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COMPRESSIBILITY BEHAVIOR OF BENTONITES BY STERN THEORY BASED ON CONSTANT SURFACE CHARGE CONDITIONS

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ABSTRACT

The compressibility behavior of clays is governed by the electrical double layer formed around the clay particles. The Gouy-Chapman diffuse double layer theory is often utilized to predict the compressibility behavior of clays. The theory, however, does not consider the effect of the size of the cations and thus predicts unrealistically small void ratios for compacted bentonites under large mechanical pressures expected in high-level nuclear waste repository applications. In this study, the Stern layer was introduced to incorporate the cations size effect in the prediction of the compressibility behavior of bentonites. The overall diffuse double-layer thickness at large pressures was found to be much smaller than the initially assumed Stern layer thickness based on the exchangeable cation size for all the studied bentonites. A compressible Stern layer was, therefore, considered for the first time in the prediction of the compressibility behavior of bentonites. The compression behavior of the Stern layer under the applied loading is influenced by the ratio of the mid-plane to the Stern potential, which is dependent on the type and composition of the exchangeable cations on the clay surface. Stern layer compression was initiated when the potential ratio is in the range of 0.65-0.75 for bentonites with different surface cations characteristics. The incorporation of cation size and compressible Stern layer provided significant improvements over the existing models in predicting the compressibility behavior of bentonites over a wide pressure range. The predicted compressibility data by the proposed model showed a very good agreement with the measured data of five different bentonites from the literature in the pressure range of 0.1-42 MPa.

Keywords: Bentonites, compressibility behavior, cation size effect, diffuse double layer theory

INTRODUCTION

Bentonites are predominantly comprised of the expansive smectite group of minerals and exhibit attractive features such as high ion adsorption capacity, high swelling capacity, and very low hydraulic conductivity (Benson et al., 1994; Glatstein and Francisca, 2015; Kaufhold et al., 2015; Chen et al., 2016). Bentonites are widely used in various Geotechnical and Geoenvironmental engineering field applications. Compacted bentonites have been considered as buffer and backfill materials for underground high-level nuclear waste repository systems in many countries (Butcher & Mu¨ller-Vonmoos, 1989; Ishikawa et al., 1990; Japan Nuclear Cycle Development Institute, 1999; ENRESA, 2000; Tripathy et al., 2004; Bharat et al., 2013; Pusch, 2015; Zheng et al., 2017). These facilities are being planned at a depth of ~ 500 to 1000 m below the ground level in different countries (Atomic Energy of Canada Limited (AECL), 2002; Enviros, 2003). The geostatic stress at such depth is expected to be in the range of 9 to 40 MPa (Tripathy & Schanz, 2007). The magnitude of stress in landfill liners and tailing impoundments are usually expected to be in the range of 0.36 to 6 MPa (Peirce et al., 1986; Timmons et al., 2012). Several studies considered the stress range of 3 to 42 MPa for studying the compressibility behavior of bentonites in these applications (Baille et al., 2010; Marcial et al., 2002; Tripathy & Schanz, 2007; Pusch et al., 2011; Bharat et al., 2013; Ye et al., 2014). Laboratory estimation of compressibility behavior at high pressures, however, is highly time-consuming and expensive as it requires specialized heavy equipment and loading mechanisms (Ng et. al., 2006; Tripathy & Schanz, 2007).

Empirical models have been proposed in the past to predict the compressibility behavior of natural soils (Nagaraj & Srinivasa Murthy, 1986; Burland, 1990; Bharat & Sridharan, 2015). The applicability of these models, however, is limited to a certain range of soil plasticity and lower ranges of applied pressures. The Gouy-Chapman model for interacting parallel clay-water-ion system has been used to predict the compressibility behavior of clays (Bolt, 1956; Sridharan & Jayadeva, 1982; Tripathy et al., 2007; Bharat & Sridharan, 2015). Discrepancies have been observed between theoretical predictions and the measured compressibility data primarily due to the assumption of the parallel arrangement of the clay platelets and the treatment of the cations as point charges in the theory (Bolt, 1956; Warkentin et al., 1957). Stern (1924) incorporated the effect of the size of cations by introducing a thin and compact layer of cations next to the clay platelet surfaces to the original Gouy-Chapman model DDL. The Stern model has been utilized to study the electrical potential distribution of non-interacting clay platelet systems (Verwey & Overbeek, 1948; van Olphen, 1977; Shang et al., 1994; Sridharan & Satyamurthy, 1996) and the compressibility behavior of bentonites based on the constant surface potential (CSP) condition (Tripathy et al., 2014). The Stern theory at constant surface charge condition (CSC) is, however, favored for the clays as their basal surfaces possess constant/permanent charges. Prediction of the clay compressibility behavior using the interacting Stern theory at CSC condition is not available so far as the mathematical formulation of electrostatic potential distribution remains to be established.

In this study, an improved predictive model was presented for the compressibility behavior of bentonites by considering the effect of the size of cations. The Stern DDL theory of CSC condition was utilized based on the postulation that clay platelets were in a parallel arrangement under high applied pressures. The Stern layer thickness, however, is still not well-defined for clays. Although, most of the available studies consider the Stern layer to be incompressible, in the present study it was shown based on the measured void ratios that the DDL thickness at large applied pressures is much smaller than the Stern layer thickness.

The proposed model, thus, incorporates the compressibility of the Stern layer thickness which depends on the ratio of mid-plan to Stern potential as identified in this study. The measured compressibility data of five different bentonites representing a wide range of surface area and surface cations in the pressure range of 0.1– 42 MPa were considered from the literature to validate the proposed model. The Gouy-Chapman model and the Stern model for CSP conditions were also considered for the comparative assessment.

