alonso et al., 1999) to characterise $d\epsilon_{M-m}$ (Sánchez et al., 2012; Vilarrasa et al., 2016). $d\epsilon_m$ is usually determined with models based on the microstructural volumetric strain increment $d\epsilon_{V,m}$ (see, for instance, Sánchez et al., 2005), which can be defined using the increase of the microstructural void ratio e_m (volume of intra-aggregate voids per volume of minerals):

$$d\epsilon_{V,m} = -\frac{de_m}{1+e} \quad (2)$$

where e is the total void ratio (total volume of voids per volume of minerals). If the microstructure is assumed to be saturated (see, for example, Gens and Alonso, 1992; Yong, 1999; Mašín and Khalili, 2016), e_m can be obtained from the water retention properties of the microstructure (Navarro et al., 2015). Several proposals were presented to characterise such properties, differentiating them from those of the macrostructure (Della Vecchia et al., 2013; Navarro et al., 2015; Dieudonné et al., 2017). In all cases, the water retention model of the microstructure was characterised using experimental values that correspond to high suctions (higher than 10 MPa for MX-80 bentonite; Villar, 2007), when a large fraction of the soil water content is inside the clay particle aggregates (Romero et al., 2011). Subsequently, the model is used to predict e_m for intermediate and low suction values. However, it is not easy to validate the model for the latter suctions, since the macrostructural water content starts to be significant, and it is difficult to differentiate between micro- and macrostructural water. Thus, strategies to inspect the validity of the extrapolation are of interest.

Molecular dynamics models (MDM) can be used as an inspection tool. Works like those of Teppen et al. (1997), Cygan et al. (2009) and Song and Wang (2019) showed that such models are helpful for improving the qualitative description of the microstructural behaviour of clays. However, the MDM results must be interpreted or quantitatively

applied with caution, since the data are obtained in systems of limited size and complexity, and their use for continuum modelling is not immediate. This article analyses such use to obtain information that allows for the inspection of the extrapolation of e_m .

To this end, the MDM and the tests used to obtain e_m data are first described. Second, the analogy between the MDM considered and the bulk behaviour of bentonite is analysed. That is, the conceptual basis to convert the information provided by MDM to a continuous media model are revised. Finally, the results obtained are reviewed and discussed.

2. Materials and methods

MDM adopt a simplified idealisation of clays at an atomic and molecular scale, analysing interactions as equivalent force fields (see Fig. 1).

Fig. 1. Atomic level structure of Na-montmorillonite and idealisation of the MDM. The bottom montmorillonite layer is fixed, the sketched springs cause the external pressure, t is the average layer thickness and d is the average basal spacing between layers. The colour code for atoms:

yellow - silicon, pink - aluminium, green - magnesium, red - oxygen, white - hydrogen and blue
- sodium.

In the two models analysed in this work, Sun et al. (2015a) and Akinwunmi et al. (2020), the CLAYFF force field (Cygan et al., 2004) was used to define the interaction forces, representing water molecules with the SPC model (Berendsen et al., 1981). The interaction between two montmorillonite layers was simulated. Both layers were composed of eight unit cells with the chemical formula $M_{0.5n}(Si_8)(Al_{3.5}Mg_{0.5})O_{20}(OH)_4$ per cell (where “M” is a cation with charge “n”). The system also included some 6000 water molecules and a variable number of NaCl molecules to simulate different salinity conditions. An external pressure P_s was also introduced, which opposed to the separation of montmorillonite layers. In the considered system (Fig. 1), t is the layer thickness and d is the basal spacing between layers.

The value of P_s and d at equilibrium for different salinity conditions were obtained (Fig. 2, adapted from Sun et al., 2015a, and Akinwunmi et al., 2020), that is, when P_s counterbalances the swelling pressure developed between layers.

Since isolated montmorillonite layers were considered, effects arising from the arrangement of the layers into particles, and their interaction, were not taken into account. Consequently, the analogue defined in the MDM cannot reproduce the subdivision of particles that, as pointed out by several authors (Cases et al., 1992; Saiyouri et al., 2004; Salles et al., 2009), plays an important role in clay hydration.

Thus, the quantitative information derived from MDM is more reliable for values of d greater than 1.8 nm, when, according to the model of Sun et al. (2015b), the interlayer hydration is very developed, and the subdivision of particles has practically finished (Cases et al., 1992). In addition, taking into account that in the MDM particles are considered to be formed by isolated clay layers, the quantitative results are more reliable

when Na-montmorillonites are analysed, since under the hydration conditions considered a reduced number of layers forms their particles. Cases et al. (1992) considered, in advanced hydration conditions, particles of 6 layers, while Neretnieks et al. (2009) suggested that, upon hydration, particles could break up into individual layers. Based on this, the current analysis focuses on the MDM results in Figs. 2 a and 2 b (adapted from Sun et al., 2015a and Akinwunmi et al., 2020), corresponding to Na-montmorillonites ($M = \text{Na}$ and $n = 1$ in each unit cell) in pure water and solutions with different NaCl concentrations.

