A model for hydraulic conductivity of compacted bentonite – inclusion of microstructure effects under confined wetting

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Hydraulic behaviour of compacted smectite-rich clays is of practical interest in geological disposal of high-level nuclear waste, as the buffer component of the engineered barrier system. Despite several decades of research, a sound theoretical description of the unsaturated hydraulic conductivity of clay buffer (compacted bentonite) and its performance remains challenging. This is evidenced by experimental data on unsaturated hydraulic conductivity, which, albeit limited, show that the hydraulic behaviour of compacted bentonite during confined wetting is considerably different from that typically observed in non-expansive clays. This work addresses the challenge by proposing a predictive model for the saturated and unsaturated hydraulic conductivity of compacted smectite under confined wetting. By considering the microstructure evolution of compacted smectite, a theoretical description of its pore system variations with relative humidity is presented based on a geochemical modelling approach. The Kozeny–Carman (KC) relationship for hydraulic conductivity of compacted smectites is revisited as a basis to derive a new model, which also incorporates more accurately the effects of key properties, such as porosity, specific surface area and tortuosity. The model predictions for saturated hydraulic conductivity for four types of bentonite clays (GMZ, Kunigel-V1, MX-80 and FEBEX) show close correlations with the experimental data. The results of model prediction for unsaturated hydraulic conductivity of compacted bentonite are in close agreement with the experimental data over a large range of suction values.

KEYWORDS: chemical properties; clays; microscopy; permeability; radioactive waste disposal; water flow

INTRODUCTION

Despite significant efforts in the last few decades, developing a sound theoretical description of the hydraulic properties of compacted highly swelling clays such as smectite-rich clays has remained a challenge. Experimental observations have indicated strong influences of microstructure and physical/chemical interactions in the clay–water–chemical system on the overall flow behaviour in compacted smectite. The subject is important in various environmental applications of bentonite, such as containment systems, and in particular in the context of geological disposal of high-level nuclear waste. For example, in the latter case, the use of compacted bentonite is envisaged as part of the engineered barrier system (Pusch & Yong, 2006). In this context, a wealth of knowledge has been developed in the last 30 years or so on the behaviour of compacted bentonite buffer (e.g. Gens, 2010; Pusch, 2015). An accurate description of the flow behaviour of compacted bentonite is crucial for a realistic assessment of the long-term moisture flow and chemical transport in compacted bentonite barriers in support of developing a sound safety case for geological disposal.

Pioneering works demonstrate the importance of strongly coupled thermal, hydraulic, chemical/geochemical and mechanical phenomena on the flow behaviour of clay buffer (e.g. Gens *et al.*, 1998; Thomas *et al.*, 1998; Dixon *et al.*, 1999; Guimarães *et al.*, 2006; Thomas & Sedighi, 2012). Note that the overall safety assessment of a nuclear waste disposal site involves a much wider scope of processes and issues; however, understanding the flow phenomena in the buffer system and key properties associated with them is one of the critical aspects that requires careful evaluation.

The applications of conventional relationships for determining unsaturated hydraulic conductivity in numerical analysis of the re-saturation of compacted smectite (bentonite) have demonstrated deviations from experimental observations in the literature (e.g. Thomas *et al.*, 2003; Xie *et al.*, 2004; Cai *et al.*, 2014; Sedighi *et al.*, 2018). For example, Thomas *et al.* (2003) showed that the modelling of moisture transport using traditional unsaturated hydraulic conductivity relationships, which assume an increase in hydraulic conductivity with increasing water content, over-predicts the rate of saturation of the buffer when compared to a full-scale experiment. These authors found that only by a significant modification of the hydraulic conductivity relationship (explained by the microstructure effects), can the analysis provide a reasonable prediction against experimental data. The expansion of the microstructure of bentonite during re-saturation reduces the void spaces available for the free water flow and thereby observation of an unconventional behaviour of hydraulic conductivity under confined swelling should be expected (e.g. Thomas *et al.*, 2003). Modifications to a hydro-mechanical model by including microstructure swelling in porosity and permeability relationships were reported by Xie *et al.* (2004), demonstrating considerable improvements in the accuracy of these parameters. In a study of coupled thermal, hydraulic and chemical modelling of compacted bentonite, Sedighi *et al.* (2018) showed that the inclusion of

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microstructure effects provided good predictions of water flow and chemical transport against heating and hydration experiments of compacted bentonite. Experimental measurements of the evolution of hydraulic conductivity of compacted bentonite are very limited and those reported are mainly based on back-analysis of re-saturation tests alongside in situ relative humidity measurements (e.g. Cui *et al.*, 2008; Ye *et al.*, 2009, 2014; Wang *et al.*, 2013).

In this paper, the effects of microstructure evolution of compacted bentonite are revisited based on a number of theoretical developments related to the key effective properties. The aim is to provide an alternative approach based on a modified Kozeny–Carman relationship (Kozeny, 1927; Carman, 1937) for calculating the unsaturated hydraulic conductivity of compacted bentonite by advancing the theoretical aspects of microstructure evolution and incorporating the state-of-the-art knowledge of the material behaviour. First, the evolution of the microstructure and porosity system of compacted bentonite based on a solid solution geochemical reaction of the interlayer hydration/dehydration is presented. Second, new insights into the dynamics of water, pores and particles during the water uptake and their effects on the conductivity are presented. Third, validations of the models, starting from the micro porosity evolution of compacted bentonite for four types of bentonite clays are presented, followed by discussions of the results of hydraulic conductivity with respect to experimental data reported in the literature. Finally, to demonstrate the capability of the modified hydraulic conductivity relationship, numerical simulations of a water infiltration test with compacted bentonite are presented.

EVOLUTION OF MICROSTRUCTURE OF COMPACTED SMECTITE DURING WETTING

Pore classification and structure of compacted bentonite

The microstructure and charged surfaces of swelling clay minerals provide a highly reactive porous medium and dynamic fabric, which dictates complex governing phenomena to the fluid flow regime (Sedighi & Thomas, 2014). The microstructure of compacted bentonite consists of an assemblage of basic unit layers (i.e. tetrahedral–octahedral–tetrahedral (TOT)) that form clay particles, aggregates and clusters (Tournassat *et al.*, 2011; Jacinto *et al.*, 2012; Chen *et al.*, 2019).

