

## Swelling pressure of a divalent-rich bentonite: Diffuse double-layer theory revisited

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[1] Physicochemical forces are responsible for the swelling pressure development in saturated bentonites. In this paper, the swelling pressures of several compacted bentonite specimens for a range of dry density of 1.10–1.73 Mg/m<sup>3</sup> were measured experimentally. The clay used was a divalent-rich Ca-Mg-bentonite with 12% exchangeable Na<sup>+</sup> ions. The theoretical swelling pressure–dry density relationship for the bentonite was determined from the Gouy-Chapman diffuse double-layer theory. A comparison of experimental and theoretical results showed that the experimental swelling pressures are either smaller or greater than their theoretical counterparts within different dry density ranges. It is shown that for dry density of the clay less than about 1.55 Mg/m<sup>3</sup>, a possible dissociation of ions from the surface of the clay platelets contributed to the diffuse double-layer repulsion. At higher dry densities, the adsorptive forces due to surface and ion hydration dominated the swelling pressures of the clay. A comparison of the modified diffuse double-layer theory equations proposed in the literature to determine the swelling pressures of compacted bentonites and the experimental results for the clay in this study showed that the agreement between the calculated and experimental swelling pressure results is very good for dry densities less than 1.55 Mg/m<sup>3</sup>, whereas at higher dry densities the use of the equations was found to be limited.

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### 1. Introduction

[2] Bentonites are clays that are composed of mineral crystals of montmorillonite commonly arranged in stacks of several unit layers. Water and electrolytes can enter into the interlayer space between the unit layers thereby causing significant expansion of the clay. Compacted bentonites are increasingly in use in many countries as the barrier and backfilling materials in toxic waste disposal repositories and in landfill cover systems [Rowe *et al.*, 1995; Pusch and Yong, 2006]. High-swelling ability, high ion adsorption capacity, and low coefficient of permeability are some of the important properties that bentonites offer in restricting migration of contaminants to groundwater and environment.

[3] Upon allowed imbibing water and electrolytes under restrained boundary condition, initially unsaturated bentonites commonly exhibit swelling pressures. Therefore, for the prevailing conditions where the volume of the compacted bentonites remains nearly unchanged during the saturation process, the determination and assessment of swelling pressures form an important issue in engineering analyses. A number of studies in the past have focused on the laboratory determination of swelling pressures of compacted bentonites for constant volume condition [Müller-Vonmoos and Kahr, 1982; Pusch, 1982; Dixon and Gray, 1985; Swedish Nuclear Fuel and Waste Management Company,

1983; Komine and Ogata, 1996; Empresa Nacional de Residuos Radiactivos SA, 2000].

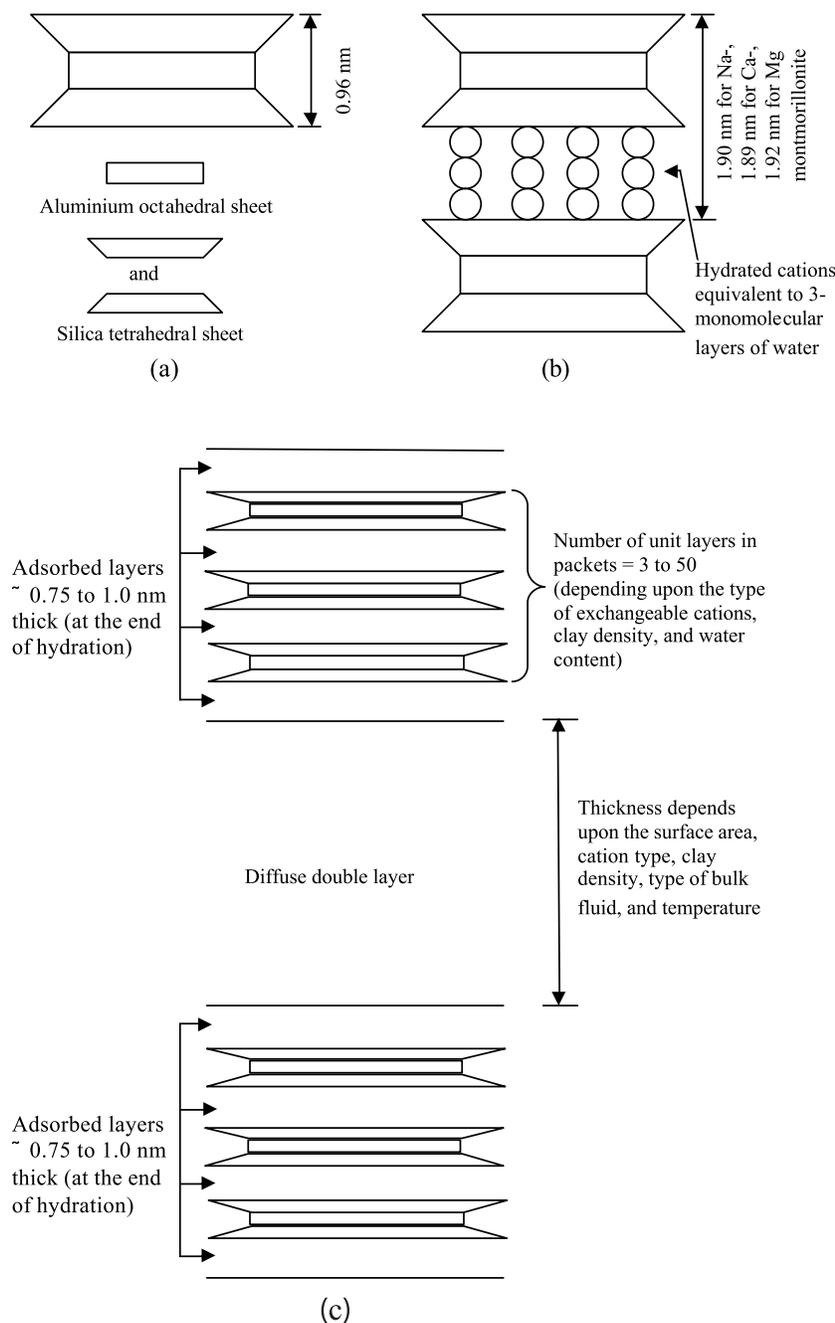
[4] Physicochemical forces are known to be responsible for the swelling pressure development in saturated bentonites [Bolt, 1956; van Olphen, 1977; Mitchell, 1993]. Some studies reported recently attempted to study the swelling pressures of compacted bentonites on the basis of the physicochemical forces in clay-water ion systems. The diffuse double-layer repulsive pressure formed the basis in these studies [Komine and Ogata, 1996; Tripathy *et al.*, 2004].