Fig. 2. The swelling pressures from the MDM by Sun et al. (2015a) and by Akinwunmi et al. (2020) for (a) Pure water and (b) different NaCl concentrations.

To obtain the e_m model to be inspected, experimental results from Cases et al. (1992), Bérend et al. (1995), Montes-H et al. (2003) and Salles et al. (2009), see Fig. 3, were used. Although they were not pure montmorillonites, all the analysed bentonites had a montmorillonite content greater than 79% (see Table 1). The tests considered in Fig. 3 were conducted with sodium exchanged samples obtained using a process similar to that followed by Rytwo et al. (1996). The samples were prepared with de-ionised water, and the suction was controlled using the vapour equilibrium technique (Pintado et al., 2009). The results used correspond to wetting paths. To define e_m , it was assumed that, in the suction range considered in the tests (Fig. 3), all the soil water content was contained in the saturated microstructure.

Table 1. Properties of the sodium-exchanged MX-80 bentonites in the tests used to derive the model proposed by De la Morena et al. (2018).

Type	Reference	Amount of smectite (%)	X_{Na} (%)	X_{Ca} (%)	CEC (mol _c /kg)
Sodium	Cases et al. (1992)	97.2	100	0	0.95
Sodium	Bérend et al. (1995)	99	97.6	2	0.996
Sodium	Montes-H et al. (2003)	79.2	100	0	0.83
Sodium	Salles et al. (2009)	100	100	0	0.95

Fig. 3. Experimental data for e_m obtained from Cases et al. (1992), Bérend et al. (1995), Montes-H et al. (2003) and Salles et al. (2009).

3. Theoretical background

To make the analogue provided by MDM useful, a functional relationship must be defined between the variables used at the two scales. In the MDM tests the void ratio can be computed as:

$$\text{Microscopic void ratio: } \frac{\text{Microscopic void volume}}{\text{Volume of minerals}} = \frac{d-t}{t} = \frac{d}{t} - 1 \quad (3)$$

where d and t (Fig. 1) have the statistical meaning of the average values of the basal spacing and the montmorillonite layer thickness, respectively. The microscopic void ratio is equal to e_m only if the montmorillonite particles are formed by isolated parallel clay layers, and there are no significant heterogeneities in the aggregates. Although this is not strictly true, it was assumed that, for the d values analysed in this work, Eq. (3) provides a valid functional relationship, linking the x-axis in Fig. 2 with the y-axis in Fig. 3:

$$e_m = \frac{d-t}{t} = \frac{d}{t} - 1 \quad (4)$$

To define the relationship between the y-axis in Fig. 2 with the x-axis in Fig. 3, the meaning of the magnitudes used in the figures must be explained. As described in Section 2, the pressure Ps in Fig. 2 has a purely mechanical meaning: the pressure that had to be added in the MDM to the interparticle forces to avoid the separation of the montmorillonite layers (Fig. 1). In the macroscopic model, the analogue to the separation, or d increase, is the increase of e_m . The latter occurs when water enters the microstructure from the macrostructure. This process of mass exchange is controlled by the value of the water chemical potential in the two structural levels. The chemical potentials of macrostructural and microstructural water, μ_M and μ_m respectively, can be defined as (Karnland et al., 2005; Navarro et al., 2018):

$$\mu_M = \mu_{VO} - \frac{WMM}{\rho_W} (s_M + s_{MO}) \quad (5)$$

and:

$$\mu_m = \mu_{VO} + \frac{WMM}{\rho_W} (p - \pi) + \Delta\mu_{mNCC} \quad (6)$$

where μ_{VO} is the chemical potential of pure free water, WMM is the water molar mass and ρ_W is the density of water. At equilibrium, $\mu_M = \mu_m$ holds, and consequently:

$$\pi = (p + s_M) + (s_{MO} - \Delta s_{mNCC}) \quad (7)$$

where π is the thermodynamic swelling pressure (equivalent to the thermodynamic osmotic pressure of Lewis 1952), p is the net mean stress (defined as the mean stress minus the gas pressure, P_G), s_M is the macrostructural suction (identified with the capillary suction: $s_M = P_G - P_L$, where P_L is the liquid pressure), s_{MO} is the osmotic suction of the macrostructure, and Δs_{mNCC} defines the increase in chemical potential $\Delta\mu_{mNCC}$ expressed in terms of suction ($\Delta s_{mNCC} = -\rho_W \Delta\mu_{mNCC} / WMM$) due to the ions (cations and anions) present in the microstructure in excess of the cation exchange capacity.