Based on the convention established in physical chemistry, three categories of pores (with a range of diameters) in compacted bentonite have been defined: (a) micro pores with diameters smaller than 2 nm; (b) meso pores with diameters from 2 to 50 nm; and (c) macro pores with diameters larger than 50 nm (Salles *et al.*, 2009; Xiong *et al.*, 2016a). Although different pore classifications for compacted clays have been reported (e.g. Gens & Alonso, 1992; Pusch & Yong, 2006), the inter-aggregate pores commonly refer to the pores between aggregates. The intra-aggregate pores are the pores existing within aggregates, which are also called inter-particle pores. Intra-particle pores refer to voids within particles, which is the same as ‘interlayer pores’ for bentonite. Figure 1 presents a schematic diagram of the pore system concept of compacted bentonite considered in this study.

The pore size distribution (PSD) of compacted bentonite has been studied using mercury intrusion porosimetry (MIP). This method is capable of retrieving the pore sizes within the range from 500 μm down to 3.7 nm (Delage *et al.*, 2006; Xiong *et al.*, 2016b). The classification based on MIP specific PSD has received greater attention in recent years. A variety of pore thresholds and PSD models have been discussed for compacted bentonite (Romero *et al.*, 2011; Romero, 2013; Seiphoori *et al.*, 2014; Delage, 2019). A bimodal PSD curve

is a common observation, which indicates that the average inter-aggregate pores and the intra-aggregate diameters create the two peaks on the PSD curves. The transition boundary between the inter-aggregate pores and intra-aggregates is the lowest area between two peaks, which represents less probability of a wide range of pore sizes between the two ranges. Multimodal curves have been reported for the expansive clay mixtures with a maximum of three clear peaks detected through MIP (Romero, 2013), where the right-most peak on the MIP curve corresponds to average (inter-particle) macro pores. This method does not identify pores smaller than 3.7 nm. Therefore, the pores between the individual clay platelets (i.e. interlayer pores) or those pores between the particles, which are smaller than 3.7 nm, cannot be identified by MIP.

From the point of view of fluid flow, the water molecules, which are adsorbed between the interlayer pores (interlayer water) have a negligible contribution to the overall flow of water in compacted bentonite (Pusch & Yong, 2006). However, the contribution of micro pores to the total porosity and water content of compacted bentonite is considerable and increases with the degree of compaction (Bourg *et al.*, 2003; Sedighi & Thomas, 2014). This research adopts a pore classification based on the mobility of water. In this classification, the pore spaces between the unit layers of smectite are called micro pores (or interlayer pores) and these are assumed to trap water but without contributing to the long-range water transport process. However, the pore spaces between particles or aggregates, which are larger than 1 nm, are considered macro pores (or inter-particle pores) and these are assumed to form the free pathways for long-range water transport (see Fig. 1).

In summary, the water flow occurs only in inter- and intra-aggregate pores, which correspond to macro and meso pores separately in Fig. 1. The immobile water is present in pores that are classified as micro pores or interlayer pores. Thereafter, macro and meso pores are unified as macro pores and the interlayer pores also called micro pores, forming a new definition of the double-pore system. Other definitions based on the physical state of water in bentonite are compatible with the assumptions made in this study. For example, from the physical state of water, three categories of water in compacted bentonite have been reported, which include the interlayer water, water affected by the diffuse double layer (DDL) and the free water (Bradbury & Baeyens, 2003; Pusch & Yong, 2006). The water in interlayers is immobile, while the water in the inter-aggregate pores is free to flow, for which there is a consensus. The water in the inter- and intra-aggregate pores can be divided into free water and DDL water. The intra-aggregate pores (i.e. inter-particle pores) can contain both DDL water and partly free water (Bradbury & Baeyens, 2003; Wersin *et al.*, 2004; Pusch & Yong, 2006). Although the DDL water can be partially constrained due to the interactions with charged surfaces, it has larger mobility than that in the interlayer pores and therefore the water in intra-aggregate pores has been categorised under the mobile water in this paper.

The multi-scale fabric of compacted smectite is dynamic and evolves with the water adsorption and desorption, controlled by the changes in the soil water potential (suction), temperature and pore fluid chemical composition. Observations of Komine & Ogata (1999) on the re-saturation of a smectite–sand mixture system under constrained swelling by scanning electron microscope indicate that, upon water supply, the clay particles are hydrated, resulting in the swelling of the interlayer distance of bentonite (micro pores) and consequent reduction of macro pores in the sand–bentonite system. This would result in reduced water flow through the macro porosity. In addition, by increasing the water content,

Fig. 1. Schematic diagram of pore system of compacted bentonite and its evolution during confined wetting

the average number of unit layers forming a single particle decreases; that is, the larger particles/aggregates are divided into smaller particles/aggregates (Musso *et al.*, 2013; Romero, 2013), which affects both the specific surface area and tortuosity of the system, and thus the hydraulic properties. This is demonstrated in Fig. 1 by way of a schematic representation of the evolution of microstructure of compacted smectite during confined re-saturation.

In this paper, theoretical models for the key microstructural processes involved during saturation are proposed, in preparation for the development of a constitutive relationship for hydraulic conductivity of compacted bentonite in the following section.

Evolution of micro porosity

Prediction of the micro porosity evolution during wetting or drying of compacted bentonite is important in order to develop a sound hydraulic model and the way the pore-water system evolves. This work presents a generic predictive model, which can describe the evolution of micro porosity due to macroscopic and measurable boundary variables such as temperature, relative humidity or ionic effects. The formulation presented by Sedighi & Thomas (2014), which is based on a solid solution geochemical model of interlayer hydration by Ransom & Helgeson (1994) to develop an understanding of the micro pore evolution during saturation, is extended.

Adsorption and desorption of water molecules to the interlayer space is referred to as hydration and dehydration of the microstructure. The interlayer hydration process can only alter the distance between the clay microstructure units (interlayer space) by adding discrete layers of water molecules. During dehydration of the microstructure, discrete layers of water are expelled from the micro pores, but a two-phase air–water system (or capillary effect) is not formed in the micro pores. The micro pores are therefore considered to be saturated and interlayer water hydration/dehydration only changes the size of the micro pores. It is noted that during interlayer

hydration one to three (or four) mono layers of water have been reported to be adsorbed in the interlayer of smectite. Notably, four water layers are not common, only observed in MX-80 (Holmboe *et al.*, 2012). The thickness of a single unit layer of smectite (d_0) is 0.95–1.0 nm. The diameter of a water molecule is 0.3 nm at standard temperature and pressure (Hillel, 2003). With the assumption that the adsorbed water is stacked layer by layer and a particle of smectite adsorbs three layers of adsorbed water molecules in its interlayer, the maximum basal spacing can increase from 0.95 to 1.85 nm. The interlayer water is considered to be immobile and bonded to the mineral internal surfaces, which forms a hydrated mineral (Romero *et al.*, 1999; Pusch & Yong, 2006) and the basic unit microstructure of smectite remains stable during the hydration and dehydration reaction (Ransom & Helgeson, 1994). Ransom & Helgeson (1994) proposed that the silicate structure of smectite can be regarded as a solvent, whereas the water can be considered as the solute dissolved in the solvent. This is described by a solid solution reaction of hydration/dehydration of the interlayer conceptually written as (Ransom & Helgeson, 1994)

where n_c is the stoichiometric number of moles of interlayer water in one mole of the hydrous smectite.