[5] The swelling pressure may be considered equivalent to the double-layer repulsive pressure only when double-layer repulsion is the single operating force, or by far the dominant force in the clay. However, at close separation of the clay platelets and the restricted diffuse double-layer swelling in case of divalent montmorillonites [Kjellander *et al.*, 1988], the hydration energy due to surface and ion hydration are the major contributing factors for the swelling pressure development [Verwey and Overbeek, 1948; van Olphen, 1977; Yong, 1999].

[6] In this paper, the swelling pressures of several compacted bentonite specimens for a dry density range of 1.10 to 1.73 Mg/m<sup>3</sup> were measured experimentally. The clay used in this study was a mixed valent (Ca and Mg 88%, Na 12%) divalent-rich bentonite from Germany. The theoretical swelling pressure–dry density relationship for the clay was determined following the Gouy-Chapman diffuse double-layer theory. A comparison of experimental results and theoretical swelling pressures from the theory was carried out in the context of literature review on clay-water cation

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**Figure 1.** Schematic diagrams of the unit layer arrangement for montmorillonite (a) unit layer without polar molecules and (b) hydrated cations within unit layers (thickness data from *Grim* [1968] and *Norrish* [1954]) and (c) arrangement of unit layers, adsorbed layer, and diffuse double layer.

system and the range of applicability of the diffuse double-layer theory to divalent-rich montmorillonites. The swelling pressures were also determined using the modified diffuse double-layer equations proposed by *Tripathy et al.* [2004] for mixed valent bentonites and compared with the experimental results.

## 2. Literature Review

[7] Commonly, bentonites contain mixture of several types of exchangeable cation [*Newman*, 1987]. The type and amount of exchangeable cations present in a bentonite

depends upon various factors, such as the environment at which the clay was formed, abundance of a particular type of ion or several types of ion, and the extent of isomorphous substitution [*Lambe and Whitman*, 1969]. Studies on the characteristics of homoionized montmorillonites have been well researched in the past [*Grim*, 1968]. The thickness of unit layer of montmorillonite (silica tetrahedron-aluminum octahedron-silica tetrahedron) in the absence of any polar molecules is about 0.96 nm (Figure 1a).

[8] Swelling of montmorillonitic clays exposed to water or electrolytes is primarily on account of two mechanisms: (1) the crystalline swelling and (2) the diffuse double-layer

swelling [van Olphen, 1977]. The crystalline swelling occurs because of the hydration of ions and surfaces of the clay platelets. The nature of adsorbed fluid present on the surface of the clay in terms of its density, viscosity, and thickness has been brought out by several researchers in the past [Low, 1959; Martin, 1960]. Under ordinary conditions (relative humidity between 30–80%) a montmorillonite with Na<sup>+</sup> as the exchangeable ion frequently has a thickness equivalent to one monomolecular layer of water on its surface and a *c* axis spacing of about 1.25 nm; with Ca<sup>2+</sup> there are frequently two monomolecular layers of water and a *c* axis spacing from about 1.45 to 1.55 nm. The *c* axis spacing is about 1.9 nm with an equivalent three monomolecular layers of water on the surface of the clay unit layer, irrespective of the exchangeable cation type present in the montmorillonite (Figure 1b). Upon further ingress of water, the hydrated cations dissociate from the surface of the clay platelets into the solution to form the electrical diffuse double layer. The volume change of the clay beyond the crystalline swelling is due to the osmotic phenomenon and is associated with the interactions of the diffuse double layers [van Olphen, 1977].