After introducing the following definitions:

$$\pi_{B,HM} = p + s_M; \quad \pi_{B,S} = s_{MO} - \Delta s_{mNCC}; \quad \pi_B = \pi_{B,HM} + \pi_{B,S} \quad (8)$$

Eq. (7) can be rewritten as:

$$\pi = \pi_B \quad (9)$$

Both $\pi_{B,HM}$ and $\pi_{B,S}$ can be understood as components of the “boundary pressure” π_B that the macrostructure exerts on the microstructure. The first component, subscript HM, is of hydro-mechanical nature, while the second, subscript S, is caused by salinity (Navarro et al., 2018). When the microstructural pressure π overcomes π_B , e_m will grow. For this swelling to be prevented, under constant salinity conditions, $\pi_{B,HM}$ will have to

increase. Then, provided that e_m is the analogue for d , $\pi_{B,HM}$ is the analogue for Ps .

Consequently, to compare Figs. 2 and 3, in addition to converting the values of d in Fig.

2 to values of e_m following Eq. (4), π is computed from Ps , following Eqs. (8) and (9),

as:

$$\pi = Ps + (s_{MO} - \Delta s_{mNCC}) \quad (10)$$

Therefore, for pure water, $\pi = Ps$, and pressures from MDM can be directly compared

with pressures in the water retention curves. In the simulations with non-negligible

salinity, Fig. 2 b, the macrostructural liquid is an aqueous solution of sodium chloride of

a concentration under 1 M. Then, according to Garrels and Christ (1965), the

macrostructural osmotic suction can be computed as:

$$s_{MO} = -\frac{\rho_w}{WMM} R T \ln(1 - 0.017 [c_{Cl,M} + c_{Na,M}]) \quad (11)$$

where $c_{Cl,M}$ and $c_{Na,M}$ are the molalities of chloride and sodium and R is the universal

gas constant. Since electroneutrality holds, $c_{Cl,M} = c_{Na,M}$. As $c_{Na,M}$ is known in each

MDM simulation, see Fig. 2 b, s_{MO} can be computed using Eq. (11), and then π can be

obtained with Eq. (10).

Δs_{mNCC} in Eq. (10) is a function of the concentration of the non-charge-compensating

ions (Cl^- and Na^+) present in the microstructure. To compute these concentrations, the

strategy adopted by Karnland et al. (2005) and Tournassat and Appelo (2011) may be

followed, which is based on the Donnan equilibrium approach (Helfferich, 1962). If the

Donnan porespace is assumed to correspond to the microporosity, the ion

concentrations in the two continua are linked through a partition function B (Navarro et

al., 2017):

$$C_{Cl,m} = \frac{C_{Cl,M}}{B} \quad ; \quad C_{Na,m} = B C_{Na,M} \quad (12)$$

where $C_{i,j}$ is the molar concentration of ion “i” ($i = \text{Cl}, \text{Na}$) in the continuum “j” ($j = \text{m}, \text{M}$). In addition, meeting electroneutrality in the microstructure will imply:

$$C_{\text{Na,m}} - C_{\text{Cl,m}} - q = 0 \quad (13)$$

where the surface charge density q (mol_c/L) is defined as:

$$q = \frac{CEC \cdot \rho_{\text{mineral}}}{e_m} \quad (14)$$

being CEC the cation exchange capacity and ρ_{mineral} the clay mineral density. After this definition, and taking into account $c_{\text{Cl,M}} = c_{\text{Na,M}}$, B is obtained from Eqs. (12) and (13):

$$B = \frac{b + \sqrt{b^2 + 4}}{2}, \quad b = \frac{q}{C_{\text{Na,M}}} = \frac{CEC \rho_{\text{mineral}}}{e_m C_{\text{Na,M}}} \quad (15)$$

For all Cl^- concentrations, $C_{\text{Cl,m}}$ is non-charge-compensating, because the anions do not compensate the negative charge q : $C_{\text{Cl,m}} = C_{\text{Cl,mNCC}}$. Then, this concentration is equal to $C_{\text{Na,mNCC}}$, sodium cations that do not compensate q , given that $C_{\text{Na,m}} = C_{\text{Na,mNCC}} + C_{\text{Na,mCC}}$. The latter concentration corresponds to the sodium cations in exchange positions compensating q . $C_{\text{Cl,m}}$ for each of the macrostructural salinities were calculated (see Fig. 4), assuming an average mineral density, ρ_{mineral} , of 2780 kg/m³ (Navarro et al., 2017), and considering two CEC values, 0.996 and 0.83 mol_c/kg (Table 1). In all cases exposed in Fig. 4 a, the concentrations in the microstructure are lower than those in the macrostructure. For this reason, the formulation of Garrels and Christ (1965) has also been used to estimate Δs_{mNCC} as:

$$\Delta s_{\text{mNCC}} = -\frac{\rho_w}{WMM} R T \ln \left(1 - 0.017 \left[c_{\text{Cl,m}} + c_{\text{Na,mNCC}} \right] \right) \quad (16)$$

