A theoretical method for predicting swelling pressures of compacted bentonite

Jing Ma[1,3], Yong-gui Chen[*,1,2]

[1]*Department of Geotechnical Engineering, College of Civil Engineering, Tongji University, Shanghai 200092, PR China* [2]*State Key Laboratory of Disaster Reduction in Civil Engineering, College of Civil Engineering, Tongji University, Shanghai 200092, PR China* [3]*Ecole Nationale des Ponts et Chausssées, Navier Laboratory/CERMES, 6 et 8 avenue Blaise Pascal, 77455 Marne La Vall´ ee cedex 2, France*

[*]*Corresponding author's email:* cyg@tongji.edu.cn

Abstract: In the deep geological repository of high-level radioactive waste (HLW), swelling pressure is a critical parameter for bentonite-based buffer. To obtain an analytic expression of swelling pressure, a theoretical model is proposed. It reveals the swelling mechanisms in compacted bentonite by introducing a crystalline swelling term (P_{cry}) and a diffuse double-layer swelling term (P_{ddl}). By comparing the calculated results with the experimental data, the performance of this model is clarified, and the coefficient of determination (R^2) is revealed to be 0.97. On this basis, the effects of dry density and exchangeable-cation composition are analyzed. The main mechanism of bentonite swelling is found to have a shift from the DDL swelling to crystalline swelling with the increase of dry density. The critical point is evaluated around 1.55 $\mathrm{Mg/m^3}$ for GMZ bentonite. In addition, the double diffuse layer (DDL) develops with the decline of the cation valence and the reduction of dry density. The P_{ddl} is promoted by the development of DDL due to cation valence, but inhibited by the development of DDL caused by dry density.

Introduction

In the deep geological repository for high-level radioactive waste (HLW), bentonite has been selected as the most ideal buffer material for engineered barriers, owing to its strong swelling potential, low permeability, and good radionuclide retardation capacity. Among these properties, swelling pressure, as one of the most significant parameters in construction, is required to exceed 2 MPa according to the reports of the KBS-3V repository[1].

The swelling pressure models of compacted bentonite have been widely investigated. They can be divided into three types, empirical models, mechanical constitutive models, and hydration theoretical models. For the empirical models, swelling pressure is empirically expressed as an exponential function with dry density[2]. For the mechanical constitutive models, the effects of suction and net stress on expansive soil are analyzed by the Barcelona basic model (BBM)[3]. Then, the double-porosity characteristics were investigated[4], and the Barcelona expansive model (BExM) was presented for the compacted expansive soil. The BExM model reveals the microstructural volumetric behavior, and the coupling behavior between macro- and microstructure. Further details were studied, like the macro- and micro-pores boundary[5], the water-absorbed order[6], and the application of stress-strain functions on the prediction of swelling pressures[7]. However, the mechanical constitutive models cannot directly reveal the physicochemical process in compacted bentonite.

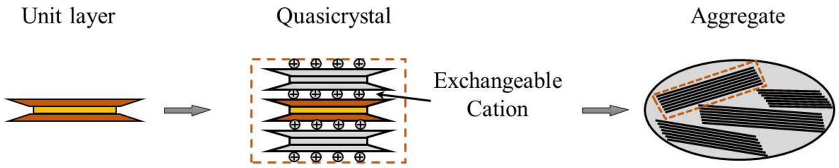
For the physicochemical models, the theory of diffuse double layers was presented by Gouy [8] and Chapman[9], that negative charges on the external surface of mineral layers attract the surrounding cations in pore water. Two charged mineral layers are simplified to be parallel plate capacitors[10]. Thus, the swelling pressure can be calculated by the sum of the electrostatic repulsion and the van der Waals attraction forces[11,12]. On this basis, Komine and Ogata[13,14] gradually defined the basic variables (e.g. montmorillonite swelling deformation), and confirmed the mineral parameters (e.g. specific surface of each mineral). The original Gouy-Chapman and DLVO theory was then expanded to the theoretical swelling models. However, the models can merely reveal the properties of the compacted soil at low dry density or for samples with low montmorillonite content. It referred to the underestimation of the crystalline swelling process for coupling hydration mechanisms in multi-scale structures of compacted bentonite[15].