The interlayer water hydration/dehydration reaction is analogous to a regular solid solution reaction, which yields the mass action law in an expanded form as (Ransom & Helgeson, 1994)

$$\log K_{eq} = \log \left(\frac{1 - X_{hs}}{X_{hs}} \right) + \frac{W_s}{2.303RT} (2X_{hs} - 1) + n_c \log a_{\text{H}_2\text{O}} \quad (2)$$

where K_{eq} is the equilibrium constant of the interlayer hydration reaction; X_{hs} is the mole fraction of the hydrous

smectite; W_s denotes the Margules parameter of the solid solution reaction; R and T are the gas constant (8.31 J/(mol/K)) and absolute temperature (K), respectively; and $a_{\text{H}_2\text{O}}$ is the activity of the water.

On the basis of the above solid–solution model, one mole of the hydrous smectite contains one mole of the counterpart anhydrous smectite and n_c moles of the adsorbed interlayer water (water in micro porosity). The total volume of the interlayer water – that is, the micro pore volume – can therefore be calculated by way of (Sedighi, 2011; Sedighi & Thomas, 2014)

$$V_1^{\text{il}} = X_{\text{hs}} n_c \frac{\rho_d^{\text{sm}}}{M_{\text{sm}}} V_t V_{\text{il}} \quad (3)$$

where ρ_d^{sm} is the bulk dry density of smectite (kg/m^3); M_{sm} is the molar mass of dry smectite (kg/mol); V_t is the total volume of the clay (m^3); and V_{il} is the specific molar volume of the interlayer water (m^3/mol).

For a given dry density and total volume of the clay, the only variable involved in equation (3) is X_{hs} , which is the mole fraction of the hydrous smectite that is calculated from equation (2). M_{sm} is calculated based on the chemical formulation of smectite and V_{il} has been reported in the literature to be slightly different from the specific molar volume of the bulk water (Ransom & Helgeson, 1995). The value of the specific molar volume of interlayer water is $17.22 \text{ cm}^3/\text{mole}$, which was adopted from Ransom & Helgeson (1995).

The micro porosity (ϕ_{micro}) or the interlayer volumetric water content (θ_1^{il}) of the clay can be described as follows

$$\phi_{\text{micro}} = \theta_1^{\text{il}} = X_{\text{hs}} \frac{n_c \rho_d^{\text{sm}} V_{\text{il}}}{M_{\text{sm}}} \quad (4)$$

Equation (4) is a generic model, which can be used to quantify the micro porosity or interlayer pore water for a given dry density and smectite at different relative humidity and temperature values, which are represented by X_{hs} , which is calculated by equation (2).

The macro porosity (ϕ_{macro}) can then be calculated from the total porosity (ϕ_{total}) and the micro porosity

$$\phi_{\text{macro}} = \phi_{\text{total}} - \phi_{\text{micro}} \quad (5)$$

where

$$\phi_{\text{total}} = 1 - \frac{\rho_d}{G_s} \quad (6)$$

where ρ_d is the dry density of the clay and G_s is the specific gravity of clay.

Evolution of specific surface area

The unit layers interact with each other through repulsive and attractive forces to form stacked layers, which are referred to as crystal particles, as shown in Figs 2(a) and 2(b) (Tournassat *et al.*, 2011; Holmboe *et al.*, 2012; Leão & Tuller, 2014; Tachi & Yotsuji, 2014; Joekar-Niasar *et al.*, 2019). The external specific surface area (A_{ext}) and interlayer specific surface area (A_{int}) of smectite can be determined if the average number of stacked unit layers (n) in a particle is known. The specific surface area of edges, A_{Edges} , of a particle has been reported to be approximately 1 to 5% of the external surface area (Tournassat *et al.*, 2003; Holmboe *et al.*, 2012), and thus A_{Edges} has negligible effect in the calculation of average total external surface area.

Considering a pure smectite to be two dimensional, and neglecting the surface area of the layer edges, A_{Edges} , the relationships between the external specific surface area, A_{ext} , internal specific surface area, A_{int} , and the total specific surface area, A_{total} , can be established on the basis of the lamellar structure of smectite

$$A_{\text{total}} = A_{\text{ext}} + A_{\text{int}} + A_{\text{Edges}} \quad (7a)$$

$$A_{\text{int}} = \frac{2n-2}{2n} A_{\text{total}} = \frac{n-1}{n} A_{\text{total}} \quad (7b)$$

Fig. 2. The structure of a bentonite particle and average numbers of stacked unit layers of a single bentonite with suction: (a) smectite unit layers; (b) particle aggregates consisting of n unit layers (modified from Tournassat *et al.* (2011)); (c) average numbers of stacked unit layers of a single particle with suction for Na-smectite and (d) for Ca-smectite

$$A_{\text{ext}} = \frac{2}{2n} A_{\text{total}} = \frac{A_{\text{total}}}{n} \quad (7c)$$

where the total specific surface area of smectite, A_{total} , can be measured experimentally, and n is the average number of stacked unit layers per particle, which can vary from several layers up to hundreds of layers and can be measured by X-ray diffraction (XRD) analysis or calculated by the structural formula of smectite (Dixon *et al.*, 1999; Saiyouri *et al.*, 2004).

The total specific surface area (A_{total}) can be measured through the ethylene glycol monoethyl ether (EGME) technique. The external specific surface (A_{ext}) area is measured by the gas sorption test or calorimetric methods. The specific surface area of edges can be estimated by atomic force microscopy (AFM) (Cadene *et al.*, 2005). The inter-layer specific surface area (A_{int}) is derived as the difference between the total and external areas (Jacinto *et al.*, 2012).

Data related to the number of stacked unit layers in a single smectite particle are very limited, but Saiyouri *et al.* (2004) indicated an S-shaped curve with regard to the evolution of the number of stacked unit layers with total suction, as shown in Figs 2(c) and 2(d).