This way, the suctions in Fig. 4 b were obtained for the different macrostructural salinities. Although they are always lower than s_{MO} , their values are not negligible. For $C_{\text{Cl,M}} = 1 \text{ M}$ and $CEC = 0.83 \text{ mol}_c/\text{kg}$, Δs_{mNCC} is equal to 2 MPa, a 43% of 4.6 MPa, which is the value of s_{MO} in the same conditions. For this reason, the estimation given

by Eq. (16) is introduced into Eq. (10) to obtain π . Given that the difference between the values of Δs_{mNCC} obtained with the CEC of 0.996 and 0.83 mol_c/kg is, in all cases, less than a 5% of s_{MO} , the average of the values obtained with the two CEC values is used in the calculations.

Fig. 4. (a) $C_{Cl,m}$ for all the macrostructural salinities considered and (b) Δs_{mNCC} for the same salinities. Experimental data from Akinwunmi et al. (2020).

4. Results and discussion

The results of Figs. 2 a and 3 (obtained for pure water) together with the mean macroscopic model proposed by De la Morena et al. (2018) to define e_m in a Na-montmorillonite was compared in Fig. 5.

270

271 Fig. 5. Macroscopic model proposed by for De la Morena et al. (2018) for a Na-
 272 montmorillonite, and results from Figs. 2 a (pure water) and 3 represented in terms of e_m and π .

273

274 The quality of the agreement between model and experimental data for π values greater
 275 than 10 MPa should not be surprising, since the model was fitted to these data (De la
 276 Morena et al., 2018). However, it is remarkable how closely the data obtained with the
 277 MDM model are grouped around the trend given by the model for smaller values of π .
 278 The consistency between MDM and model is greater when e_m is greater than 0.8. If $t =$
 279 1 nm (Saiyouri et al., 2004) is assumed, e_m is equal to 0.8 for $d = 1.8$. That is, the
 280 consistency is higher when the MDM data are more reliable, which is a satisfactory
 281 result.

282 The lesser consistency for lower e_m values is not essential for the inspection of the e_m
 283 model extrapolation. Nevertheless, it is of interest to analyse the better grouping
 284 obtained for values of e_m between 0.5 and 0.6, for a better understanding of the data
 285 dispersion for greater e_m values, which are relevant for this work. For values of e_m
 286 between 0.5 and 0.6, d takes values between 1.5 and 1.6, range of basal spacings in
 287 which the MDM simulates the end of the formation of the 2-layer hydrate in the
 288 montmorillonite interlayer (Sun et al., 2015b). In the idealised and simplified system in

the MDM (with no heterogeneities and at nanometre scale, Sun et al., 2015a), that is a well-defined process, along which the basal spacing barely changes, which causes the mentioned grouping. However, as the hydration progresses, the discrete system in the MDM is able to find more equilibrium situations (Fig. 6, adapted from Sun et al., 2015a, where the evolution of d_t along the modelling time is plotted).

Fig. 6. Evolution of the d_t and $[d_t]$, time-averaged value of d , along simulation time. Data adapted from Sun et al. (2015 a). LFC: Low force constant ($10 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{nm}^{-2}$), IFC: Intermediate force constant ($50 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{nm}^{-2}$), HFC: High force constant ($150 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{nm}^{-2}$).

When the time-averaged evolution of the values, $[d_t]$, is computed, a steady-state value is reached (Fig. 6), which was described, for instance, by Song and Wang (2019). This steady time-averaged value is the value of d represented in Figs. 2 a and b: $d = [d_t]$. Even if a time-averaged steady value is reached, the MDM defines different situations close to equilibrium (Fig. 6). For this reason, different values of P_s for a same value of d were obtained, depending on the initial d -value considered and on how P_s changed with d (Figs. 2 a and b). This variability could be attempted to be reduced using a MDM of larger dimensions (note that the volume of even a reduced sample 5 mm high and with a diameter of 10 mm is 12 orders of magnitude greater than that of the MDM), or

running a large number of simulations to statistically process the results. However, this is beyond the aim of this work, since the dispersion of the MDM results does not compromise their consistency with the e_m model and given that the results in Fig. 5 represent a satisfactory inspection exercise. This is even more noticeable when the information obtained in the MDM also for non-negligible salinity conditions are considered (Figs. 7 a and b). The results are similar to those in Fig. 5, but the inspection was even more demanding because it integrated a larger amount of information.