In this study, a theoretical method for predicting swelling pressures of compacted bentonite is presented. It reveals the swelling mechanisms in compacted bentonite by introducing a crystalline swelling term (P_{cry}) and a diffuse double-layer swelling term (P_{ddl}). The model performance is clarified by comparing the experimental data with the calculation results for a typical soil, GMZ bentonite produced in China. On this basis, the effects of different dry densities and exchangeable cations, as well as the differential properties between P_{cry}, P_{ddl} are analyzed.

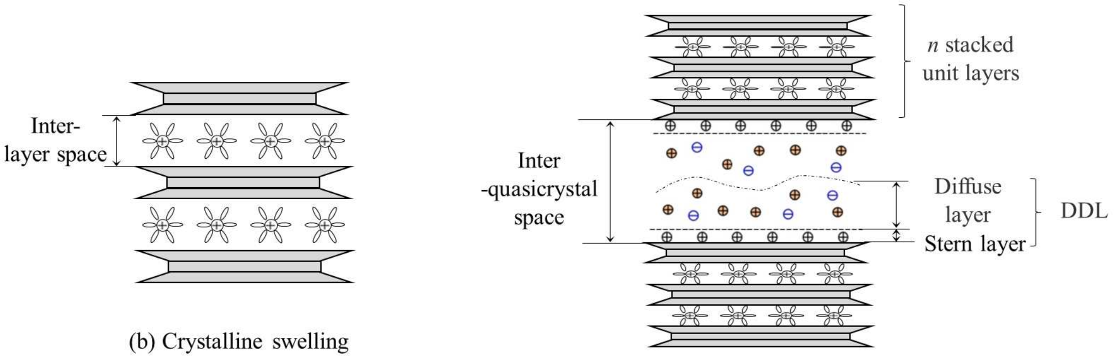
Swelling mechanism

The swelling mechanisms developed correspondingly to the microstructure investigations. For the microstructure, the bimodal pore was initially proposed. The pores in compacted clay were distinguished into inter-aggregate and intra-aggregate pores via mercury intrusion porosimetry (MIP) results[16]. However, the total pore volume tested by MIP was found less than the actual total pore volume for high-plastic clay (like compacted bentonite). It was owing to the existence of inaccessible pores at lower diameters[17]. Combined with montmorillonite studies, the trimodal pore structure was revealed in compacted bentonite. The intra-aggregate pores are further divided into inter-quasicrystal pores and intra-quasicrystal pores; the intra-quasicrystal pores are considered to be the inter-layer pores between the unit layers of montmorillonite. Thus, the micro-structure in compacted bentonite is widely analyzed as unit layers, quasicrystals, and aggregates, as shown in Fig. 1 a[18,19].

Based on the trimodal micro-structure in compacted bentonite, the swelling mechanisms of compacted bentonite are correspondingly analyzed[19,20]. Upon water infiltration, the water molecules are preferentially adsorbed into the inter-layer space. They hydrate with the interlayer cations and consequently lead to the interlayer space increasing. This process is defined as crystalline swelling (Fig. 1 b). The hydrated cations in the pore water are attracted by the negative charges on the external surface of quasicrystals, forming the diffuse double layers (DDL), including a stern layer and a diffuse layer. When two respective diffuse layers overlap, the inter-quasicrystal space increases. This process is referred to as diffuse double-layer swelling (DDL swelling) (Fig. 1 c). Both the crystalline swelling and the DDL swelling compose the swelling mechanisms in compacted bentonite hydration.



(a) Multi-scale structure in compacted bentonite



(b) Crystalline swelling

(c) DDL swelling

Figure 1: Schematic view of micro-structure and swelling mechanisms.