DIFFUSE DOUBLE LAYER THEORY

The interaction of clays with water or other electrolytes is important in understanding the engineering aspects of clays *viz*., the volume change behavior, chemical sorption, and flow-related problems. Clay-water interaction involves physicochemical forces because of the electrochemical activity of the clay surface. The Van der Waals (VdW) attractions, capillary interactions, Coulombic attraction and repulsion, and long-ranged diffuse double-layer repulsive forces are the important surface forces that are known to be existing in clays (Verwey and Overbeek, 1948; Bolt, 1956; Bishop, 1959; Lambe, 1960; Skempton, 1960; Sridharan and Rao, 1973; van Olphen, 1977, Mitchell, 1993; Lu and Likos, 2006; Lamb and Whitman, 2008; Israelachvili 2011). While the Coulombic forces are negligible in expansive clays dominated by montmorillonite minerals, the capillary forces are absent at full saturation (Schubert 1975, Lu and Likos, 2006). The VdW forces are significant at smaller inter-particle separation distances (Israelachvili, 2011), however, their influence on the compressibility behavior is not well understood so far. The VdW forces may be considered passive type forces during compression as they are compressive in nature and will remain inactive during the compression loading. The magnitude of the VdW forces, however, increases under the application of compressive stress due to the reduced separation distance or enhanced particle-particle interaction. The increased VdW forces are activated during the stress removal and significantly control the rebound or swelling response of the soil. The long-ranged diffuse double layer (DDL) repulsive forces, on the other hand, are predominant in saturated montmorillonite clays and primarily control the compressibility behavior (Bolt, 1956, Mitchell, 1960, Olson and Mesri, 1970, Sridharan and Rao, 1970, 1972). The Vdw forces are, thus, often neglected and the compressibility behavior of clays is obtained based on the equilibrium between the applied mechanical stress and the repulsive forces. The Gouy-Chapman DDL theory is commonly used to understand the clay-water-electrolyte interaction, which relates the repulsive forces to the electrostatic potential distribution in the clay-water system (Bolt,1956, Honig and Mul, 1971, Komine and Ogata, 2003, Bharat et al., 2013, Bharat & Sridharan, 2015a & b). A brief description of the diffuse double layer theory is presented below followed by the theoretical formulation of the compressibility behavior.

Net negative charges are available on the basal surfaces of clay platelets (montmorillonite minerals) due to the isomorphous substitution of Al^{3+} by Mg^{2+} in the crystal structure of the octahedral alumina sheet (Grim, 1968; Mitchell & Soga, 2005). Exchangeable cations are naturally present on the clay surface to compensate for the negative charges. In the presence of a water/electrolyte medium, the cations on the clay surface experience an additional diffusive type of force that tries to drive the cations away from the charged clay surface. The diffusive forces are developed due to the existing concentration gradient of the cationic species between the clay surface and the bulk electrolyte solution. An electric diffuse double layer (cation cloud) is formed around the clay platelets as a consequence of the competition between the strong electrostatic attraction between the cations and negatively charged clay surface, and the diffusive forces (Verwey & Overbeek, 1948; Van Olphen, 1977; Sparks, 1999). The DDL around the clay platelet primarily controls the interaction among the clay platelets and often leads to the parallel plate orientation in the saturated clays. For such a parallel plate configuration, the DDL around the clay platelets defines the separation distance among the clay platelets which is related to the macroscopic void ratio. Thus, the compressibility behavior of clays is predicted by the theoretical estimation of the thickness of the DDL around clay platelets (Bolt, 1956, Sridharan & Jayadeva, 1982, Sridharan & Choudhury, 2002, Tripathy et al. 2007).

An illustration of the interacting parallel-plate clay-water-electrolyte system under applied mechanical pressure by the Gouy-Chapman DDL model (Gouy, 1911; Chapman, 1913) is presented in Fig.1. As the two clay platelets approach each other under the action of applied mechanical stress, repulsive pressure (P_R) develops between the clay platelets due to the interaction of the similarly charged DDL around the clay platelets. The separation distance between two neighboring clay platelets continues to decrease under the applied mechanical stress until it reaches an equilibrium state. Under this condition, the repulsive pressure is equal to the applied mechanical pressure (P) on the system (Bharat & Sridharan, 2015a; Bharat & Das, 2017). The electrostatic potential distribution within the interacting system is represented by the curve y(x) with a minimum potential (u) at the mid-plane as shown in Fig. 1. The midplane potential is related to the repulsive pressure between the two platelets or the applied mechanical pressure at equilibrium as per the equation given by Langmuir (1938) presented below (van Olphen, 1977; Mitchell & Soga, 2005),

$$P_R = P = 2nkT\left(\cosh\left(u\right) - 1\right) \tag{1}$$

where n is the concentration of cations in the electrolyte solution in ions/m^3, k is the Boltzmann constant ($= 1.38 \times 10^{-23} J/K$), and T is the temperature in K. The mid-plane potential is uniquely related to the separation distance between the clay platelets and represents the degree of interaction in the system. The relationship between the mid-plane potential and the separation distance is given by the Poisson-Boltzmann's equation as (van Olphen, 1977)

$$t_{DDL} = -\frac{1}{\kappa}\int_{y_0}^{u} (2\cosh(y) - 2\cosh(\mathrm{u}))^{-1/2}\, dy \tag{2}$$

where, t_{DDL} is the DDL thickness, which is equal to half of the separation distance (d) in the Gouy-Chapman DDL model, $\frac{1}{\kappa}$ ($\kappa = \sqrt{\frac{8\pi q^2 v^2 n}{\varepsilon D_0 kT}}$) is the Debye length (Verwey & Overbeek, 1948; van Olphen, 1977; Bharat & Sridharan, 2015b), q is the electronic charge ($= 1.6\times10^{-19} C$), v is the valence, ε is the dielectric constant, D_0 is the dielectric permittivity of vacuum ($= 8.854\times10^{-12} C^2 / N - m^2$), y_0 is the normalized electrostatic potential at the clay surface. The surface potential estimated for a given soil surface and electrolyte properties given by

$$\left(\frac{dy}{d\xi}\right)_{x=0} = \sqrt{2\cosh\left(y_0\right) - 2\cosh\left(u\right)} = \sigma\sqrt{\frac{1}{2\varepsilon D_0 nkT}} = 0.96352\frac{C_e}{S_a}\sqrt{\frac{1}{2\varepsilon D_0 nkT}} \tag{3}$$

where $\left(\frac{dy}{d\xi}\right)_{x=0}$ is the slope of the potential distribution curve near the clay surface, σ is the total surface charge density on the clay surface, C_e is the cation exchange capacity in meq/100g, and S_a is the specific surface area in m^2/g. The macroscopic void ratio is related to the inter-platelet separation distance as per the following equation (Bolt, 1956; Bharat & Das, 2017),

$$e = G\rho_w S_a \, {}^{d}\!/_{2} \tag{4}$$

where, ${}^{d}\!/_{2}$ is the half of the separation distance between two parallel clay platelets, G is the specific gravity. The void ratio at any given pressure, thus, can be estimated using Eq. 1-3 assuming a parallel plate orientation of the clay platelets. The integral involved in Eq. 2 is elliptic, which is to be solved numerically to establish the relationship between mid-plane potential and separation distance (Bharat et al., 2013).