Fig. 7. (a) Macroscopic model proposed by for De la Morena et al. (2018) for a Na-montmorillonite, and results from Figs. 2 b (different NaCl concentrations) and 3 represented in terms of e_m and π and (b) the same, together with the data in Fig. 2 (pure water) terms of e_m and π .

322

323 The correlation between all the e_m values obtained with the MDM (data in Figs. 2 a and
324 b), e_{mMDM} , and the e_m values obtained with the model by De la Morena et al. (2018) for
325 the π values corresponding to e_{mMDM} , e_{mMOD} was estimated (Fig. 8).

326

327

328 Fig. 8. Correlation between the e_m values obtained with the MDM, e_{mMDM} , and those obtained
329 with the model by De la Morena et al. (2018), e_{mMOD} , for the π values corresponding to e_{mMDM} .

330

331 A satisfactory Pearson correlation coefficient of 0.91 was obtained, which brings
332 confidence in the capability to contrast the consistency of the model with the MDM
333 results.

334 To end this section, it is worth noting the global robustness of the macroscopic
335 conceptual model, in which the definition of π as state variable builds a framework to
336 process jointly all the information independently of the salinity conditions for which it
337 was obtained.

338

5. Conclusions

The bimodal pore size distribution of compacted bentonites suggests the application of double porosity models to predict the chemo-mechanical behaviour. In doing so, for high enough suction values (greater than 10 MPa for an MX-80 bentonite, Villar 2007), the macroscopic determination of water content allows defining the changes of microstructural void ratio with respect to its thermodynamic swelling pressure (Navarro et al., 2018) in wetting paths using a state surface (De la Morena et al., 2018). This state surface plays a key role in the macroscopic models used to solve boundary value problems at an engineering scale, since it controls to a large extent the swelling behaviour of bentonite. However, it is difficult to assess the validity of the surface for lower values of suction, as the water content information integrates, in this case, also information on the water retention capacity of the macrostructure.

Molecular dynamics models contribute valuable information for such suction ranges, when the interlayer hydration is largely developed, and the subdivision of particles has then practically finished (Cases et al., 1992). For sodium montmorillonites there are particles formed by a reduced number of clay layers, being more reliable molecular dynamics models based on isolated montmorillonite layers.

From the viewpoint of a double porosity model, when describing the interaction between layers, the information obtained by the MDM is related to the modelling of the effect of the microstructural continuum level (microstructure). To assess the scope of such information, it is necessary to represent jointly the results from microscopic molecular dynamics models and from macroscopic models. To this end, an analogy between the variables characterising each of the scales must be defined. This way, Eq. (4) links for hydrated Na-montmorillonites the variables that define spatial organisation: average basal spacing at the microscopic scale and microstructural void ratio at the

macroscopic scale. Eq. (10) defines the relationship between thermodynamic forces: pressure P_s and thermodynamic swelling pressure π . In addition, Eq. (10) integrates the effect of salinity, making it possible to analyse the results obtained with all the salinities considered jointly.

Once Eqs. (4) and (10) are introduced, the simultaneous plot of the results from Sun et al. (2015a) and Akinwunmi et al. (2020) and the extrapolation of the bulk state surface from De la Morena et al. (2018), Figs. 5 and 7, reveals the consistence between both approaches in the suction range studied. The encouraging correlation between the bulk model and the results of molecular dynamics models, Fig. 8, depicts the practical use of molecular dynamics models to evaluate the validity of extrapolating the state surface for lower suction values. Thus, the applicability of molecular dynamics models as a support element in the continuum modelling of the microstructure of compacted bentonites is illustrated.

Acknowledgements

This study was funded by Posiva Oy. We are also grateful for the support received from the Spanish Ministry of Education [FPU15/02655] through the grant awarded to Ms. De la Morena, and from the Spanish Ministry of Science, Innovation and University [IJC-2018-035212] through the grant awarded to Dr. López-Vizcaíno. The data provided by Dr. Linlin Sun is greatly appreciated. The authors express their gratitude to Dr. Seppo Kasa for managing and following up on the project.