Model development

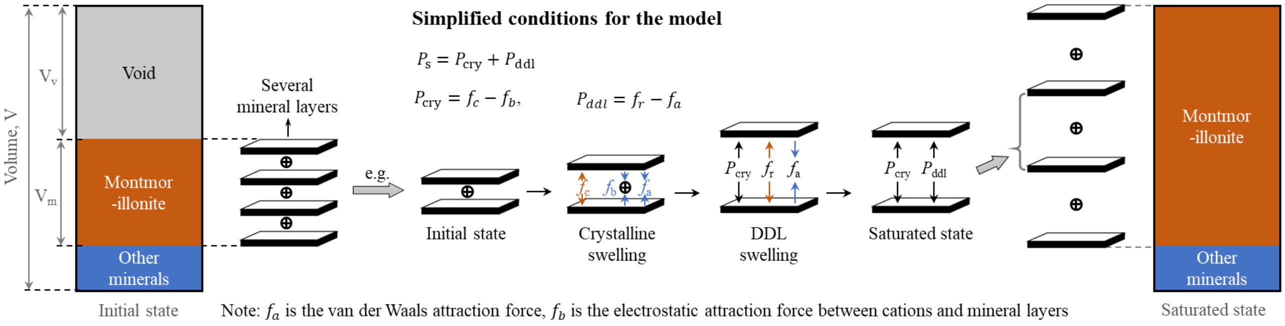
New framework

Based on the swelling mechanisms of compacted bentonite, an accordingly theoretical model is presented. The new framework reveals the coupling effects of crystalline swelling and DDL swelling by introducing a crystalline swelling term and distinguishing the influence of different exchangeable cations on the DDL swelling term.

For the sake of simplicity, crystalline swelling and DDL swelling are simplified as two independent terms and they are at a similar magnitude when the unit layers of montmorillonite are considered to be uniformly and directionally filling throughout the soil.

Fig. 2 shows the conceptualization of the theoretical model. The composition of compacted bentonite contains voids, montmorillonite minerals, and other minerals. Upon water infiltration under constant volume conditions, the spaces between the mineral layers increase, filling up the initial voids. Then, the final pressure can be calculated by the summation of the crystalline swelling term (P_{cry}) and DDL swelling term (P_{ddl}). The P_{cry} focuses on the hydrated repulsion (f_{c})

due to the hydration of both the cations and the negative surface charge sites. The P_{ddl} focuses on the electrostatic repulsion (f_{r}) between the hydrated cations in the diffuse layers.



Note: f_a is the van der Waals attraction force, f_b is the electrostatic attraction force between cations and mineral layers

Figure 2: Concept of the new method for compacted bentonite swelling prediction.

Theoretical approaches

As Fig. 2 reveals, the volume percentage of swelling deformation of montmorillonite ($\varepsilon_{\mathrm{sv}}{}^{*}$) is the ratio of void volume (V_{v}) and montmorillonite volume (V_{m}) under the constant volume conditions. They can be derived as a function of void ratio (e_0):

$$\varepsilon_{\mathrm{sv}}^{*} = \frac{V_{\mathrm{v}}}{V_{\mathrm{m}}} \times 100\% = e_0 \frac{100\rho_{\mathrm{m}}}{C_{\mathrm{m}} \cdot \rho_{\mathrm{solid}}} \tag{1}$$

$$e_0 = \frac{\rho_{\mathrm{solid}}}{\rho_{\mathrm{d0}}} - 1 \tag{2}$$

$$\rho_{\mathrm{solid}} = \frac{\frac{100}{C_{\mathrm{m}}}\rho_{\mathrm{m}}}{1 + \left(\frac{100}{C_{\mathrm{m}}} - 1\right)\frac{\rho_{\mathrm{m}}}{\rho_{\mathrm{nm}}}} \tag{3}$$

where ρ_{d0} (Mg/m^3) is the dry density; ρ_{m}, ρ_{nm} (Mg/m^3) are the particle density of montmorillonite and other minerals respectively; C_{m} (%) is the mass percentage of montmorillonite.

Then, based on the new framework of theoretical model, the final pressure is simplified to the summation of the crystalline swelling term (P_{cry}, kPa) and the DDL swelling term (P_{ddl}, kPa):

$$P_{\mathrm{s}} = P_{\mathrm{cry}} + P_{\mathrm{ddl}} \tag{4}$$

P_{cry} contains the hydration repulsion, electrostatic forces, and van der Waals forces based on the thermodynamic study by Laird[21] and Liu[15]. A general expression is used as follows:

$$P_{\mathrm{cry}} = \alpha \exp\left(\frac{-e_0}{\psi_0}\right) \tag{5}$$

where α (kPa) and ψ_0 (-) depend on the sorption isotherm. They are constants for the specific bentonite, which can be obtained by empirically fitting in this model.