[9] Figure 1c shows the schematic diagram of the unit layer arrangement, adsorbed layer, and the diffuse double layer for saturated montmorillonites. In general, several mineral crystals of montmorillonite together form a clay particle. The number of unit layers in a clay particle depends upon the types of exchangeable cation present in the clay, the clay density, and the initial water content. The thickness of diffuse double layer in case of Na-montmorillonite can extend up to a distance of about 12.0 nm, or even more under certain conditions [Grim, 1968; van Olphen, 1977]. Several researchers in the past [Barshad, 1952; Tamura et al., 2000] have shown that the water uptake capacities of Ca- and Mg-montmorillonites are not very dissimilar. Norrish [1954] stated that the osmotic repulsive pressure is much less for divalent cations, therefore montmorillonite particles separated by large distances (>2.5 nm) will collapse together if this force is insufficient to counterbalance the van der Waals attractive forces. Ca-montmorillonite has a considerable range of stability with two molecular layers of water and it has substantially no expansion beyond a *c* axis dimension of about 1.9 nm [Aylmore and Quirk, 1959; Blackmore and Warkentin, 1960; Iñigo et al., 2000].

[10] In a mixed valent montmorillonite, the exchangeable cations within the interlayers and in between the clay particles may comprise either a single cation species or a mixture of all cation types available in the clay [Mering and Glasser, 1954; Keren and Shainberg, 1979; Meleshyn and Bunnenberg, 2005]. The repulsive energy due to hydration of divalent exchangeable cations is significantly greater than that for monovalent ions [MacEwan, 1954].

[11] The pore size distribution studies for initially unsaturated compacted bentonites by Delage et al. [2006] showed that the total pore volume of compacted unsaturated bentonites comprising pores of different sizes, such as the interlayer pores between the unit layers, interparticle pores between the clay particles inside the aggregates, and inter-aggregate pores between aggregates made up of clay particles. Microscopic studies of bentonites by several researchers showed that within the clay aggregates, the clay fabric is mostly oriented, with the planar clay platelets

remaining in a face to face arrangement [Blackmore and Warkentin, 1960; Grim, 1968; Barclay and Thompson, 1969; Tessier, 1984; Saiyouri et al., 2000; Iñigo et al., 2000]. With an increase in the water content, the swelling of montmorillonitic clays is characterized by an increase in the interparticle spacing that is manifested on the reduction of the interaggregate pores [Delage et al., 2006].

[12] Several researchers in the past have emphasized the development of swelling pressure for compacted expansive soils during the water uptake process. Brackley [1973] and Komine and Ogata [1994] observed that the evolution of swelling pressure with time during the saturation process was affected by the initial water content and dry density of the clay specimens. For compacted specimens with higher initial water content, the increase in swelling pressure with time was smooth, whereas for very low water content specimens a collapse followed by an increase in swelling pressure was noted. Pusch [1982] stated that a decrease in swelling pressure during saturation process is due to loss of shear strength at the aggregate level, whereas a further increase in the swelling pressure is attributed to the redistribution of clay particles to a more homogenous and dispersed state. Imbert and Villar [2006] reported the swelling pressure development for French FoCa bentonite (50/50% bentonite pellets/powder mixture) compacted at different dry densities. Their results showed that irrespective of the initial dry density, the swelling pressure of the clay specimens increased and then decreased during the initial phase of water uptake process. Further, with an elapsed time, the swelling pressure increased and then stabilized. The decrease in swelling pressure was attributed to a collapse of the macrostructure on suction decrease, whereas a further increase in the swelling pressure interpreted as due to the redistribution of water toward the microstructure.

### 3. Theoretical Swelling Pressure–Dry Density Relationship

[13] According to Bolt [1956], the swelling pressure is the difference between the osmotic pressure in the central plane between clay platelets and the osmotic pressure in the equilibrium solution. The osmotic pressure at the central plane between the clay platelets for a given bulk fluid chemistry and properties of the clay can be calculated from the Gouy–Chapman diffuse double-layer theory [Verwey and Overbeek, 1948; Bolt, 1956; van Olphen, 1977; Sridharan and Jayadeva, 1982]. The following equations are used to establish the theoretical swelling pressure–dry density relationship:

$$p = 2n_0kT(\cosh u - 1) \quad (1)$$

$$-\left(\frac{dy}{d\xi}\right)_{x=0} = \sqrt{2 \cosh z - 2 \cosh u} \\ = \left(\frac{B}{S}\right) \sqrt{\left(\frac{1}{2\varepsilon_0 D n_0 k T}\right)}; \text{ at } x = 0, y = z \quad (2)$$

$$\int_z^u \frac{1}{\sqrt{2 \cosh y - 2 \cosh u}} dy = \int_0^d d\xi = -Kd \quad (3)$$

$$K = \left( \frac{2n_0 e^2 v^2}{\varepsilon_0 D k T} \right)^{\frac{1}{2}} \quad (4)$$