Stern DDL theory

The finite size of the cations at the particle surface limits the closest approachable distance to the charged clay surface (Stern, 1924). This results in a relatively compact and immobile layer of counter-ions close to the surface, which is followed by a diffused layer of the counter-ions. Thus the electric double layer in a clay-water system is characterized by the Stern layer and the outer diffused layer consisting of the Gouy layer. The center of the spherical cations in the Stern layer is at a distance of approximately equal to their hydrated radius away from the clay surface (Guven & Pollastro, 1992), which is defined as the outer surface of the Stern layer (Shang et al., 1994). The charge within the Stern layer is constant and the electrostatic potential varies linearly from a maximum value (y_0) at the clay surface to y_δ at a distance equal to the Stern thickness (δ) at the Stern-Gouy interface where the potential is termed the Stern potential. The dielectric constant of water within the Stern layer is significantly reduced to 3-6 as the water molecules are tightly bound to the clay surface (Verwey & Overbeek, 1955; Sridharan, 1962; van Olphen, 1977; Sposito, 1984; Hunter, 1987; Shang et al., 1994; Sridharan & Satyamurty, 1996). A graphical illustration of the Stern model for the interacting clay-water system is presented in Figure 2. The inter-platelet separation distance, *d*, in the Stern model is the summation of the Stern layer thickness δ and the thickness of the Gouy diffuse layer, t_{DDL}.

$$d = 2(\delta + t_{DDL}) \tag{5}$$

The electrostatic potential distribution within the Stern layer is dependent on the surface charge density and the dielectric properties of the pore fluid as given in Eq. (6)

$$\sigma = \frac{\varepsilon^{'} kT}{4\pi\delta vq}\left(y_0 - y_\delta\right) \tag{6}$$

Within the Gouy layer, the electrostatic potential distribution varies non-linearly between Stern potential (y_δ) at the x = δ and mid-plane potential (y_d) at x = *d/2*, which is represented by the Poisson-Boltzmann equation:

$$\kappa t_{DDL} = -\int_{t_{DDL}-\delta}^{t_{DDL}} d\xi = -\int_{y_\delta}^{u} (2\cosh(y) - 2\cosh(\mathrm{u}))^{-1/2}\, dy \tag{7}$$

Evaluation of the Stern potential (y_δ) is prerequisite for the estimation of Gouy layer thickness (t_{DDL}). The relationship between the charge density and potential distribution is utilized to determine the Stern potential for a given clay-water-electrolyte system. The Stern layer charge (σ_1) and Gouy layer charge (σ_2) together balance the total negative surface charge (σ) on the clay platelets:

$$\sigma = -(\sigma_1 + \sigma_2) \tag{8}$$

The clay platelets are treated as constant-charged plates (Grim 1968), for which the total surface charge density can be expressed as,

$$\sigma = 0.96352\frac{C_e}{S_a}\ \mathrm{C/m^2}$$

where C_e is the cation exchange capacity of soil expressed in $meq/100g$ and S_a is the specific surface area expressed in m^2/g. The charge density in the Stern layer can be obtained as (Verwey & Overbeek, 1948);

$$\sigma_1 = \frac{N_1 vq}{1+\left(N_A/Mn\right)\exp\left(-\left(y_\delta + {}^{\psi vq}\!/_{kT}\right)\right)} \tag{9}$$

where N_1 = no. of adsorption spot per 1 cm^2 area of the clay surface, v is the valence of ions, N_A = Avogadro's number, M = molecular weight of the solvent (water), y_δ = Stern potential at the plan separating Stern and Gouy layer, ψ = specific adsorption potential on the counter-ions at the surface. The charge in the Gouy layer can be derived as (Verwey and Overbeek, 1948; van Olphen, 1977);

$$\sigma_2 = \sqrt{2nkT\varepsilon}\sqrt{2\cosh y_\delta - 2\cosh u} \tag{10}$$

Combining Eqs. 6 and 8-10, the Stern potential can be expressed as a function of the mid-plane potential and the pore fluid parameters, which in turn can be used along with Eqs. 1 and 6 to estimate the void ratio at a given pressure. Equation (9) is only valid for non-interacting systems (van Olphen, 1973) and requires modification for applying to the interacting clay-water system. The number of available spots in the bulk solution, N_1 is dependent on the volume of the diffuse layer which is subjected to change with the change in the degree of interaction under the applied pressure. van Olphen (1973) presented the following equation to replace Eq. 9 for an interacting system,

$$\sigma_1/\sigma_2 = \left[\delta\Big/\left(\frac{d}{2}-\delta\right)\right]\exp\left[y_\delta + \left(\psi/kT\right)\right] \tag{11}$$

The inter-particle distance can be estimated from Eq. 12,

$$\kappa t_{DDL} = -\int_{\delta}^{d/2} d\xi = -\int_{y_\delta}^{u} (2\cosh(y) - 2\cosh(u))^{-1/2} dy \tag{12}$$

Eq. 11 is derived based on the assumption that statistical charge distribution between the Stern and Gouy layer is proportional to their respective volumes or their respective thickness. The equation, however, leads to erroneous estimation of electrostatic potential distribution as it does not utilize the correct volume of the Gouy diffused layer.

The interacting Stern model is utilized for predicting the compressibility behavior of clays by assuming the clay surface potential to be constant (Tripathy et al., 2014). Since montmorillonites possess constant surface charge (Grim, 1968), the assumption of constant surface potential may not be tenable. Therefore, estimation of Stern potential and DDL thickness requires modification of the Stern theory, which has been dealt with in this study.

STERN-GOUY MODEL FOR CONSTANT SURFACE CHARGE

van Olphen (1963) suggested that the charges in the Stern and Gouy layers can be proportional to their respective areas under the electrostatic potential distribution curve (Eq. 14).

$$\frac{\sigma_1}{\sigma_2} = \frac{\text{Area of the Stern layer } (\text{A}_\text{s})}{\text{Area of Gouy layer } (\text{A}_\text{Gouy})} \tag{14}$$

The estimation of Stern layer charge (σ_1) in an interacting system for CSC conditions is not available due to the difficulties involved in estimating the two parameters, such as the number of available adsorption sites and specific adsorption potential on the counter-ions at the clay surface (see Eq. 9). The influence of platelet interaction on the number of available adsorption sites is not understood yet. Further, the specific adsorption potential, ψ for a given clay-water-electrolyte system is difficult to estimate under varying DDL interaction. In this study, estimation of σ_1 was eliminated and the following equation was developed to determine the Stern potential at a given pressure by knowing the soil surface and pore-fluid properties. (*Detail derivation is presented in the Appendix*)

$$\sigma A_{Gouy} = \sqrt{2nkT\varepsilon}\sqrt{2\cosh y_\delta - 2\cosh u}\left(\left(y_\delta + \left(vq\sigma 2\pi\delta/\varepsilon' kT\right)\right)\delta + A_{Gouy}\right) \qquad (15)$$