P_{ddl} includes the electrostatic repulsive force (f_{r}, kPa) and the van der Waals attraction force (f_{a}, kPa), influenced by the exchangeable cation i (i denotes either Na$^+$, Ca^{2+}, K$^+$, or Mg^{2+}). The equations are expressed as:

$$P_{\mathrm{ddl}} = \frac{1}{CEC} \sum_{i=\mathrm{Na}^{+},\mathrm{Ca}^{2+},\mathrm{K}^{+},\mathrm{Mg}^{2+}} \left\{EXC_i[(f_{\mathrm{r}})_i - (f_{\mathrm{a}})_i]\right\} \tag{6}$$

where CEC (mequiv./g) is the cation exchange capacity of bentonite.

The influence of initial exchangeable-cation composition is evaluated by the exchange capacity, the radius, and the ionic valence of each exchangeable cation[14]:

$$(f_{\mathrm{r}})_i = 2nkT(\cosh u_i - 1) \times 10^{-3} \tag{7}$$

$$(f_{\mathrm{a}})_i = \frac{A_{\mathrm{h}}}{24\pi}\left[\frac{1}{d_i^3} + \frac{1}{(d_i + t)^3} - \frac{2}{(d_i + \frac{t}{2})^3}\right] \times 10^{-3} \tag{8}$$

where T (K) is the temperature; k (J/K) is the Boltzmann constant; n (Number/m^3) is the effective concentration; t (m) is the thickness of the unit layer; A_{h} is the Avogadro constant; u_i, z_i can be calculated by:

$$u_i = 8\tanh^{-1}\left[\exp(-\kappa_i d_i)\tanh\left(\frac{z_i}{4}\right)\right] \tag{9}$$

$$z_i = 2\sinh^{-1}\left(\frac{96.5EXC_i}{S}\sqrt{\frac{1}{8\varepsilon n kT}}\right) \tag{10}$$

where EXC_i (mequiv./g) is the exchange capacity of cation i; S (m^2/g) is the specific surface of bentonite; ε (C^2·J^{-1}·m^{-1}) is the actual dielectric constant of fluid.

The characteristics of each exchangeable cation are revealed by the diffuse double-layer parameter (κ_i, m^{-1}) and the half distance between two separated quasicrystals (d_i, m):

$$\kappa_i = \sqrt{\frac{2nv_i^2 e'^2}{\varepsilon kT}} \tag{11}$$

$$d_i = \varepsilon_{\mathrm{sv}}^{*}[t + (R_{\mathrm{ion}})_i] + (R_{\mathrm{ion}})_i \tag{12}$$

where $(R_{\mathrm{ion}})_i$ (m) is the radius of the exchangeable cation i; v_i is the ionic valence of cation i; e' (C) is the constant of the electron charge.

The concentration of cations in pore water decreases with the swelling of montmorillonite minerals during the hydration. Thus, the effective concentration for the saturated samples can be obtained as follows:

$$n = \frac{n_0 \cdot N_{\mathrm{A}}}{1 + \varepsilon_{\mathrm{sv}}^{*}} \tag{13}$$

where n_0 (mol/m^3) is the ion concentration in montmorillonite; N_{A} is Avogadro's number.

Therefore, after defining the fundamental terms of bentonite (e_0, $\varepsilon_{\mathrm{sv}}^{*}$), the swelling terms ($P_{\mathrm{cry}}$, P_{ddl}) are calculated by the empirical equations of thermodynamic theory and the modified equations of Gouy-Chapman theory.

Model performance

The applicability of this theoretical model has been confirmed by the experimental results. Take the GMZ bentonite for example, the experimental data of swelling pressures with different dry densities and the exchangeable-cation composition of soil can be obtained from the tests of Jia et al.[22], Ye et al.[23] and Ma et al.[19].

Outline of materials and experiments

Previous works by Jia et al.[22], Ye et al.[23] and Ma et al.[19] used the GMZ bentonite, which has been selected as the most ideal material for buffer barriers of the HLW repository in China. The soil was sodium-dominated montmorillonite. Tables 1 and 2 list the basic properties of soil, environmental parameters, and physical constants[13,15,22].

Fig. 3 shows the schematic of the test apparatus. The samples were located in the test cell, clamped between the upper lid and the pedestal. The pressure sensor was fixed under the lid and in contact with the top of the piston. The hydration processes were under constant volume conditions. For more details, please see Ye et al.[23].