$$e = G \rho_w S d \times 10^6 \quad (5)$$

$$\rho_d = \frac{G \rho_w}{1 + e} \quad (6)$$

where  $p$  is swelling pressure in  $\text{N/m}^2$ ,  $n_0$  is the ionic concentration of the bulk fluid in  $\text{ions/m}^3$ ,  $u$  is the nondimensional midplane potential,  $k$  is the Boltzmann's constant ( $=1.38 \times 10^{-23} \text{ J/K}$ ),  $T$  is the absolute temperature in Kelvin,  $\xi$  is the distance function,  $y$  is the nondimensional potential at a distance  $x$  from the clay surface,  $z$  is the nondimensional potential function at the surface ( $x=0$ ),  $B$  is the cation exchange capacity ( $\text{meq}/100\text{g}$ ),  $S$  is the specific surface area ( $\text{m}^2/\text{g}$ ),  $\varepsilon_0$  is the permittivity of vacuum ( $=8.8542 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$ ),  $D$  is the dielectric constant of bulk fluid ( $=80.4$  for water),  $K$  ( $1/\text{m}$ ) is the diffuse double-layer parameter,  $e'$  is the elementary electric charge ( $=1.602 \times 10^{-19} \text{ C}$ ),  $v$  is the valency of exchangeable cations,  $e$  is the void ratio of the clay specimen,  $G$  is the specific gravity of soil solids,  $d$  is the half the distance between clay platelets in meters,  $\rho_d$  is the dry density, and  $\rho_w$  is the density of water.

[14] For given properties of the clay, and for known bulk fluid properties, the predictions of swelling pressures for a range of dry densities is done by relating the  $u$  values obtained from equation (1) with the values of the non-dimensional distance function,  $Kd$  [Sridharan and Jayadeva, 1982; Tripathy *et al.*, 2004]. For a range of assumed swelling pressures, the  $u$  values can be calculated from equation (1). The corresponding values of  $z$  can be calculated from equation (2). Knowing  $z$  and  $u$  for any given swelling pressure, equation (3) can be used to calculate  $Kd$ . Knowing  $Kd$  and  $K$  from equation (4),  $d$  is determined, and  $e$  from equation (5). The dry density can be calculated from equation (6).

[15] Equation (5) relates the half distance between clay platelet to the overall void ratio of the saturated clay system [Bolt, 1956]. For two parallel clay platelets of plan area,  $A$ , and thickness,  $t$ , separated by an average distance of  $2d$ , equation (5) can be derived using equations (7)–(12) (see Figure 2):

volume of void

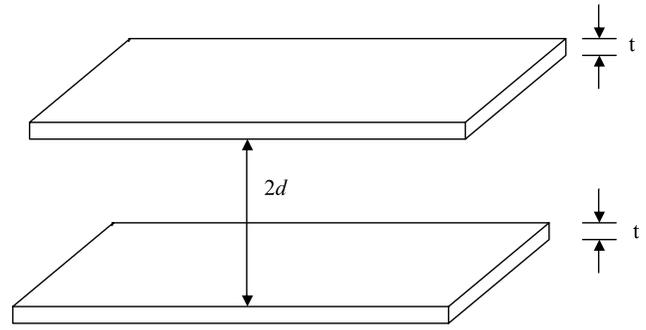
$$V_v = 2Ad \quad (7)$$

volume of soil solids

$$V_s = At \quad (8)$$

void ratio

$$e = \frac{V_v}{V_s} = \frac{2d}{t} \quad (9)$$



**Figure 2.** A representative unit layer separation for parallel clay platelets.

Neglecting the contribution due to the edges, the specific surface area (i.e., surface area per unit mass),  $S$ , is

$$S = \frac{2A}{M_d} \quad (10)$$

Specific gravity of soil solids is

$$G = \frac{M_d}{V_s \rho_w} \quad (11)$$

Mass of the dry soil solids is

$$M_d = G V_s \rho_w = \frac{2AdG\rho_w}{e} \quad (12)$$

Substituting  $M_d$  from equation (12) in equation (10) gives equation (5). Equation (5) is valid for all water contents and spacing between the clay platelets [Muhunthan, 1991].

#### 4. Application of Diffuse Double-Layer Theory for Compacted Bentonite Systems

[16] The Gouy-Chapman diffuse double-layer theory has been used by several researchers in the past to assess the compressibility behavior of initially saturated clays [Bolt, 1956; Sridharan and Jayadeva, 1982; Mitchell, 1993]. Some of the factors that may arise while applying the theory to determine the swelling pressures of compacted bentonite systems are: (1) poorly developed or partially developed diffuse double layers, (2) reduced specific surface area because of formation of clay particles, (3) surface and ion hydration at close platelet spacing, (4) nonuniform size of clay platelets, (5) existence of electrical attractive forces, (6) presence of various types of exchangeable cation, and (7) presence of minerals other than montmorillonite in the clay.

[17] For compacted bentonites, there is a space deficit for the clay particles to freely disintegrate and form a thicker diffuse double layer owing to the restrictions posed by the initial dry density and confinement during the saturation process. Therefore, the application of the diffuse double-layer theory may be considered to be limited for conditions where the interparticle distance is very small. Although the theory can be used to compute swelling pressure for any given spacing between the clay platelets; however, at close separation distance, the effects of ion and surface hydration

**Table 1.** Properties of the Bentonite Used in This Study

Properties of the Material	Value
Liquid limit (%)	178.0
Plastic limit (%)	56.1
Specific gravity of soil solids, $G$	2.8
Specific surface area, $S$ (m <sup>2</sup> /g)	650.0
Cation exchange capacity, $B$ (meq/100 g)	74.0 <sup>a</sup>

<sup>a</sup>Na<sup>+</sup>, 9.0 meq/100g; Ca<sup>2+</sup>, 33 meq/100g; Mg<sup>2+</sup>, 32 meq/100g.

may significantly influence the swelling pressure of compacted bentonites.