The area under the hyperbolic potential distribution curve for the Gouy layer (A_{Gouy}) is a function of Stern and mid-plan potentials which can be calculated by following the method of slices (See Appendix). Therefore, Eq. (15) provides an implicit solution for the Stern potential. For a known value of mid-plan potential, Stern potential is obtained through optimization. The objective function to determine the Stern potential based on Eq. (16) is given as,

$$f\left(y_\delta\right) = \sigma A_{Gouy} - \left\{\sqrt{2nkT\varepsilon}\sqrt{2\cosh y_\delta - 2\cosh u}\left(\left(y_\delta + \left(vq\sigma 2\pi\delta/\varepsilon' kT\right)\right)\delta + A_{Gouy}\right)\right\} \qquad (16)$$

The 'fminbnd' function, which is based on the golden section search and parabolic interpolation method, was used to obtain the optimized value of Stern potential from the objective function (Eq. 16) in Matlab. The mid-plane potential, *u*, was used as the lower boundary in the optimization, added a small value (~ 10^{-9}) to avoid the singularity (Bharat et al., 2013). The upper boundary was fixed at 30 for the studied pressures and pore fluid concentrations. The nature of the objective function was, further, studied at three different applied pressures and four different pore fluid concentrations. The important parameters used in the objective function evaluation are presented in Table 1. For all the cases, the true minima are preceded by a minimum at the lower boundary (i.e., *u*). The true minima approach the first minima (*u*) with the increase in the applied pressure (Fig. 3a) and pore fluid concentration (Fig. 3b). Overall, the local minimum was observed in the range of 0−10 for all the considered cases.

Electrostatic potential distribution

The potential distribution for the entire DDL in the Gouy-Chapman model follows the Poisson's distribution from a maximum value at surface to a minimum at the mid-plane. In the case of Stern model, the potential starts with a maximum value at the surface, and reduce linearly to Stern potential at the Stern-Gouy interface. Beyond this, the potential follows the Poisson's distribution within the Gouy-layer to a minimum value at the mid-plane. The mid-plan potential u, at a given pressure was determined using Eq. 1. The surface potential was obtained using Eq. 3 for the Gouy-Chapman model and Eq. 6 for the Stern model after knowing the Stern potential. The Stern potential was estimated through optimization using Eq. 22 for known u.

Fig. 4a presents the potential distributions for both models from the surface to mid-plane distance under two different applied pressure at equilibrium. The parameters considered in the computation are presented in Table 1. At the lower applied pressure (0.01 MPa), the influence of the size of the cations was only visible near the clay surface up to a distance of ~ 20 Å. At higher applied pressure, the effect of cations size on the potential distribution was more pronounced due to the increased DDL interaction as the separation distance reduced significantly.

Fig. 4b presents the variation of Stern potential, mid-plane potential, and the DDL thickness (on the third axis) of an interacting clay-water system with the applied pressure by the proposed Stern model. The values of all parameters considered in the simulation were presented in Table 1. The applied pressure varied in the range of 0.01 MPa to 40 MPa. The DDL thickness decreased exponentially with the applied pressure and attained a minimum thickness of 7.9 Å (hydrated radius of Na^+ cation), equivalent to the Stern thickness at ~ 5 MPa. This indicated the full compression of the diffused Gouy-layer leading to compact layers of cations around the clay platelets. The DDL thickness, thus, remained constant with a further increase in the pressure. The mid-plane potential linearly increased with the increase in the applied pressure on the semi-log scale due to the increased DDL interaction. The Stern potential, on the other hand, showed a relatively slower rise in magnitude as compared to the mid-plan potential. The two potential curves eventually converged beyond ~ 7-8 MPa pressure as the mid-plane coincided with the Stern boundary after the elimination of the Gouy-layer. The ratio between the Stern potential and the mid-plan potential, thus, is a useful parameter to understand the compressibility behavior of the DDL under the applied pressure.

Stern layer thickness at large pressure

Choosing an appropriate thickness of the Stern layer is crucial for predicting the pressure-void ratio relationship, especially in the higher-pressure range, where the Gouy diffused layer gets compressed significantly. The minimum possible void ratio (i.e., the minimum separation distance between two interacting clay platelets) in clays is controlled by the thickness of the Stern layer. A well-defined value for the Stern layer thickness, however, is not available for the clays (Verwey & Overbeek, 1948; van Olphen, 1973; Shang et al., 1994; Sridharan & Satyamurhty, 1996). The type of exchangeable cations, charge distribution, and size and shape of the siloxane cavity on the surface of the montmorillonite influence the adsorption of cations on the clay surface (Sposito, 2008), which can significantly influence the Stern layer thickness. Most of the available studies consider the Stern layer to be incompressible and equivalent to the radius of the hydrated cations, but the interaction between the particles considered in such studies is weak or negligible. The behavior of the Stern layer at large applied pressure, however, is not studied so far.

Experimentally determined compressibility data of seven different bentonites from the literature were considered in this study to understand the minimum achievable separation distance between the clay platelets (DDL thickness) under the applied mechanical pressures. The relevant properties of the bentonites are presented in Table 2. The DDL thickness was derived from the experimental void ratio for these bentonites from the literature using Eq. 4 by considering the parallel plate assumption. The void ratio of the bentonites considered in this study was in the range of ~0.4–1 under the studied pressure range. The parallel arrangement of the clay platelets has been well reported for heavily consolidated clays at such small void ratios (Delage & Lefebvre, 1984). Strong DDL repulsion brings the clay platelets towards a parallel arrangement as the soil is heavily compressed at large pressure. The DDL thickness was plotted against the applied pressure and presented in Fig. 5a. Variation of the DDL thickness with the applied pressure for all the bentonites suggested that the thickness of the DDL is compressed to the smallest value of 2.3 Å in the pressure range of 10 MPa- 40 MPa for different bentonites. The minimum possible separation distance between the two clay platelets surrounded by a rigid Stern layer is shown in Fig. 5b(i). When the DDL thickness or the half of the separation distance is decreased beyond the value equivalent to the diameter of the exchangeable cation, the Stern layer thickness consequently got compressed. The Stern layer compression is facilitated by the penetration of the surface cations into the siloxane cavities of the clay surface (Fig. 5b (ii)) once the diffuse layer is eliminated from the system at a large applied pressure. Generally, the diameter of the siloxane cavity is about 2.6 Å, which is approximately 1/3rd of the hydrated size of Na^+ (Sposito, 2008) and about similar in size as that of water molecules. The Stern layer, thus, get compressed at a high applied pressure to facilitate further volumetric compression of clays once the Gouy-layer is compressed significantly.