Referring to the pseudo-first kinetic equation (Yao *et al.*, 2019), a fit to the data presented by Saiyouri *et al.* (2004) is developed in the present work to describe a relationship between the average number of stacked unit layers per particle, n , and the total suction, s . The mathematical expression of the fit is given by

$$n = \frac{n_{\text{max}}}{1 + (n_{\text{max}}/n_{\text{min}} - 1)e^{zs}} \quad (8)$$

where n_{min} , n_{max} and z are dimensionless material-dependent parameters. The fits for the two materials are shown in Figs 2(c) and 2(d), with fitting parameters for Na-smectite $n_{\text{min}} = 10$, $n_{\text{max}} = 350$ and $z = -0.17$, and for Ca-bentonite $n_{\text{min}} = 10$, $n_{\text{max}} = 100$ and $z = -0.14$. Notably, z is a parameter controlling the decreasing rate of average numbers of stacked unit layers with suction.

Evolution of tortuosity

The effects of microstructure need to be reflected in the tortuosity factor. The tortuosity factor for a porous medium is defined as the ratio of the effective path length (L_e) to the sample length (L) ($\tau = (L_e/L)$) (the effective flow path as illustrated in Fig. 1) (Carman, 1937, 1939). Carman (1937) presented an approximate derivation of tortuosity as $(L_e/L) = \sec(\alpha)$, where α is the average angle between the flow pathway and apparent direction of flow for cubic packing of equal-sized spheres. Normally α is considered to be 45° and $(L_e/L) = \sqrt{2}$ is commonly used as the value of tortuosity in non-swelling soils. However, this approach may not be suitable for unsaturated cases, as it does not relate the tortuosity parameter to the evolving clay micro/macrostructure. It is appropriate to start with a relationship such as the one proposed by Boudreau (1996) and Ghanbarian *et al.* (2013)

$$\tau^2 = 1 - p \ln(\phi) \quad (9)$$

where p is a fitting constant (Boudreau, 1996; Ghanbarian *et al.*, 2013). For the case of particles with fine granular and lamellar structure, Weissberg (1963) proposed $p = 0.5$, which provides a close agreement with experimental data (Weissberg, 1963; Boudreau, 1996).

Equation (9) has been formulated based on experiments on coarse-grained soils (non-swelling soils) and therefore may not be fully relevant to smectite, where evolving micro/macro

structure is expected. Considering a two-scale porosity system of compacted bentonite, the interlayer porosity increases with increasing water content, whereas the macro porosity (as the main conduit for water flow) decreases. This work therefore employs the replacement of the total porosity by the macro porosity in the relationship proposed by Boudreau (1996) and Ghanbarian *et al.* (2013); however, keeping the same p value

$$\tau_{\text{macro}}^2 = 1 - 0.5 \ln(\phi_{\text{macro}}) \quad (10)$$

The above implies that as macro porosity decreases due to wetting, there is an increase in the tortuosity and thereby a decrease in hydraulic conductivity.

HYDRAULIC CONDUCTIVITY OF COMPACTED SMECTITE

The majority of constitutive models developed for describing the hydraulic conductivity of unsaturated soils are based on relationships or correlations with the soil water potential or suction or water content (Mualem, 1976). An example is the description of the unsaturated hydraulic conductivity as a function of a reference value (which is commonly the saturated hydraulic conductivity) and a relative hydraulic conductivity (e.g. Mualem, 1976). This formulation is applied in conjunction with the experimental soil water retention curve (SWRC) to describe the evolution of hydraulic conductivity with suction or water content. Such a relationship has been employed extensively in calculating the unsaturated hydraulic conductivity of soils and acceptable agreements with experimental observations in coarse-grained and non-swelling soils has been demonstrated (van Genuchten, 1980; Agus *et al.*, 2003; Chapuis, 2012, 2017).

An established approach to calculate the saturated hydraulic conductivity of porous media is the Kozeny–Carman (KC) relationship (Kozeny, 1927; Carman, 1937). The KC equation provides a theoretical description for the saturated hydraulic conductivity k_{sat} as a function of the porosity, specific surface area, tortuosity factor and a shape factor, given as

$$k_{\text{sat}} = \left(\frac{\gamma_w}{\mu_w} \right) \left(\frac{C_s}{\rho_d^2 \tau^2 A_{\text{total}}^2} \right) \frac{\phi_{\text{total}}^3}{(1 - \phi_{\text{total}})^2} \quad (11)$$

where C_s is a dimensionless shape constant recommended as 0.2 for soils (Carman, 1939; Wyllie & Gregory, 1955; Chapuis & Aubertin, 2003); A_{total} is the specific surface area of soil (m^2/g); γ_w is the unit weight of the fluid (N/m^3); ρ_d is the dry density of the soil (kg/m^3); η is the fluid viscosity ($\text{N s}/\text{m}^2$); and τ is the tortuosity of soil.

It has been shown that the KC equation for compacted clays does not provide a good correlation with experimental observations (Carrier III, 2003; Chapuis & Aubertin, 2003; Chapuis, 2012). The saturated hydraulic conductivity relationship for compacted smectite is revisited by considering the microstructure effects on porosity, external specific surface area and tortuosity. It is assumed in this paper that the proportion of the pore water that is adsorbed in the interlayer of smectite (micro pores) is an immobile phase (Bradbury & Baeyens, 2003; Pusch & Yong, 2006). Therefore, the system studied is a dual-pore system in which the micro porosity (i.e. interlayer porosity) accommodates the immobile water, while the macro porosity contributes to the flow.

In the hypothesis considered in this work, the total porosity in KC relationship should be replaced by the macro porosity and tortuosity and external specific surface

area, which are dependent on porosity to provide a realistic description of the pore system of compacted smectite. A modified KC relationship for saturated hydraulic conductivity of compacted bentonite is therefore proposed, which reflects the effects of microstructure on flow behaviour through the use of macro porosity in the relationship

$$k_{\text{sat}} = \left(\frac{\gamma_w}{\mu_w} \right) \left(\frac{C_s}{\rho_d^2 \tau_{\text{macro}}^2 A_{\text{ext}}^2} \right) \frac{\phi_{\text{macro}}^3}{(1 - \phi_{\text{macro}})^2} \quad (12)$$

As described earlier and as a widely applied approach in this field, the unsaturated hydraulic conductivity (k_{unsat}) of compacted bentonite can be presented as a function of its saturated hydraulic conductivity and relative permeability, given as (Brooks & Corey, 1964; Mualem, 1976)

$$k_{\text{unsat}} = k_r k_{\text{sat}} \quad (13)$$

where k_r is the relative permeability, which is commonly described as a function of water content (Mualem, 1976)

$$k_r = \left(\frac{\theta_1 - \theta_r}{\theta_{\text{sat}} - \theta_r} \right)^\alpha \quad (14)$$

where θ_{sat} and θ_r are the saturated and residual volumetric water contents, respectively; θ_1 is the total volumetric water content; and α is a constant parameter, which is assumed to be 3.5 as an average widely adopted for soils in the literature (Brooks & Corey, 1964; Lu & Likos, 2004). The constant 3.5 has been used for α in the entire content of the present work.