References

- Akinwunmi, B., Hirvi, J.T., Kasa, S., Pakkanen, T.A., 2020. Swelling pressure of Na- and Ca-montmorillonites in saline environments: A molecular dynamics study. *Chem. Phys.* 528, 110511, <https://doi.org/10.1016/j.chemphys.2019.110511>.
- Alonso, E., Hoffmann, C., 2007. Modelling the field behaviour of a granular expansive barrier. *Phys. Chem. Earth A/B/C* 32 (8-14), 850-865, <https://doi.org/10.1016/j.pce.2006.04.039>.
- Alonso, E.E., Gens, A., Josa, A., 1990. A constitutive model for partially saturated soils. *Géotechnique* 40(3), 405–430, <https://doi.org/10.1680/geot.1990.40.3.405>.
- Alonso, E.E., Vaunat, J., Gens, A., 1999. Modelling the mechanical behaviour of expansive clays. *Eng. Geol.* 54(1-2), 173-183, [https://doi.org/10.1016/S0013-7952\(99\)00079-4](https://doi.org/10.1016/S0013-7952(99)00079-4).
- Bérend, I., Cases, J.M., François, M., Uriot, J.P., Michot, L., Masion, A., Thomas, F., 1995. Mechanism of adsorption and desorption of water vapor by homoionic montmorillonites: 2. The Li^+ , Na^+ , K^+ , and Cs^+ -exchanged forms. *Clays Clay Miner.* 43(3), 324-336, <https://doi.org/10.1346/CCMN.1995.0430307>.
- Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., Hermans, J., 1981. Interaction models for water in relation to protein hydration. In: Pullman B (ed.) *Intermolecular forces*, Reidel Publishing, pp. 331-342, https://doi.org/10.1007/978-94-015-7658-1_21.
- Cases, J.M., Bérend, I., Besson, G., François, M., Uriot, J.P., Thomas F., Poirier, J.E., 1992. Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite. 1. The sodium-exchanged form. *Langmuir*. 8(11), 2730-2739, <https://doi.org/10.1021/la00047a025>

410 Chen, G.J., Ledesma, A., 2009. Coupled thermohydromechanical modeling of the full-
 411 scale in situ test “Prototype Repository”. *J. Geotech. Geoenviron. Eng.* 135(1),
 412 [https://doi.org/10.1061/\(ASCE\)1090-0241\(2009\)135:1\(121\)](https://doi.org/10.1061/(ASCE)1090-0241(2009)135:1(121)).

413 Cygan, R.T., Liang, J.J., Kalinichev, A.G., 2004. Molecular models of hydroxide,
 414 oxyhydroxide, and clay phases and the development of a general force field. *J. Phys.*
 415 *Chem. B* 108(4), 1255-1266, <https://doi.org/10.1021/jp0363287>.

416 Cygan, R.T., Greathouse, J.A., Heinz, H., Kalinichev, A.G., 2009. Molecular models
 417 and simulations of layered materials. *J. Mater. Chem.* 19(17), 2470-2481,
 418 <https://doi.org/10.1039/b819076c>.

419 De la Morena, G., Asensio, L., Navarro, V., 2018. Intra-aggregate water content and
 420 void ratio model for MX-80 bentonites. *Eng. Geol.* 246, 131-138,
 421 <https://doi.org/10.1016/j.enggeo.2018.09.028>.

422 Delage, P., Marcial. D., Cui, Y.J., Ruiz, X., 2006. Ageing effects in a compacted
 423 bentonite: a microstructure approach. *Géotechnique*. 56(5), 291-304,
 424 <https://doi.org/10.1680/geot.2006.56.5.291>.

425 Della Vecchia, G., Jommi, C., Romero, R., 2013. A fully coupled elastic-plastic
 426 hydromechanical model for compacted soils accounting for clay activity. *Int. J. Numer.*
 427 *Anal. Meth. Geomech.* 37, 503-535, <https://doi.org/10.1002/nag.1116>.

428 Dieudonné, A.C., Della Vecchia, G., Charlier, R., 2017. Water retention model for
 429 compacted bentonites. *Can. Geotech. J.* 54(7), 915-925, [https://doi.org/10.1139/cgj-](https://doi.org/10.1139/cgj-2016-0297)
 430 2016-0297.

431 Garrels, R.M., Christ, C.H., 1965. *Solutions, minerals, and equilibria*. Harper and Row.
 432 New York.

433 Gens, A., Alonso, E.E. 1992. A framework for the behaviour of unsaturated expansive
 434 clays. *Can. Geotech. J.* 29(6), 1013-1032, <https://doi.org/10.1139/t92-120>.

435 Gens, A., Sánchez, M., Guimarães, L.N., Alonso, E.E., Lloret, A., Olivella, S., Villar,
 436 M.V., Huertas, F., 2009. A full-scale in situ heating test for high-level nuclear waste
 437 disposal: observations, analysis and interpretation. *Géotechnique*. 59(4), 377-399,
 438 <https://doi.org/10.1680/geot.2009.59.4.377>.