The total DDL thickness at large pressure was, therefore, corrected through the incorporation of the Stern layer compression. The compressibility of the Stern layer was, however, incorporated only into the void ratio computation in Eq. 4. The effect was not considered in the computation of Stern potential and the thickness of the Gouy-layer, as the theoretical formulation for such a complex interaction is not available. The ratio of mid-plan to Stern potential (u/y_δ) during the compression of the DDL thickness under the applied pressure was studied for three different bentonites namely Na-Kunigel, Ponza, and Na-Ca-MX80 (Fig. 6). The three bentonites represented a wide range of surface cation characteristics and surface charge density (σ). The ratio between the two potentials indicated the degree of interaction between the two interacting clay platelets. The relevant properties of the respective bentonites and other parameters related to the pore-fluid and Stern layer used in the estimation are presented in Table 2 & 3, respectively. A cationic concentration of 0.0001N was used to represent water as pore fluid (Das & Bharat, 2021). The Stern layer thickness was taken as the hydrated radius of Na^+ for Na-dominated bentonite. For the divalent dominated and mixed-valence bentonites, the larger cationic size (i.e., Ca^{2+}) was considered as the Stern layer thickness.

The potential ratio increased with the applied pressure for all the three bentonites as the DDL thickness was compressed resulting in a higher degree of DDL interaction. The Stern layer compression began when the potential ratio was ~ 0.65 for the di-valence-dominated Ponza bentonite as well as the mixed-valent Na-Kunigel bentonite (Fig. 6a). On the other hand, Stern layer compression was observed at ~ 0.75 for the Na-dominant Na-Ca-MX80 bentonite. The observed difference in the potential ratio at the beginning of the Stern layer compression for different bentonites was related to the variation in the surface cation characteristics and surface charge density. Stern layer compression started early for the bentonites containing higher surface charge densities and di-valent cations. Overall, the Stern layer compression begins when the potential ratio was in the range of 0.65-0.75 for different bentonites.

An S-curve relation between the Stern layer thickness (δ) and the ratio between the mid-plan and Stern potential was assumed to predict the void ratio, which follows the typical compressibility behavior of clays, as given by

$$\delta = r \exp^{-\left\{a\left(\frac{u}{y_\delta} - R_y\right)\right\}} \qquad ; \frac{u}{y_\delta} - R_y > 0 \tag{23}$$

where r is the hydrated radius of cation in Å, R_y is the potential ratio at which Stern layer thickness starts getting compressed, varies in the range of 0.65-0.75, depending on the surface charge characteristics of the clays. The parameter '*a*' defines the slope of the curve, which was determined based on the observed minimum achievable thickness of the Stern layer (~2.3 Å) when the potential ratio becomes unity, as given by

$$a = (R_y - 1)\ln\left(\frac{2.3\,\mathring{A}}{r}\right) \tag{24}$$

The above correction for Stern layer thickness was incorporated into the void ratio computation through Eq. 5 when the potential ratio reaches a specified value under the applied pressure for a given soil.

VALIDATION OF THE PROPOSED STERN MODEL

The proposed compressible Stern model was validated on five different bentonites from the literature and the validation results were presented in Fig. 8. A flowchart for the computation of the pressure-void ratio relationship based on the proposed approach was presented in Fig. 7. The predicted compressibility data of these bentonites from the Gouy-Chapman model and the Stern model for CSP conditions (Tripathy et al., 2014) were also presented along with the proposed model to carry out a comparative analysis.

Table 2 presents the relevant properties of the bentonites used in the prediction of the compressibility data of the bentonites using the three models. The valence was taken as 1 for Na-dominated bentonites and 2 for Ca or other divalent cations–dominated bentonites in the Stern interacting CSP model as considered by Tripathy et al. (2014), while weighted average valence (ν_{avg}) was considered in the prediction by the Gouy-Chapman and the proposed model. The initial Stern layer thickness (δ_0) at zero pressure was considered to be equivalent to the hydrated radius Na^+ cation for the Na-dominated Na-Ca-MX80 bentonite and Mexico montmorillonite in the proposed model. For the other bentonites, which have either mixed-valence or divalent-dominated surface cations, the hydrated radius of Ca^{2+} cation was taken as the Stern layer thickness, being the largest among the available exchangeable cations. The Stern layer compression was applied when the potential ratio (u/y_δ) reached a specified value (R_y) for the given bentonite. However, a fixed value of 5 Å was used as the Stern thickness for all the bentonites in the CSP model by Tripathy et al. (2014). The pore fluid parameters and other relevant parameters used in the three models were presented in Table 3.

The predicted compressibility data by the proposed model and the two existing models were compared with the measured data for five different bentonites as presented in Fig. 8. The CSP model by Tripathy et al. (2014) was not in good agreement with the measured data in the studied pressure range for the studied bentonites. The CSP model was in close agreement with the measured data for the Na-Kunigel bentonite briefly in the lower pressure range of 0.1 – 0.5 MPa, however, deviated significantly at higher pressures (Fig. 8b). For the other studied bentonites, the

CSP model was far away from the measured data as compared to the proposed model (Fig. 8a, 8c-8e). The observed discrepancies were attributed to the issue with the assumption of constant surface potential conditions in the model, as discussed earlier. Overall, the Gouy-Chapman model was relatively close to the measured data as compared to the CSP model, however, severely underestimated the void ratios at large pressures. This was primarily due to not considering the effect of the size of the cation in the Gouy-Chapman theory. The proposed model based on the Stern theory at CSC condition showed a better agreement with the measured data in the studied pressure range in comparison to the existing two models. The proposed model significantly improved the prediction at large pressures as the predicted void ratios were higher than the Gouy-Chapman model due to the incorporation of the size of the cations and were very close to the measured data. Further, treatment of the compressible Stern layer provided a realistic void ratio variation with pressure at very large pressures unlike the earlier Stern model at CSP condition. Overall, the proposed model showed a better prediction at pressures higher than 0.1 MPa for the studied bentonites, however, overpredicted at a lower pressure range (0.01 MPa- 0.1 MPa). The observed discrepancies at lower pressures were attributed to the dominant presence of the edge-face clay platelets orientation as the theory is based on the parallel arrangement of the clay platelets.

CONCLUSIONS

The effect of cations size was incorporated into the prediction of clay compressibility behavior using the Stern theory at CSC condition for the first time. A mathematical model was developed to establish the potential-distance relationship for the interacting Stern model at the CSC condition. The compressibility of the Stern layer was further incorporated into the theory for the first time to provide a more realistic prediction of the compressibility behavior of bentonites in the high-pressure range. Based on the detailed analysis of the compressibility data of different bentonites from the literature using the proposed Stern theory, the following conclusion was drawn.

Under the application of load, the diffused Gouy layer initially undergoes significant compression, while the Stern layer remains unaffected. The compression of the Stern layer starts in the pressure range of 0.5–1 MPa for different bentonites once the thickness of the Gouy layer is significantly reduced. The thickness of the Stern layer reaches a minimum value equivalent to the water molecule size at a pressure of ~40 MPa. The siloxane cavities on the surface of the clay platelets accommodate the cations at such high pressure to facilitate the Stern layer compression. The void ratio corresponding to the minimum Stern layer thickness at such high pressure is ~0.4.