The relative permeability relationships reported in the literature are mainly expressed based on the experimental measurements in coarse-grained soils where the entire porosity is available for water flow. However, in the case of compacted smectite, where a considerable proportion of water is immobile caused by a high percentage of interlayer porosity (Delage *et al.*, 2006), considering the total porosity and water content available for the flow is unrealistic and does not represent the porous system of compacted smectite. The physical state of water in the interlayer has been shown to be different from that which exists in macro pores (Pusch & Yong, 2006). Water flow occurs in macro pores in the form of free water or water affected by the electrical diffuse layer (Bradbury & Baeyens, 2003). A revised

relationship for the relative permeability is therefore proposed by replacing the total water content by the water content of macro pores, given as

$$k_r = \left(\frac{\theta_{\text{macro}} - \theta_{\text{macro},r}}{\phi_{\text{macro}} - \theta_{\text{macro},r}} \right)^\alpha \quad (15)$$

where θ_{macro} is the volumetric water content in macro pores and $\theta_{\text{macro},r}$ is the residual water content in macro pores. The volumetric water content in macro pores (θ_{macro}) is calculated from ϕ_{macro} as shown in equation (5).

Therefore, the proposed relationship incorporates the key microstructure features of the dual-porosity system of compacted smectite at Darcy's scale of flow.

VALIDATION OF THE MODELS

Micro porosity evolution in compacted bentonite

The model proposed for calculating the micro porosity of compacted smectite is assessed by applying it to four types of bentonite clays: GMZ, Kunigel-V1, MX-80 and FEBEX. Table 1 presents the basic properties of the clays studied. The variation of water content with suction (SWRC) is important to establish the macro and micro pore water evolution (equation (5)) and subsequently the variation of hydraulic conductivity (equations (12)–(15)). The van Genuchten's relationship (van Genuchten, 1980) has been adopted for this purpose

$$\theta = \theta_r + \frac{\theta_{\text{sat}} - \theta_r}{[1 + (as)^{1/(1-m)}]^m} \quad (16)$$

where a and m are fitting parameters. The parameters required for the relationships are provided in Table 2. Fig. 10 presents the SWRCs for the compacted bentonite clays used in this study. It is acknowledged that the role of microstructure in the water retention behaviour of bentonite, which is a multimodal pore system, is significant. In the current authors' approach, the water retention component governed by the microstructure water interaction (interlayer hydration) is isolated through the solid solution geochemical model. However, in the new hydraulic conductivity relationships, a single porosity system has been adopted and the effects of microstructure are introduced by the

Table 1. Properties of bentonite clays used in this study

	GMZ	Kunigel-V1	MX-80	FEBEX
Montmorillonite: %	Cui <i>et al.</i> (2008), Ye <i>et al.</i> (2014)		Villar (2007)	
Particles < 2 µm: %	75.4	48	65–90%	92
Specific surface area: m ² /g	60	64.5	76–90%	67
Specific gravity of soil, G_s	570	687	760	725
Primary exchangeable cations	2.66	2.79	2.82	2.70
Cation exchange capacity (CEC): meq/100 g	Na-Ca	Na-Ca	Na-Ca	Ca-Mg
Liquid limit: %	77.3	73.2	75–82	96–102
Plastic limit: %	313	474	526	102
	38	27	46	53

Table 2. Parameters for the SWRCs of compacted bentonite clays

	GMZ	Kunigel-V1	MX-80		FEBEX		
Dry density: g/cm ³	1.7	2.0	1.3	1.6	1.6	1.65	1.7
α : 1/MPa	0.080	0.309	0.069	0.054	0.018	0.016	0.014
m	0.264	0.188	0.415	0.348	0.415	0.377	0.309
θ_{sat}	0.425	0.270	0.380	0.422	0.408	0.389	0.369
θ_r	0	0	0	0	0	0	0

Table 3. Parameters related to the micro porosity calculations of compacted clays

Bentonite	GMZ	Kunigel-V1	MX80		FEBEX		
ρ_d : g/cm ³	1.7	2.0	1.3	1.6	1.6	1.65	1.7
$\log K_{eq}$ *	-0.85	1.23	0.96	1.64	-1.90	-2.11	-1.49
W_s : kcal/mol*	-2618	-1849	1.153	1.103	-2.615	-4.451	-3.316
$\phi_{total}^\dagger$	0.361	0.283	0.380	0.422	0.4	0.4	0.4
M_{sm} : g/mol‡				378.79			
M_w : g/mol§				18.05			
V_{il} : cm ³ /mol				17.22			
n_c ¶				5.5			
X_{hs} (RH = 100%)**	0.606	0.323	0.688	0.649	0.701	0.666	0.643

*Provided in Appendix 1.

†Calculated by equation (6).

‡Average value reported by Gailhanou *et al.* (2007).

§From Liu & Lin (2005).

||Based on values reported by Ransom & Helgeson (1994).

¶Based on Jove-Colon (2015) and Vieillard *et al.* (2011).**Calculated by equation (6) and using linear interpolation relationship to derive X_{hs} for dry densities of MX80 and FEBEX between the given values.

mobile/immobile water concept in the overall hydraulic properties. The effects of microstructure are reflected in the new hydraulic conductivity relationships, – that is equations (12) and (15) – by way of replacing θ_{sat} with ϕ_{macro} , and replacing θ_l with θ_{macro} .

In order to calculate the micro porosity of compacted bentonite, the hydration/dehydration model (Ransom & Helgeson, 1994; Sedighi & Thomas, 2014) was used (equation (2)). The thermodynamic parameters (i.e. the equilibrium constant (K_{eq}) and Margulus parameter (W_s) of the reaction) required for the model were obtained based on the procedure described by Ransom & Helgeson (1994). Appendix 1 presents the details of the derivation of thermodynamic parameters of the model required for calculating the micro porosity and pore water evolution. Based on the procedure, Table 3 includes a summary of the thermodynamic parameters of the solid solution model for the compacted bentonite clay studied.

Using the thermodynamic parameters derived and following the procedure described in the Appendix, the variations of mole fraction of hydrous smectite (X_{hs}) and suction have been established. The results are presented in Fig. 3. The water content of micro pores decreases with the increase in suction, which is reflected in the decrease in X_{hs} in the solid solution model. In the suction range between 0 and 80, the behaviour is linear. However, at higher suction (lower relative humidity values), the behaviour is non-linear (see Fig. 3).