[18] According to the diffuse double-layer theory, the void ratio and hence the dry density of saturated clay controls the distance between the clay platelets and the ionic concentration at the central plane between the clay platelets. Equation (5) is based on the assumption that the clay platelets are uniformly dispersed throughout the clay system giving rise to an equivalent half spacing between the clay platelets. A possible reduction of the specific surface area due to the formation of the clay particles has not been considered in the theory. On the basis of the review of literature on the macro and microstructural changes due to swelling of compacted bentonites [Pusch, 1982; Saiyouri et al., 2000; Imbert and Villar, 2006; Delage et al., 2006], it can be considered that upon saturation, a more homogenous clay fabric is attained and hence equation (5) can be used in the analyses. However, it is to be noted that equation (5) is valid for monomineral systems. Therefore, the presence of various other mineral types in the clay may influence the predicted swelling pressure–dry density relationship. Similarly, the effects of various types of exchangeable cation present in the clay and their effects on the ionic concentration distribution between the clay particles are not very well researched. In this context, Tripathy et al. [2004] and Tripathy and Schanz [2007] considered the weighted average valency of exchangeable cations present in clays for the diffuse double-layer calculations.

## 5. Modified Swelling Pressure Equations

[19] Tripathy et al. [2004] compared the experimental swelling pressure results for several mixed valent compacted bentonites with the swelling pressures determined from the diffuse double-layer theory. It was noted that the relationships between the nondimensional midplane potential function ( $u$ ) and nondimensional distance function ( $Kd$ ) derived from the theory and that were back calculated from the experimental results differed significantly leading to the disagreement between the theoretical predictions and experimental results. On the basis of the experimental swelling pressure results of several compacted bentonites, they proposed modified  $u$ - $Kd$  relationships to be considered in equation (1) for determining the swelling pressures of compacted bentonites. The following swelling pressure equations were proposed:

$$p = 2n_0kT[\cosh(-7.277 \log_{10} Kd - 2.91) - 1] \quad (13)$$

(for  $\nu = 1.14$  to  $1.5$ )

$$p = 2n_0kT[\cosh(-10.427 \log_{10} Kd - 7.72) - 1] \quad (14)$$

(for  $\nu = 1.66$  to  $1.73$ )

$$p = 2n_0kT[\cosh(-9.190 \log_{10} Kd - 3.26) - 1] \quad (15)$$

(for  $\nu = 1.97$ )

[20] Tripathy et al. [2004] noted that equations (13)–(15) could be used for several bentonites on the basis of the weighted average valency of exchangeable cations present in the clay. In particular, equation (15) was based on the results for a divalent bentonite with specific surface area of 493 m<sup>2</sup>/g. For other bentonites considered by them, the specific surface area varied between 525 and 725 m<sup>2</sup>/g. Equation (13) was found to be suitable for bentonites containing a greater percentage of Na<sup>+</sup> ions, with the weighted average valency of exchangeable cations of 1.14 and 1.5. Similarly, equation (14) was found to be suitable for bentonites with the values of the weighted average valency of exchangeable cations of 1.66 and 1.73. In the latter, the bentonites contained a greater percentage of divalent exchangeable cations. For any given dry density of the bentonite,  $e$ ,  $d$ , and  $K$  can be calculated from equations (6), (5), and (4). The swelling pressures can be calculated from equations (13)–(15).

## 6. Material and Methods

[21] The bentonite used in this study is from Bavaria, Germany. The bentonite contains about 80% of montmorillonite mineral. More than 85% of the exchangeable cations in the clay are found to be divalent calcium and magnesium ions with about 12% exchangeable sodium ions. The weighted average valency of exchangeable cations [Tripathy and Schanz, 2007] was found to be 1.9 for the clay. The specific surface area was measured following Ethylene Glycol monoethyl Ether method [Cerato and Lutenecker, 2002]. The cation exchange capacity of the clay was determined by Silver Thiourea method [Pleysier and Juo, 1980]. The properties of the bentonite are shown in Table 1.

[22] The swelling pressure of compacted swelling clays can be measured in the laboratory following different procedures for the oedometric condition [Sridharan et al., 1986]. There are two different ways the swelling pressure of compacted clays can be measured in the laboratory employing the constant volume tests: (1) by applying external load to the clay specimen when it imbibes water or electrolytes while without allowing any volume change to take place ( $K_0$  condition) and (2) by fixing the top of the odometer cell, the swelling pressure can be measured using a load cell sandwiched between the restraint and top of the clay specimen during the saturation process (isochoric condition). In the former, the clay specimen undergoes a hysteresis effect due to the swelling and compression processes [Warkentin and Schofield, 1958]. In the present study, the swelling pressures of compacted clay specimens for several dry densities were determined employing the isochoric condition. In all cases, the initial water content of the specimens was 9.9%. The initial total suction for the clay specimens measured using chilled-mirror dew point technique was found to be 126 MPa.