439 Helfferich, F., 1962. Ion exchange. McGraw-Hill, Series in Advanced Chemistry. New
 440 York.

441 Karnland, O., Muurinen, A., Karlsson, F., 2005. Bentonite swelling pressure in NaCl
 442 solutions. Experimentally determined data and model calculations. In: Alonso, E.E.,
 443 Ledesma, A. (Eds.) *Advances in Understanding Engineered Clay Barriers: Proceedings*
 444 *of the International Symposium on Large Scale Field Tests in Granite, Sitges,*
 445 *Barcelona, 12-14 November 2003.* Taylor and Francis Group, London, pp. 241-256.

446 Lewis, D.R., 1952. Ion exchange reactions in clays. *Clays Clay Miner.* 1(1), 54-69,
 447 <https://doi.org/10.1346/CCMN.1952.0010107>.

448 Lloret, A., Villar, M.V., Sánchez, M., Gens, A., Pintado, X., Alonso, E.E., 2003.
 449 Mechanical behaviour of heavily compacted bentonite under high suction changes.
 450 *Géotechnique*. 53(1), 27-40, <https://doi.org/10.1680/geot.2003.53.1.27>.

451 Mašín, D., Khalili, N., 2016. Swelling phenomena and effective stress in compacted
 452 expansive clays. *Can. Geotech. J.* 53(1), 134-147. [https://doi.org/10.1139/cgj-2014-](https://doi.org/10.1139/cgj-2014-0479)
 453 0479.

454 Montes-H, G., Duplay, J., Martinez, L., Mendoza, C. 2003. Swelling–shrinkage kinetics
 455 of MX80 bentonite. *Appl. Clay Sci.* 22(6), 279-293, [https://doi.org/10.1016/S0169-](https://doi.org/10.1016/S0169-1317(03)00120-0)
 456 1317(03)00120-0.

457 Musso, G., Romero, E., Della Vecchia, G., 2013. Double structure effects on the
 458 chemo-hydro-mechanical behaviour of compacted active clay. *Géotechnique*. 63(3),
 459 206-220, <https://doi.org/10.1680/geot.SIP13.P.011>.

460 Navarro, V., Asensio, L., De la Morena, G., Pintado, X., Yustres, Á., 2015.
 461 Differentiated intra-and inter-aggregate water content models of MX-80 bentonite.
 462 *Appl. Clay Sci.* 118, 325-336, <https://doi.org/10.1016/j.clay.2015.10.015>.

463 Navarro, V., De la Morena, G., Yustres, Á., González-Arteaga, J., Asensio, L., 2017.
 464 Predicting the swelling pressure of MX-80 bentonite. *Appl. Clay Sci.* 149, 51-58,
 465 <https://doi.org/10.1016/j.clay.2017.08.014>.

466 Navarro, V., De la Morena, G., González-Arteaga, J., Yustres, Á., Asensio, L., 2018. A
 467 microstructural effective stress definition for compacted active clays. *Geomech. Energy*
 468 *Envir.* 15, 47-53, <https://doi.org/10.1016/j.gete.2017.11.003>.

469 Neretnieks, I., Liu, L., Moreno, L., 2009. Mechanisms and models for bentonite erosion.
 470 SKB Technical Report TR-09-35. Svensk Kärnbränslehantering AB.

471 Pintado, X., Lloret, A., Romero, E., 2009. Assessment of the use of the vapour
 472 equilibrium technique in controlled-suction tests. *Can. Geotech. J.* 46(4), 411-423,
 473 <https://doi.org/10.1139/T08-130>.

474 Pusch, R., 1994. *Waste Disposal in Rock. Developments in Geotechnical Engineering*
 475 76. Elsevier, Amsterdam, pp 490.

476 Romero, E., Gens, A., Lloret, A., 1999. Water permeability, water retention and
 477 microstructure of unsaturated compacted Boom clay. *Eng. Geol.* 54(1-2), 117-27,
 478 [https://doi.org/10.1016/S0013-7952\(99\)00067-8](https://doi.org/10.1016/S0013-7952(99)00067-8).

479 Romero, E., Della Vecchia, G., Jommi, C., 2011. An insight into the water retention
 480 properties of compacted clayey soils. *Géotechnique* 61(4), 313-328,
 481 <https://doi.org/10.1680/geot.2011.61.4.313>.

482 Rytwo, G., Banin, A., Nir, S., 1996. Exchange reactions in the Ca-Mg-Na-
 483 montmorillonite system. *Clays Clay Miner.* 44(2), 276-285,
 484 <https://doi.org/10.1346/CCMN.1996.0440212>.