Table 1: Parameters ascertained by the fundamental properties of compacted GMZ bentonite.

Parameters	Value	Parameters	Value	Parameters	Value
ρ_{solid} (Mg/m^3)	2.66	S (m^2/g)	570	t (m)	9.6×10^{-10}
CEC (mequiv./g)	0.773	C_m (%)	75.4	v (Na$^+$)	1
EXC_{Na^+} (mequiv./g)	0.4336	R_{ion} (Na$^+$) (nm)	0.098	v (Ca^{2+})	2
$EXC_{Ca^{2+}}$ (mequiv./g)	0.2914	R_{ion} (Ca^{2+}) (nm)	0.1115	v (K$^+$)	1
EXC_{K^+} (mequiv./g)	0.0251	R_{ion} (K$^+$) (nm)	0.133	v (Mg^{2+})	2
$EXC_{Mg^{2+}}$ (mequiv./g)	0.1233	R_{ion} (Mg^{2+}) (nm)	0.0835		

Note: Parameters determined based on the values summarized from earlier papers[13,24].

Table 2: The environmental parameters and physical constants.

Environmental conditions		Physical constants			
Parameters	Value	Parameters	Value	Parameters	Value
ε (C^{2}J^{-1}m^{-1})	7.083×10^{-10}	e' (C)	1.602×10^{-19}	N_A	6.023×10^{23}
T (K)	295	k (J/K)	1.38×10^{-23}	α (kPa)	1.94×10^{5}
n_0 (mol/m^3)	55	A_h (J)	2.2×10^{-20}	ψ_0	0.14

Note: n_0 is an empirical value fitted based on studies of Jia et al.[22], Komine and Ogata[13]. α, *and* ψ_0 are fitted based on studies of Jia et al.[22] and Liu[15].

Calculation results

The swelling pressures of compacted bentonite with different dry densities were calculated by this theoretical model. The calculation results (P_{s_cal}, kPa) were compared with the experimental data tested by Ye et al.[23] (P_{s_test}, kPa), listed in Table 3. The coefficient of determination (R^2) is 0.969, which means the reasonable performance of this theoretical model.

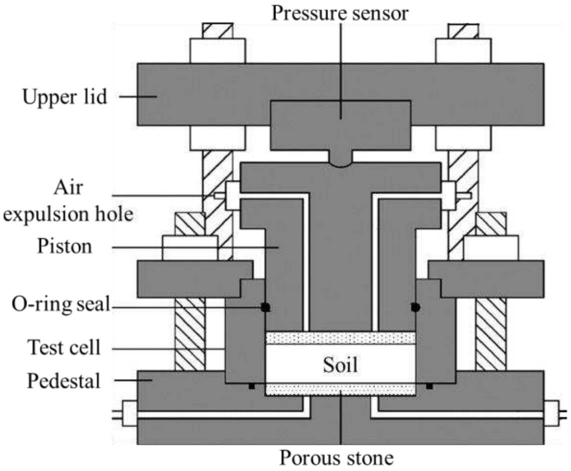


Figure 3: Schematic view of the test device.

Table 3: Calculated results of swelling pressures (simplified version).

ρ_{d0} (Mg/m^3)	ε^*_{sv}	P_{ddl} (kPa)	P_{cry} (kPa)	P_{s_cal} (kPa)	P_{s_test} (kPa)
1.5	1.068	1022.6	774.5	1797.0	1244.0
1.6	0.915	1364.1	1709.3	3073.4	2973.0
1.7	0.780	1797.3	3437.0	5234.3	5344.0
1.8	0.660	2336.0	6395.0	8731.0	9688.0

Discussion

Effect of different dry densities and exchangeable cations

Fig. 4 (a) shows the development of DDL and the corresponding evolution of P_{ddl} with dry density, as well as the different contributions of each exchangeable cation. The ‘thickness’ of the DDL (m) is defined as the reciprocal of κ. It increases with the decline of the cation valence or the reduction of dry density. For the increase of DDL thickness due to cation valence, the repulsive force of P_{ddl} correspondingly increases. However, for the increase of DDL thickness due to dry density, the P_{ddl} decreases. It is owing to the rapid attenuation of DDLs with distance according to the characteristics of Boltzmann distribution.