The variations of micro and macro porosity with suction are calculated using equations (4)–(6), which are functions of mole fraction of hydrous smectite (Fig. 3). The variations of ϕ_{micro} and ϕ_{macro} with suction are presented in Fig. 4. In the case of GMZ bentonite, with decreasing suction (wetting path), ϕ_{micro} increases to approach a maximum value 0.240, while ϕ_{macro} decreases to approach a minimum value of 0.124. At saturation (very low suction), ϕ_{micro} is approximately two times larger than that of ϕ_{macro} ; however, the latter only accounts for 34% of the total porosity ($\phi_{total} = 0.361$). In the case of Kunigel-V1 bentonite, the maximum ϕ_{micro} is 0.11 and the corresponding minimum ϕ_{macro} is 0.17. The ϕ_{macro} constitutes 62% of the total porosity ($\phi_{total} = 0.283$).

Despite the fact that the total porosity of Kunigel-V1 bentonite is smaller than that of GMZ because of higher dry density, at very low suction, its macro porosity of 0.17 is slightly larger than the macro porosity of GMZ, which is 0.12. This is related to differences between the compositions

Fig. 3. Variations of mole fraction of hydrous smectite (X_{hs}) with suction

of the two clays, which are reflected in the properties and thermodynamic parameters of the model, especially the dry density (ρ_d) and equilibrium constant of the solid solution reaction (K_{eq}). According to the calculations, the GMZ has a larger percentage of micro porosity showing higher water apportionment and swelling capacity, in comparison with Kunigel-V1 bentonite. The results from the proposed model are compared with an alternative approach proposed by Likos & Lu (2006), which utilises the variation of basal spacing with suction to calculate the porosity associated with the interlayer space. In the proposed approach by Likos & Lu (2006), the interlayer porosity is calculated as

$$\theta_{micro} = \frac{d_{iw}}{d_{iw} + d_0} \quad (17)$$

where d_{iw} is the thickness of the interlayer water molecules based on a maximum of two water layers in bentonite, and the value of basal spacing ($d_{iw} + d_0$) is fitted based on measured data from water-controlled XRD by Likos & Wayllace (2010).

Comparing the calculations based on the approach proposed by Likos & Lu (2006) (LL) and the proposed

Fig. 4. Variations of micro and macro porosity of compacted bentonite with suction, including comparison with the Likos & Lu (2006) approach: (a) compacted GMZ bentonite; (b) compacted Kunigel-V1 bentonite

approach (based on equation (4)), it is shown that for the GMZ bentonite, the porosity evolution is similar. The maximum micro porosity and minimum macro porosity in the LL method are 0.224 and 0.137, respectively, in comparison with 0.237 and 0.124 in the present model. In addition, when suction is between 20 MPa and 100 MPa, the two scales of porosity calculated by both methods are almost the same. However, with respect to the results of Kunigel-V1 bentonite and at very low suction, the results of micro and macro porosity in the LL method are 0.108 and 0.175, respectively. Using the proposed approach, the values are 0.174 and 0.109, respectively. The prediction of the micro porosity and macro porosity in the saturated situation are inverse to each other using these two methods. The reason for this discrepancy is that the LL approach is based on the analysis of basal spacing variations ($d_{iw} + d_o$) from experiments and most of the experiments used to develop this approach are limited to dry densities from 1.3 to 1.6 g/cm³. The dry density of GMZ-bentonite in this paper is 1.7 g/cm³, which is close to the ones used in experiments validating LL, whereas that of Kunigel-V1 is 2.0 g/cm³, which is substantially higher. The larger differences with statistics create more inaccuracy in the calculation. In addition, the LL method assumes that the maximum number of water layers between the unit layers of smectite is two, whereas the present method considers three water layers in smectite as a maximum, which is much closer to most experimental observations of bentonites (Saiyouri *et al.*, 2004; Holmboe *et al.*, 2012).

Fig. 5. Comparison of calculated saturated hydraulic conductivity using modified KC equation plotted against experimentally measured values for various bentonites under confined conditions

Saturated hydraulic conductivity of compacted bentonite

Equation (12) is used to predict the saturated hydraulic conductivity of several bentonite clays compacted in the range from 1.2 to 2.0 Mg/mm³. The experimental saturated hydraulic conductivities of compacted MX-80, FEBEX, GMZ and Kunigel-V1 are used to compare with the model results. The microstructure parameters required for modelling (i.e. micro/macro porosity, external surface area and tortuosity) were described in the previous section (Table 3).

Figure 5 presents the results of saturated hydraulic conductivity calculated by the proposed model against experimental data of saturated hydraulic conductivity for various dry densities and types of bentonites reported in the literature (Cui *et al.*, 2008; Lloret & Villar, 2007; Wang *et al.*, 2013; Ye *et al.*, 2014). The results indicate that the predicted values fall mostly between 1/3 and 3 times the experimentally measured values ($1/3 k_{sat_measured} < k_{sat_calculated} < 3 k_{sat_measured}$). These are well within the acceptable uncertainty range of common experimental results for hydraulic conductivity (Mbonimpa *et al.*, 2002; Chapuis, 2012). Fig. 5 shows that in the region of higher k_{sat} values (i.e. low dry density), calculated k_{sat} is above the line of equality (the middle of the three dashed lines), which means predicted values are larger than the measured values. In the case of the low k_{sat} region (high dry density), the calculated k_{sat} is typically smaller than measured k_{sat} .

Figure 6 presents saturated hydraulic conductivity calculated by the KC model considering that the total porosity is available for the flow. The results are compared with experimental data. It is seen that the predictions are poor. Other researchers have also reported that the total porosity based on the KC equation cannot predict the hydraulic conductivity of clayey soils correctly (Chapuis & Aubertin, 2003; Chapuis, 2012). It is therefore concluded that the modified KC equation, which considers the microstructure effects, yields improved results.

Unsaturated hydraulic conductivity of compacted GMZ and Kunigel-V1 bentonites

In this section, the saturated and unsaturated hydraulic conductivities of GMZ and Kunigel-V1 bentonite clays are discussed. First the hydraulic conductivity (k_{sat}) values of GMZ bentonite and Kunigel-V1 bentonite are calculated. This is followed by an investigation of the evolution of the unsaturated hydraulic conductivity of compacted GMZ

Fig. 6. Comparison of calculated values using the original KC equation (considering total porosity available for the flow) plotted against experimentally measured values of saturated hydraulic conductivity for various bentonites under confined conditions

and Kunigel-V1 against experimental data published in the literature.

The models for hydraulic conductivity of unsaturated and saturated clay (equations (12)–(15)) are applied to study the variations of hydraulic conductivity of compacted GMZ and Kunigel-V1. Investigations included the behaviour of compacted GMZ with a dry density of 1.7 g/cm^3 and compacted Kunigel-V1 with a dry density of 2 g/cm^3 .