[23] The swelling pressure tests were carried out using a device similar to that developed at the UPC Barcelona, Spain [Romero, 1999]. The device (Figure 3) consists of a pedestal, a threaded top part with a top cap and a load cell. The diameter and height of the compacted clay specimens

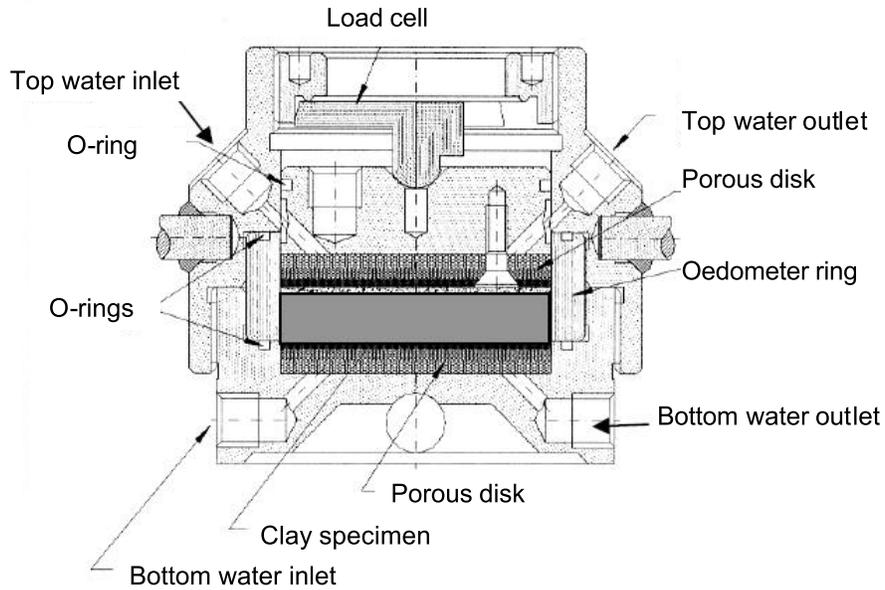


Figure 3. Schematic of the constant volume swelling pressure cell.

used were respectively 50 mm and 15 mm. Distilled water was used to saturate the clay specimens at a nominal water pressure head of about 1 kPa using a burette. The swelling pressures developed during water uptake by the compacted clay specimens were measured via the load cell. The load cell consisted of four strain gauges (full bridge configuration) attached to the top steel plate. The swelling pressure readings during a test were recorded using a data acquisition system calibrated to directly provide the transient upward thrust by the clay specimens. The final water content of the specimens was measured using oven drying method. The

calculated degree of saturation from volume-mass relationship suggested that the clay specimens were fully saturated after the swelling pressure tests.

## 7. Experimental Results and Discussion

### 7.1. Time Versus Swelling Pressure

[24] The typical time versus swelling pressure results for the specimens are shown in Figure 4. At smaller dry densities ( $<1.34 \text{ Mg/m}^3$ ), the swelling pressure developed with elapsed time was smooth with single maxima (Figure 4).

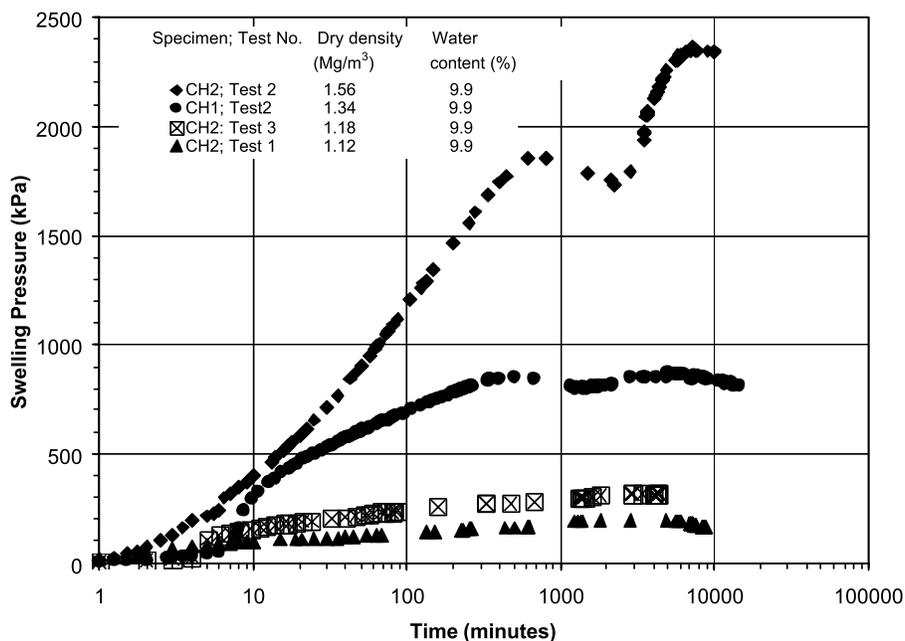


Figure 4. Typical time versus swelling pressure development for the clay specimens tested.