485 Saiyouri, N., Tessier, D., Hicher, P.Y., 2004. Experimental study of swelling in
 486 unsaturated compacted clays. *Clay Miner.* 39(4), 469-479,
 487 <https://doi.org/10.1180/0009855043940148>.

488 Salles, F., Douillard, J.M., Denoyel, R., Bildstein, O., Jullien, M., Beurroies, I., Van
 489 Damme, H., 2009. Hydration sequence of swelling clays: evolutions of specific surface
 490 area and hydration energy. *J. Colloid Interface Sci.* 333(2), 510-522,
 491 <https://doi.org/10.1016/j.jcis.2009.02.018>.

492 Sánchez, M., Gens, A., Guimarães, L.N., Olivella, S., 2005. A double structure
 493 generalized plasticity model for expansive materials. *Int. J. Numer. Anal. Method.*
 494 *Geomech.* 29(8), 751-787, <https://doi.org/10.1002/nag.434>.

495 Sánchez, M., Gens, A., Olivella, S., 2012. THM analysis of a large-scale heating test
 496 incorporating material fabric changes. *Int. J. Numer. Anal. Methods Geomech.* 36(4),
 497 391-421, <https://doi.org/10.1002/nag.1011>.

498 Sánchez, M., Gens, A., Villar, M.V., Olivella, S., 2016. Fully coupled thermo-hydro-
 499 mechanical double-porosity formulation for unsaturated soils. *Int. J. Geomech.* 16(6),
 500 [https://doi.org/10.1061/\(ASCE\)GM.1943-5622.0000728](https://doi.org/10.1061/(ASCE)GM.1943-5622.0000728).

501 Song, X., Wang, M.C., 2019. Molecular dynamics modeling of a partially saturated
 502 clay-water system at finite temperature. *Int. J. Numer. Anal. Meth. Geomech.* 43(13);
 503 2129-2146, <https://doi.org/10.1002/nag.2944>.

504 Sun, L., Hirvi, J.T., Schatz, T., Kasa, S., Pakkanen, T.A., 2015a. Estimation of
 505 Montmorillonite Swelling Pressure: A Molecular Dynamics Approach. *J. Phys. Chem.*
 506 C 119, 19863-19868. <https://doi.org/10.1021/acs.jpcc.5b04972>.

507 Sun, L., Tanskanen, J.T., Hirvi, J.T., Kasa, S., Schatz, T., Pakkanen, T.A., 2015b.
 508 Molecular dynamics study of montmorillonite crystalline swelling: Roles of interlayer
 509 cation species and water content. *Chem. Phys.* 455, 23-31,
 510 <https://doi.org/10.1016/j.chemphys.2015.04.005>.

511 Teppen, B.J., Rasmussen, K., Bertsch, P.M., Miller, D.M., Schäfer, L., 1997. Molecular
 512 dynamics modeling of clay minerals. 1. gibbsite, kaolinite, pyrophyllite, and beidellite.
 513 *J. Phys. Chem. B* 101(9), 1579-1587, <https://doi.org/10.1021/jp961577z>.

514 Tournassat, C., Appelo, C.A.J., 2011. Modelling approaches for anion-exclusion in
 515 compacted Na-bentonite. *Geochim. Cosmochim. Acta* 75(13), 3698-3710,
 516 <https://doi.org/10.1016/j.gca.2011.04.001>.

517 Vilarrasa, V., Rutqvist, J., Blanco Martin, L., Birkholzer, J., 2016. Use of a dual-
 518 structure constitutive model for predicting the long-term behavior of an expansive clay
 519 buffer in a nuclear waste repository. *Int. J. Geomech.* 16(6),
 520 [https://doi.org/10.1061/\(ASCE\)GM.1943-5622.0000603](https://doi.org/10.1061/(ASCE)GM.1943-5622.0000603).

521 Villar, M.V., 2007. Water retention of two natural compacted bentonites. *Clays Clay*
522 *Miner.* 55(3), 311-322, <https://doi.org/10.1346/CCMN.2007.0550307>.

523 Yong, R.N., 1999. Overview of modeling of clay microstructure and interactions for
524 prediction of waste isolation barrier performance. *Eng. Geol.* 54(1-2), 83-91,
525 [https://doi.org/10.1016/S0013-7952\(99\)00064-2](https://doi.org/10.1016/S0013-7952(99)00064-2).

526 Yustres, A., Jenni, A., Asensio, L., Pintado, X., Koskinen, K., Navarro, V., Wersin, P.,
527 2017. Comparison of the hydrogeochemical and mechanical behaviours of compacted
528 bentonite using different conceptual approaches. *Appl. Clay Sci.* 141, 280-291,
529 <https://doi.org/10.1016/j.clay.2017.03.006>.

530

531