Figure 7 presents the variations of unsaturated hydraulic conductivity of compacted GMZ and Kunigel-V1 bentonites with suction calculated using equations (14) and (15). The results are compared with the experimental measurements presented by Ye *et al.* (2009) for GMZ bentonite and Cui *et al.* (2008) for Kunigel-V1. The classic model (i.e. equation (14)), which is built on experiments on coarse-grained soil, considers the total porosity as the flow path (Mualem, 1976).

The model proposed here introduced microstructural corrections to the unsaturated hydraulic conductivity evolution (i.e. equation (15)). The results obtained by the proposed relationship for the relative permeability agree very well with the experimental data. Compared to the classic approach, which considers total volumetric water content (total porosity), the new relationship provides a better agreement with the experimental results for both bentonites. If microstructure effects are completely ignored, the predicted k_{unsat} is much larger than the experimental values. This indicates that, for a wide range of suctions or relative humidity, the conventional relative permeability relationship will overestimate the rate of saturation.

MODEL APPLICATION FOR LABORATORY-SCALE ISOTHERMAL WATER INFILTRATION TEST ON COMPACTED BENTONITE

A numerical simulation of a small-scale laboratory experiment of moisture transfer in compacted FEBEX bentonite has been undertaken to examine the validity of the modified hydraulic conductivity relationship. The simulation presented includes the water flow through a $400 \text{ mm} \times 70 \text{ mm}$ cylindrical compacted FEBEX bentonite. The case study is based on experimental tests and results reported by (Villar *et al.*, 2005). The soil is a FEBEX bentonite, compacted with its hygroscopic water content (about 14%) at a nominal dry density of 1650 kg/m^3 . A granitic water was injected through

Fig. 7. Variations of unsaturated hydraulic conductivity of compacted GMZ and Kunigel-V1 with suction: (a) compacted GMZ bentonite; (b) compacted Kunigel-V1 bentonite

the upper side of the sample at a pressure of 1.2 MPa . Measurements of the relative humidity values at 100, 200 and 300 mm distances from the water injection boundary for up to 30 000 h were reported by Villar *et al.* (2005). These results have been used for comparisons with the results of numerical simulation.

The Richard's equation for water flow in a single porosity system was numerically solved by the use of the classic finite-element method

$$\frac{\partial \theta_l}{\partial t} = \nabla \left[k_{\text{unsat}} \left(\frac{\nabla u_l}{\gamma_w} + \nabla z \right) \right] \quad (18)$$

where u_l is the pore water pressure; z is the elevation; and γ_w is the unit weight of water.

The vapour diffusion has a limited contribution to the overall moisture flow under isothermal and normal temperature conditions (Szymkiewicz, 2013). Therefore, the vapour flow is not considered in the simulations. The infiltration experiment is simulated using a two-dimensional (2D) axisymmetric domain. A constant pore water pressure of 1.2 MPa is prescribed at the inlet boundary. Zero flux is imposed on the remaining boundaries.

The simulations are carried out for two scenarios: (a) revised relative permeability model, equation (15); and (b) conventional relative permeability model, equation (14), in order to demonstrate the improvements offered by the revised model over the conventional model.

Fig. 8. Variation of micro and macro porosity with suction in compacted FEBEX bentonite under confined condition based on the geochemical model

The parameters of the solid solution model for FEBEX bentonite (i.e. $\log K_{eq} = -2.11$, $W_s = -4.451$ kcal/mol) is used to derive the X_{hs} under different suctions, which is then used in equations (4) and (5) to calculate the evolution of micro porosity and macro porosity. The relationship between total volumetric water content and suction was reported by Lloret & Villar (2007) (see Fig. 10(d) later). The variations of micro and macro porosities with suction are presented in Fig. 8.

The water retention curve is based on the relationship in Table 2 (i.e. $a = 0.016$ (1/MPa), $m = 0.377$, $\theta_s = 0.389$, $\theta_r = 0$). The initial suction is 117 MPa, which corresponds to the initial water content of 14%.

The saturated hydraulic conductivity is calculated theoretically based on equation (12). The calculated saturated hydraulic conductivity is 1.9×10^{-13} m/s. The experimental value of the hydraulic conductivity of compacted FEBEX bentonite at dry density of 1650 kg/m^3 and subject to granitic water is 6.4×10^{-14} m/s (Villar, 2002). The theoretically calculated saturated hydraulic conductivity is admissible given that it falls well within the known experimental uncertainty, which is approximately 3 times the experimental results (Mbonimpa *et al.*, 2002; Chapuis, 2012).

Figures 9(a) and 9(b) present the results of the simulations for each of the two scenarios, respectively. The results demonstrate that the simulation using the revised relative permeability model (equation (15)) provides much closer correlations with the measured data, while modelling using the conventional relative permeability model (equation (14)) has overestimated the rate of water flow, leading to larger values of relative humidity, especially at low water contents. The comparison of the two simulated results demonstrates the importance of incorporating the microstructure evolution of bentonite in the prediction of water flow in swelling clays.

CONCLUSIONS

A new model for calculating the unsaturated hydraulic conductivity of compacted smectite is presented. The model accounts for the microstructure evolution of smectite during wetting by considering a dual-porosity system characterised by micro porosity and macro porosity. The microstructure evolution is described in two major steps: (a) variations of micro porosity, leading to changes of macro porosity and subsequently tortuosity; and (b) variations of

Fig. 9. Variations of relative humidity with time from the numerical simulations (lines) and from experimental data presented by Villar *et al.* (2005) (symbols): (a) with consideration of microstructure evolution; (b) with conventional model

particle sizes, leading to changes of specific surface area and tortuosity.

Models are proposed for predicting the microstructure evolution based on the geochemical reaction of water with the clay microstructure. The modified KC relationship proposed for hydraulic conductivity includes corrections to the porosity system, and the tortuosity and surface area of smectite. It is demonstrated that the predictions of the new model are in close agreement with the measured saturated hydraulic conductivity of compacted bentonite for a wide range of dry densities (Fig. 5).

Furthermore, a new relative permeability relationship is proposed, which considers the macro volumetric water content instead of the total volumetric water content. It has been shown that the predictions with this new proposal are in excellent agreement with the experimental data reported for GMZ and Kunigel-V1 bentonites over a large suction range (see Fig. 7).

The comparisons between the proposed models and the available experimental data suggest that the models capture the pore system evolution at Darcy's scale in a substantially more realistic way than the equations commonly used in numerical analysis for water flow or chemical transport in compacted smectite. The new constitutive relationships proposed in this work are important for accurate prediction of flow processes in smectite-rich clays and especially for the clay buffer in the context of the geological disposal of nuclear waste.