The ratio of the midplane to Stern potential, which represents the degree of interaction in the clay-water system, influenced the compression behavior of the Stern layer under the loading. The potential ratio of the clay-water electrolyte system at any given pressure is dependent on the type and composition of the exchangeable cations on the clay surface. The Stern layer compression starts when the potential ratio is in the range of 0.65-0.75 for bentonites with different surface cations characteristics.

DECLARATION

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Conflicts of interest: All the authors declare that they have no conflicts of interest.

Availability of data: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability: The codes developed and/or used in the current study are available from the corresponding author on reasonable request.

Appendix

The estimation of Stern layer charge (σ_1) in an interacting system for CSC conditions is not available due to the difficulties involved in estimating the two parameters, such as the number of available adsorption sites and specific adsorption potential on the counter-ions at the clay surface (see Eq. 9). The influence of platelet interaction on the number of available adsorption sites is not understood yet. Further, the specific adsorption potential,ψ for a given clay-water-electrolyte system is difficult to estimate under varying DDL interaction. The σ_1 estimation was, therefore, eliminated by considering

$$\frac{\sigma}{\sigma_2} = \frac{A_{Stern}}{A_{Gouy}} + 1 \tag{A1}$$

Substituting the expression for the Gouy layer charge (σ_2) from Eq. (10) in Eq. (A1) and re-arranging gives

$$\sigma A_{Gouy} = \sqrt{2nkT\varepsilon}\sqrt{2\cosh y_\delta - 2\cosh u}\left(A_{Stern} + A_{Gouy}\right) \tag{A2}$$

The area of Stern layer was estimated from Eq. (A3).

$$A_{Stern} = \frac{\left(y_0 + y_\delta\right)}{2}\delta \tag{A3}$$

After substituting for y_0, from Eq. (6),

$$A_{Stern} = \left(y_\delta + \left(vq\sigma 2\pi\delta / \varepsilon' kT\right)\right)\delta \tag{A4}$$

Combining Eqs. (A1) and (A3), we get

$$\sigma A_{Gouy} = \sqrt{2nkT\varepsilon}\sqrt{2\cosh y_{\delta} - 2\cosh u}\left(\left(y_{\delta} + \left(vq\sigma 2\pi\delta/\varepsilon' kT\right)\right)\delta + A_{Gouy}\right) \tag{A5}$$

The area under the hyperbolic potential distribution curve for the Gouy layer (A_{Gouy}) can be calculated by following the method of slices. Dividing the entire Gouy layer thickness into N number of thin slices of equal thickness Δx, the area can be computed as,

$$A_{Gouy} = \sum_{i=1}^{N+1} \frac{\left(y_i + y_{i+1}\right)}{2}\Delta x \tag{A6}$$

where $y_{i+1} = y_i - (slope)_i \Delta x$, and *i* denotes the number of nodal points, $d = N\Delta x$. The boundary conditions are– $\mathrm{y}_i = y_{\delta}$ at *i=1*, and $\mathrm{y}_i = u$ at *i* = N+1. The slope of the potential distribution in the Gouy layer at any point can be obtained as per the following equation,

$$\left(slope\right)_i = \kappa\sqrt{2\cosh y_i - 2\cosh u} \tag{A7}$$

The Gouy area, thus, can be estimated by knowing the Stern and mid-plan potentials in an interacting clay-water-electrolyte system.

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Table 1. Parameters used to establish electrostatic potential distribution in the Gouy-Chapman model and the proposed Stern model (Fig. 3 & 4)

Parameters	**Value**
Specific gravity, G_s	2.76
Specific surface area, S_a (m^2/g)	800
Cation Exchange Capacity, C_e (meq/100g	100
Valence, ν	1
Dielectric constant of bulk pore fluid, ε	80.4
Stern thickness/hydrated cationic radius, δ (Å)	7.9
Dielectric constant of water within stern layer, ε'	6
Temperature, T (K)	298

Table 2. Relevant bentonite properties used in the theoretical prediction of compressibility behavior

Soil name	S_a (m^2/g)	**Total** C_e (meq/100g)	**Individual cations**				ν_{avg}	G	δ_0 (Å)
			Na$^+$	**Ca^{2+}**	**Mg^{2+}**	**K$^+$**			
MX80 bentonite[a]	676	90.31	51.24	28.24	9.43	1.28	1.42	2.76	9.6
Na-Ca MX80 bentonite[b]	700	68	60	5	3	-	1.12	2.65	7.9
Na-Kunigel[b]	687	73.2	40.5	28.7	3	0.9	1.45	2.79	9.6
Ponza[c]	500	85	14	22	46	-	1.76	2.77	9.6
Mexico Montmorillonite[d]	734	114	92	1	-	1	1	2.7	7.9

[a]Tripathy et al. (2014), [b]Marcial et al. (2002), [c]Di Maio (2002), [d]Low (1980),

Table 3. Parameters used in the prediction of compressibility behavior of the considered bentonites by the three models

Parameters	Value		
	GC	**Stern constant potential**	**proposed**
Cationic concentration, n (N)	0.0001	0.0001	0.0001
Valence, ν	[*]ν_{avg}	[#]1 or 2	[*]ν_{avg}
Dielectric constant of water	80.4	80.4	80.4
Stern thickness, δ (Å)	N/A	5	[$]$\delta_0$
Dielectric constant of Stern pore fluid, ε'	N/A	6	6
Surface potential, ϕ_0 (mV)	N/A	274	N/A
Normalized surface potential, y_0	N/A	10.66	N/A
Specific adsorption potential, ψ	N/A	0	N/A
Number of adsorption spot, N_1 (ions/m^2)	N/A	[&]4.10^{-17}	N/A
Density of water, ρ_w (Mg/m^3)	1	1	1
Molecular weight of solvent (water), M (Mg/mol)	N/A	18	N/A
T (K)	298	298	298

[*]weighted average valence (see Table 2), [#]1 for Na-d0minated and 2 for di-valence dominated, [$]initial Stern layer thickness at zero pressure (see table 2), [&]for Na$^+$.