Differential properties between Pcry, and Pddl

Fig. 4 (b) shows the experimental data and calculated results of swelling pressures with different dry densities. Both the P_{cry} and P_{ddl} increase with dry density. However, it is interesting to find that the main swelling mechanism evolves from the DDL swelling to crystalline swelling with dry density increasing, and this critical point is evaluated at around 1.55 Mg/m^3 for GMZ bentonite. This phenomenon successfully explains the experimental results discussed by Wang et al.[25]. The critical point also provides quantitative information for a better understanding of the main swelling mechanism for further analysis of THMC coupling. In addition, the required dry density is evaluated to be 1.52 Mg/m^3, according to the swelling pressure over 2 MPa[1].

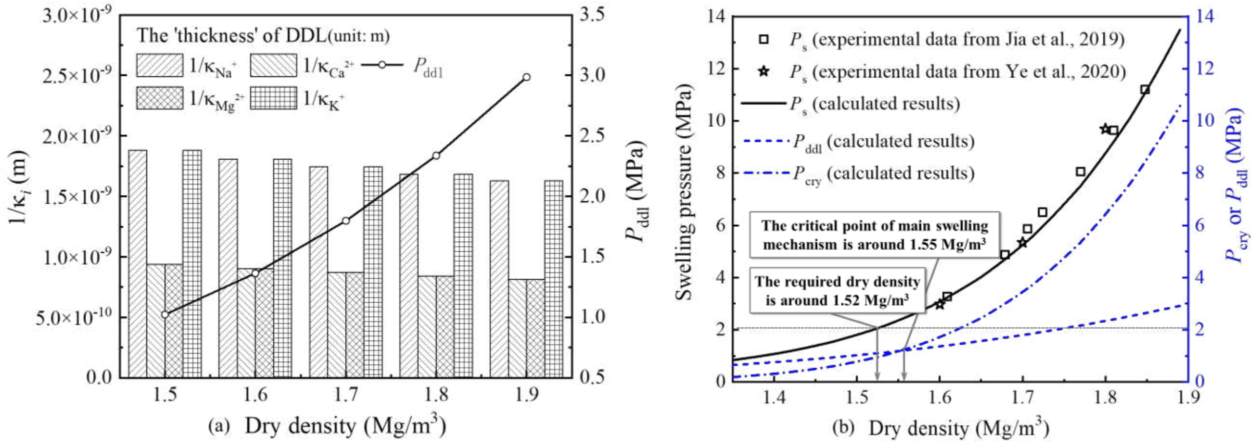


Figure 4: Modeling analysis. (a) Effect of different dry densities and exchangeable cations. (b) Model performance and differential properties between P_{cry}, P_{ddl}.

Conclusion

A theoretical method for predicting swelling pressures of compacted bentonite is proposed in this study. It reveals the coupling swelling mechanisms of multi-scale structures, by introducing a crystalline swelling term (P_{cry}) and distinguishing the influence of each exchangeable cation on the diffuse double-layer swelling term (P_{ddl}).

Based on the model, the effects of different exchangeable cations and dry densities on P_{ddl} are investigated. The ‘thickness’ of the DDL increases with the decline of the cation valence or the reduction of dry density. For the increase of DDL thickness due to cation valence, the repulsive force of P_{ddl} correspondingly increases. However, for the increase of DDL thickness due to dry density, the P_{ddl} decreases. It is owing to the rapid attenuation of DDLs with distance according to the characteristics of Boltzmann distribution.

The differential characteristics of P_{cry}, P_{ddl} with dry density are analysed. In general, both the P_{cry} and P_{ddl} increase with the rise of dry density. However, the main swelling mechanism has a shift from the DDL swelling to crystalline swelling, and the critical point is determined at around 1.55 Mg/m^3 for GMZ bentonite. This phenomenon successfully corresponds to the findings in previous experimental studies.

The model performance is clarified by comparing the experimental data with the calculated results for a typical soil, GMZ bentonite produced in China. Then, according to the requirements on swelling pressure over 2 MPa, the dry density for the bentonite buffer barrier is proposed to be 1.52 Mg/m^3.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that appear to influence the work reported in this paper.

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