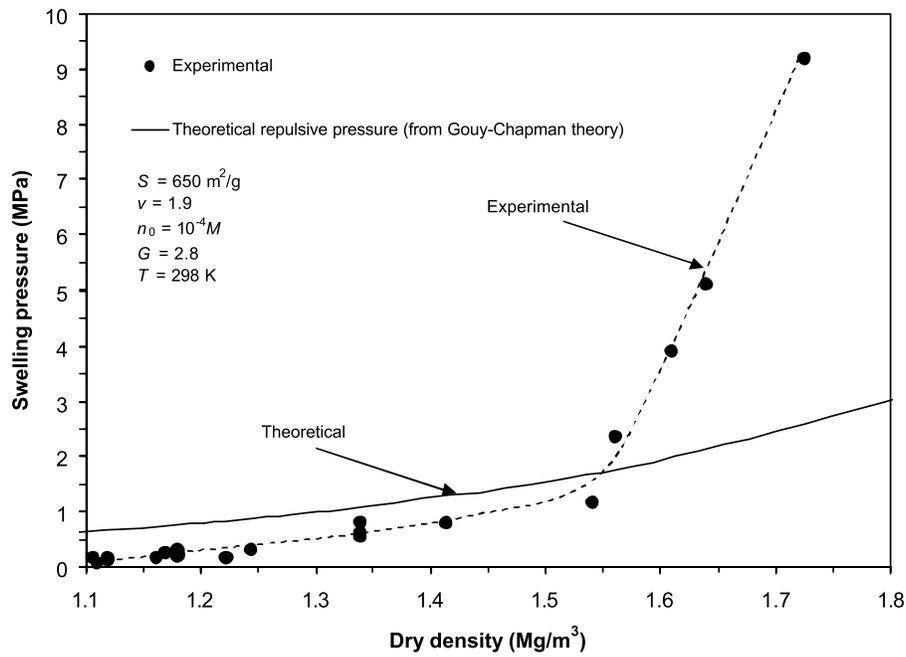


Figure 5. Experimental and theoretical swelling pressures for the clay studied.

However, as the dry density increased, the development of swelling pressure with elapsed time was found to be accompanied by two maxima (Figure 4).

[25] The magnitude of the physicochemical forces depends upon the structure and fabric of the clay [Nagaraj and Srinivasa Murthy, 1983]. Apart from the interlayer and interparticle repulsive forces within the clay aggregates, the type and amount of exchangeable cations available in the interaggregate pores and the surface area of the clay aggregates will influence the osmotic pressure development in the interaggregate pores. If the osmotic pressure in the interaggregate pores is insufficient to maintain the distance between the clay aggregates, there will be a collapse of the larger voids to compensate the osmotic pressure equilibrium. On the other hand, the interlayer pores and interparticle pores also tend to expand during the saturation process because of surface and ion hydration, and further to develop the diffuse double layers. Depending upon the initial compaction conditions, and pore size distribution, the rate of expansion of the interlayer and interparticle pores and the contraction of the larger voids will be manifested on the overall swelling pressure development in compacted bentonites.

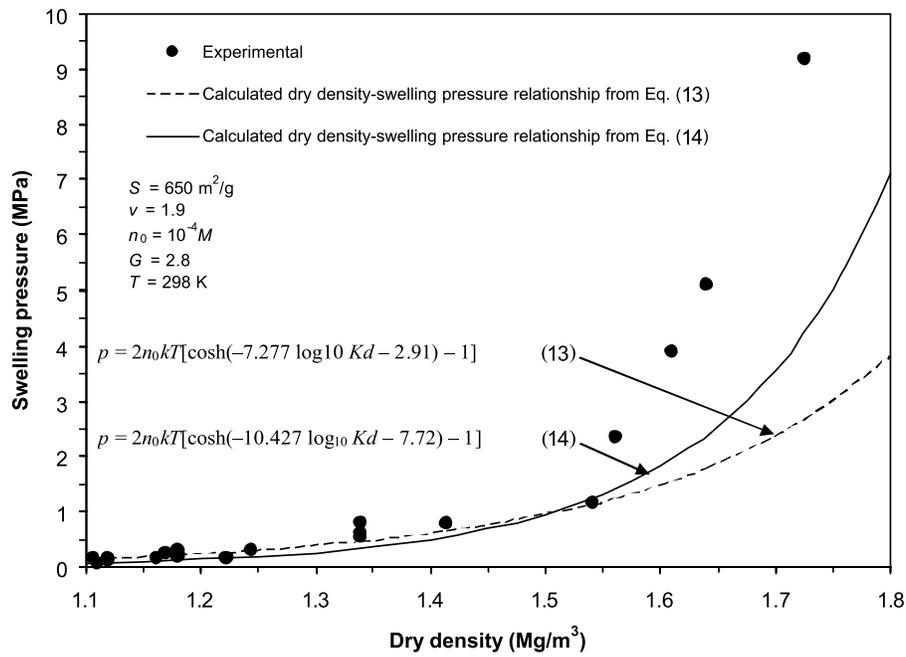
## 7.2. Experimental Versus Theoretical Swelling Pressures

[26] Figure 5 shows the experimental swelling pressure results for the corresponding dry densities of the clay considered in the study. The equilibrium swelling pressure values were considered for comparing with the theoretical swelling pressure–dry density relationship for the clay. The theoretical swelling pressure–dry density relationship was determined using equations (1)–(6). The parameters considered for determining the theoretical swelling pressure–dry density relationship are shown in Figure 5.