Table 4. List of figures

Figure	**Caption**
Fig. 1	Illustration showing interaction of DDL of two approaching clay platelets under applied mechanical pressure
Fig. 2	Electric potential distribution in Stern DDL model
Fig. 3a	Nature of objective function at 0.0001 M pore fluid concentration for three different pressure values

Fig. 3b	Nature of objective function at 10 kPa pressure for four different pore fluid concentrations
Fig. 4a	Computed electrostatic potential distribution in clay-water system (n = 0.0001M) based on GC and stern model under two different applied mechanical pressure
Fig. 4b	Variation of Stern potential and midplane potential in clay-water system (n = 0.0001M) with change in the degree of interaction (separation distance) under loading
Fig. 5a	Variation of DDL thickness with applied mechanical pressure derived from the measured compressibility data (using Eq. 4 with the parallel plate assumption) of different quality bentonites
Fig. 5b	Illustration showing cations penetrating the siloxane cavities on clay surface resulting in compression of Stern layer under very high applied mechanical pressure
Fig. 6a	Variation of double layer thickness with pressure at different degree of interaction for Ponza bentonite
Fig. 6b	Variation of double layer thickness with pressure at different degree of interaction for Na-Kunigel Bentonite
Fig. 6c	Variation of double layer thickness with pressure at different degree of interaction for Na-Ca-MX80 bentonite
Fig. 7	Flow chart showing the computation of void ratio at a given pressure using the proposed Stern model
Fig. 8a	Theoretically predicted and measured pressure-void ratio data of Na-Ca MX80 bentonite (Marcial et al., 2002)
Fig. 8b	Theoretically predicted and measured pressure-void ratio data of Na-Kunigel bentonite (Marcial et al., 2002)
Fig. 8c	Theoretically predicted and measured pressure-void ratio data of MX-80 bentonite (Tripathy et al., 2014)
Fig. 8d	Theoretically predicted and measured pressure-void ratio data of Ponza bentonite (Di Maio, 2011)
Fig. 8e	Theoretically predicted and measured pressure-void ratio data of Mexico Montmorillonite (Low 1980)

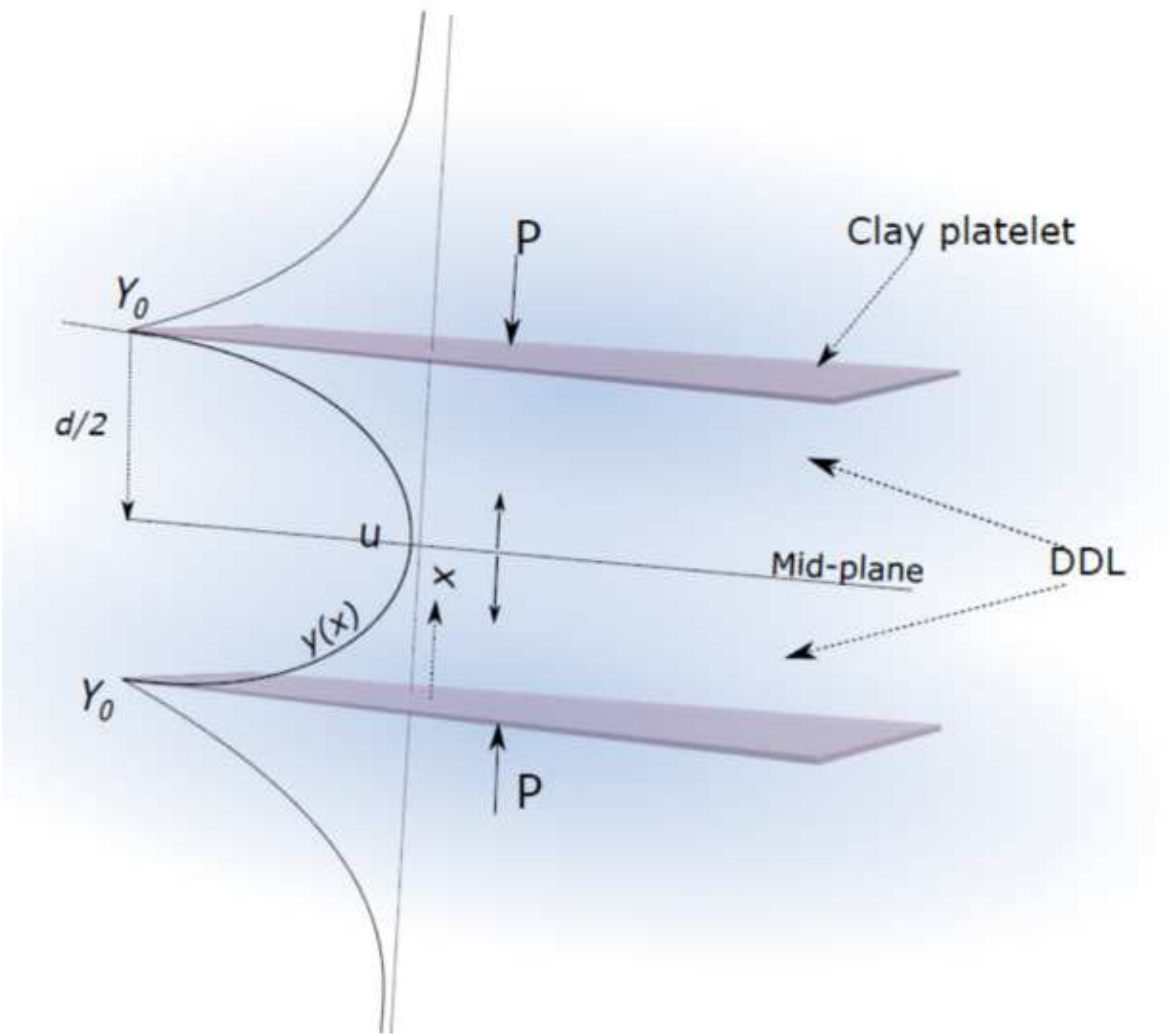
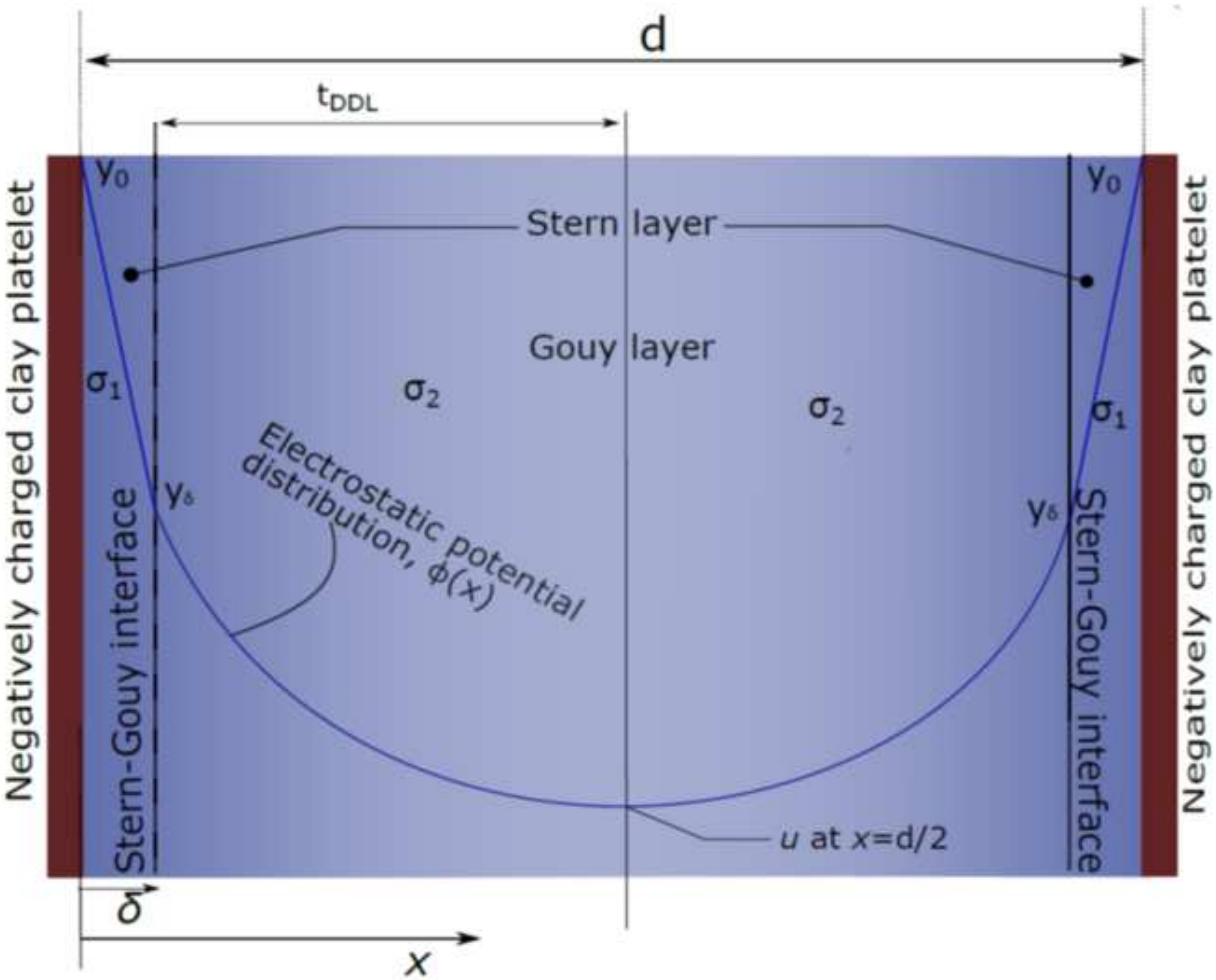