Fig. 10. Variations of the volumetric water content with suction for (a) compacted GMZ bentonite; (b) compacted Kunigel-V1 bentonite; (c) compacted MX-80 bentonite; (d) compacted FEBEX bentonite

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APPENDIX

A summary of the major steps in the determination of the thermodynamic parameters of the hydration/dehydration model is presented here. The steps taken follow the procedure described by Ransom & Helgeson (1994). Note that, for demonstration purposes, the derivations of the thermodynamic parameters of only GMZ and Kunigel-V1 bentonites are shown. However, the procedure is the same for MX80 and FEBEX.

Step 1. On the basis of the solid solution model for hydration/dehydration, Ransom & Helgeson (1994) described a theoretical derivation for the number of moles of interlayer water (n_c) considering maximum basal spacing and the molar volumes of ions and water molecules. They reported n_c to be 4.5 moles of water per $\text{O}_{10}(\text{OH})_2$. This is based on a maximum of two water layers between the individual unit layers. Others have argued that the maximum number of water layers should be three for homo-ionic smectites based on experimental evidence (Michot *et al.*, 2005; Vieillard *et al.*, 2011). Three monolayers of water in the interlayer space corresponds to 5.5 moles of water per $\text{O}_{10}(\text{OH})_2$ (Vieillard *et al.*, 2011). Vieillard *et al.* (2011) and Jove-Colon (2015) analysed and used 5.5 moles of water in their calculations. Thus, three monolayers of water with $n_c = 5.5$ is considered.

Step 2. By defining a function Φ as shown in equation (19) (which is essentially a part of equation (2)), a relationship between $\log K_{eq}$ and Φ can be stated as in equation (20) (Ransom & Helgeson, 1994)

$$\Phi = \log \left(\frac{1 - X_{hs}}{X_{hs}} \right) + n_c \log a_{\text{H}_2\text{O}} \quad (19)$$

$$\Phi = -\frac{W_s}{2.303RT} (2X_{hs} - 1) + \log K_{eq} \quad (20)$$

If data related to the activity of water and the molar fraction of hydrous smectite are available, the values of Φ can be determined. A linear relationship between Φ and $2X_{hs} - 1$ then provides the values of W_s and $\log K_{eq}$ of the reaction. The experimental water retention data of compacted GMZ, Kunigel-V1, MX80 and FEBEX from the literature (Villar, 2007; Lloret & Villar, 2007; Cui *et al.*, 2008; Ye *et al.*, 2014) are shown in Fig. 10 and Table 2 using van Genuchten model fitting. Thus, X_{hs} is determined for different relative humidity values. First of all, the number of moles of water in the interlayer spacing of partially hydrous smectite, n_{il} , is calculated using equation (21) (Ransom & Helgeson, 1994)

$$n_{il} = (g_s - 2g_k) M_{sm} / M_w \quad (21)$$

where g_s is the mass fraction of total adsorbed water in smectite (g/g); g_k is the mass fraction of adsorbed water in kaolinite (g/g), which is calculated using vapour adsorption data by Johansen (1957). M_{sm} and M_w are the molecular weights of smectites and water provided in Table 3. The mole fraction of the hydrous smectite in a partially hydrous state, X_{hs} is then calculated by way of

$$X_{hs} = \frac{n_{il}}{n_c} \quad (22)$$

Fig. 11. Linear relationship between Φ and $(2X_{hs}-1)$, which was used to obtain $-W_s/2 \cdot 30RT$ and intercept ($\log K_{eq}$): (a) compacted GMZ bentonite; (b) compacted Kunigel-V1 bentonite

Figure 11 presents a plot of Φ against $2X_{hs}-1$ based on the experimental water retention curves of compacted GMZ and Kunigel-V1.

Step 3. In this step, the Margules parameter (W_s) and equilibrium constant ($\log K_{eq}$) values are determined by linear fitting of equation (20) with the experimental data plotted in Fig. 11. Note that X_{hs} is obtained from step 2. It is acknowledged that the solid solution model adopted in this study is a linear model, which yields discrepancies against experimentally calculated values.

Adopting the above procedure, the calculated values of W_s (cal/mol) and $\log K_{eq}$ at an ambient temperature of 20°C for GMZ are -2618 and -0.85, respectively, and for Kunigel-V1 these are -1849 and 1.23, respectively. The W_s and $\log K_{eq}$ of MX80 and FEBEX for different dry densities are also shown in Table 3.

NOTATION

A_{Edges}	specific surface area of edges
A_{ext}	external specific surface area
A_{int}	interlayer specific surface area
A_{total}	total specific surface area
a_{H_2O}	activity of the water
a, m	fitting parameters in van Genuchten's model
C_s	dimensionless shape constant as assumed to be 0.2 for any soil
G_s	specific gravity of clay
g_k	mass fraction of adsorbed water in kaolinite (g/g)
g_s	mass fraction of total adsorbed water in smectite (g/g)
K_{eq}	equilibrium constant of the interlayer hydration reaction
k_r	relative permeability
k_{sat}	saturated hydraulic conductivity
k_{unsat}	unsaturated hydraulic conductivity
M_{sm}	molar mass of dry smectite (kg/mol)
M_w	molecular weight of water
n	average number of stacked unit layers in a particle
n_c	stoichiometric number of moles of interlayer water in one mole of the hydrous smectite
n_{il}	number of moles of water in the interlayer spacing of partially hydrous smectite
p	fitting constant to derive tortuosity
R	gas constant (8.31 (J/mol)/K)
T	absolute temperature (K)
V_{il}	specific molar volume of the interlayer water (m ³ /mol)
V_t	total volume of the clay (m ³)
W_s	Margules parameter of the solid solution reaction
X_{hs}	mole fraction of the hydrous smectite
z	parameter controlling the decreasing rate of average numbers of stacked unit layers with suction
α	constant parameter assumed as 3.5
γ_w	unit weight of the fluid (N/m ³)
η	fluid viscosity (N s/m ²)

θ_l	total volumetric water content
θ_l^{il}	interlayer volumetric water content
θ_{macro}	volumetric water content in macro pores
$\theta_{macro,r}$	residual water content in macro pores
θ_r	residual volumetric water content
θ_{sat}	saturated volumetric water content
ρ_d	dry density of the clay
ρ_d^{sm}	bulk dry density of smectite (kg/m ³)
τ	tortuosity of soil
ϕ_{macro}	macro porosity
ϕ_{micro}	micro porosity
ϕ_{total}	total porosity

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