[27] It can be seen in Figure 5 that the theoretical swelling pressure–dry density relationship remained above the

experimental results up to about a dry density of 1.55 Mg/m<sup>3</sup>, whereas at higher dry densities, the experimental swelling pressures are found to be greater than that predicted from the diffuse double-layer theory. The disagreement between the theoretical and experimental swelling pressure results can be attributed to the several factors that arise while applying the diffuse double-layer theory to compacted bentonites systems, as mentioned earlier. In addition, the intersection of the theoretical swelling pressure–dry density relationship with the experimental results would indicate that different phenomena are responsible for the disagreement between the experimental and theoretical swelling pressures at lower and higher densities of the clay.

[28] Considering the fact that a more uniform interparticle spacing is attained at saturation and that montmorillonites predominantly containing divalent exchangeable cations do not exhibit swelling beyond a *c* axis spacing of 1.9 nm (i.e., the distance between the clay unit layers,  $2d = 0.94$  nm), using equations (5) and (6), the dry density of the clay for  $2d = 0.94$  nm was calculated as 1.50 Mg/m<sup>3</sup>. A slightly lesser  $2d$  spacing ( $=0.88$  nm) was calculated at the intersection of the theoretical swelling pressure–dry density relationship and the experimental results. For compacted divalent clays, the swelling pressure possibly would not develop for dry densities less than 1.5 Mg/m<sup>3</sup>. On the other hand, the clay studied exhibited significant swelling pressures for dry densities less than 1.55 Mg/m<sup>3</sup>. The swelling pressures developed at lesser dry densities hence can be attributed to one of the following: (1) the clay contained 12% exchangeable sodium ions and that these ions dissociated from the surface of the clay platelets and took part in the double-layer repulsion and (2) the sodium ions remained in the crystal lattice and were unable to dissociate, whereas the divalent ions took part in the double-layer repulsion. For dry densities of the clay greater than 1.55 Mg/m<sup>3</sup>, the swelling pressures developed can be primarily attributed



**Figure 6.** Experimental swelling pressures and calculated swelling pressure–dry density relationship for the clay studied.

to the hydration forces that are much greater than that predicted from the diffuse double-layer theory.

## 8. Verification of Modified Swelling Pressure Equations

[29] The swelling pressure–dry density relationships for the clay studied were determined using the modified swelling pressure equations proposed by *Tripathy et al.* [2004] (i.e., equations (13)–(15)). On the basis of the weighted average valency of exchangeable cations present in the clay studied, equations (14) and (15) were initially used to calculate the swelling pressures of the clay. However, it was noted that the swelling pressures calculated using equation (15) were far greater than their experimental counterparts and hence are not presented. The swelling pressure–dry density relationships obtained from equations (13) and (14) and the experimental results for the clay studied are presented in Figure 6. The parameters used in equations (13) and (14) are shown in Figure 6.

[30] It can be seen in Figure 6 that the calculated relationships from equations (13) and (14) are not very dissimilar and agree well with the experimental swelling pressures for dry densities less than about 1.55 Mg/m<sup>3</sup>. The agreement between the calculated relationship from equation (13) and experimental results is found to be slightly better than that obtained from equation (14). For dry densities greater than 1.55 Mg/m<sup>3</sup>, the calculated swelling pressures from equations (13) and (14) clearly remained below the experimental results, with the results from equation (14) remaining above that calculated from equation (13) and closer to the experimental results.

[31] The results indicated that although the proposed swelling pressure equations based on the diffuse double-layer theory by *Tripathy et al.* [2004] can be used for the clay studied for dry densities less than 1.55 Mg/m<sup>3</sup>, whereas at higher dry densities the application of the equations is

limited. The disagreement between the calculated swelling pressures and experimental results at higher dry densities is attributed to the presence of significant amount of divalent exchangeable cations in the clay that produced greater hydration energy at close particle spacing. Therefore in addition to the diffuse double-layer forces at lesser dry densities, considerations of the additional repulsive pressures would be required for assessing the swelling pressures of the clay at very high densities.

## 9. Conclusions

[32] The swelling pressures of a divalent-rich bentonite were determined employing constant volume swelling pressure tests on several compacted bentonite specimens. The theoretical swelling pressure–dry density relationship was determined on the basis of the diffuse double-layer theory and compared with the experimental swelling pressure results of the clay. The results showed that the experimental swelling pressures are either smaller or greater than their calculated counterparts within different dry density ranges. The swelling pressures for the clay specimens for dry densities less than 1.55 Mg/m<sup>3</sup> are attributed to the double-layer repulsion owing to the dissociation of cations from the surface of the clay platelets. At higher dry densities, the adsorptive forces due to hydration of surfaces of the clay platelets and exchangeable cations dominated the swelling pressures of the compacted clay specimens.

[33] The predictions of swelling pressures for the clay studied using the modified diffuse double-layer equations proposed in the literature indicated a very good agreement between the calculated and experimental swelling pressures results within a dry density of 1.55 Mg/m<sup>3</sup>. On the other hand, at higher dry densities the use of the proposed equations was found to be limited. Therefore, considerations of the additional repulsive pressures would be required

for assessing the swelling pressure of the clay at very high dry densities.

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