P
Clay platelet
Y0
d/2
u
Mid-plane
DDL
x
y(x)
Y0
P

Fig.2


d
tDDL
y0
y0
Stern layer
Gouy layer
σ1
σ2
σ2
σ1
Electrostatic potential distribution, φ(x)
yδ
yδ
Negatively charged clay platelet
Stern-Gouy interface
Stern-Gouy interface
Negatively charged clay platelet
u at x=d/2
δ
x

Pasted Layer

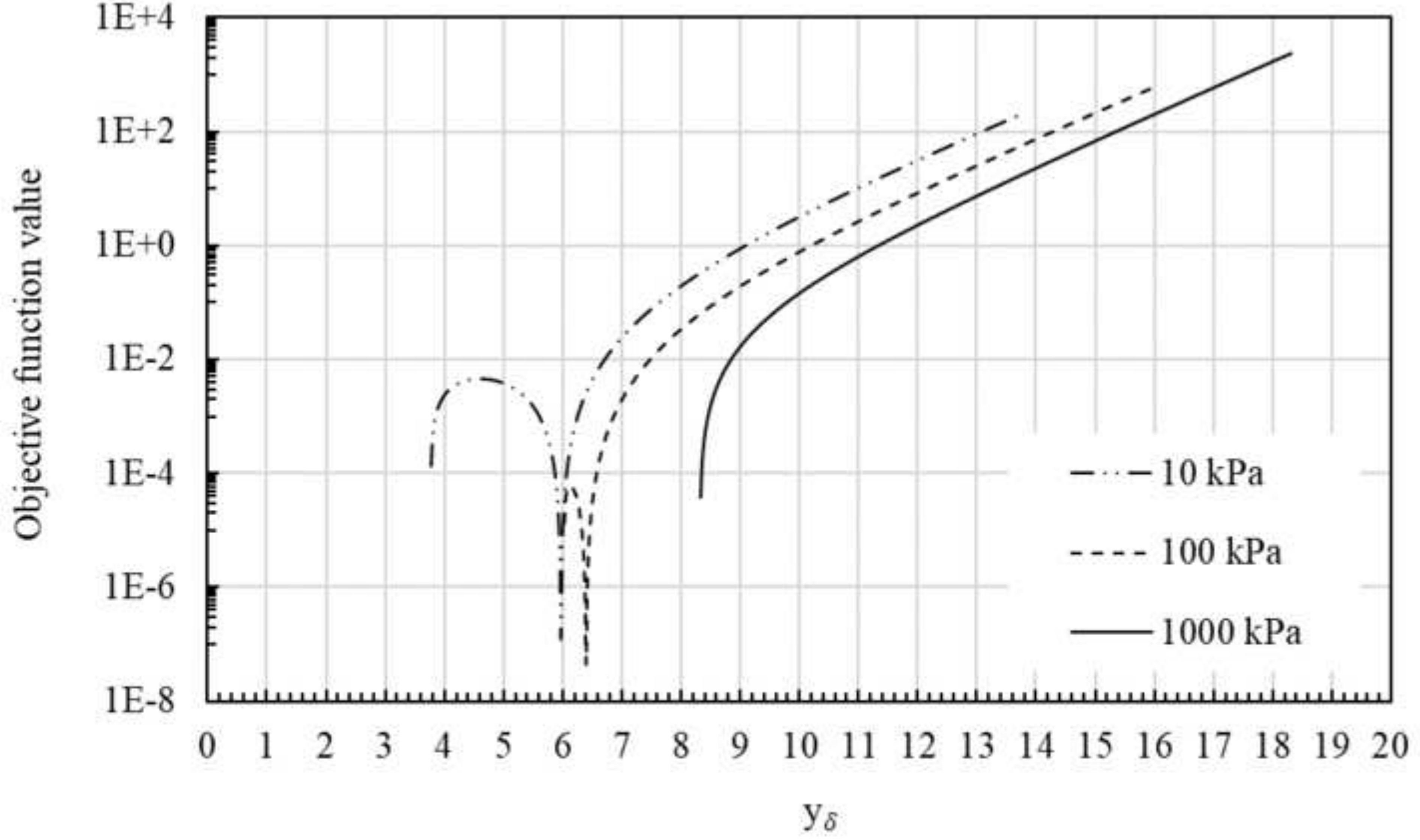
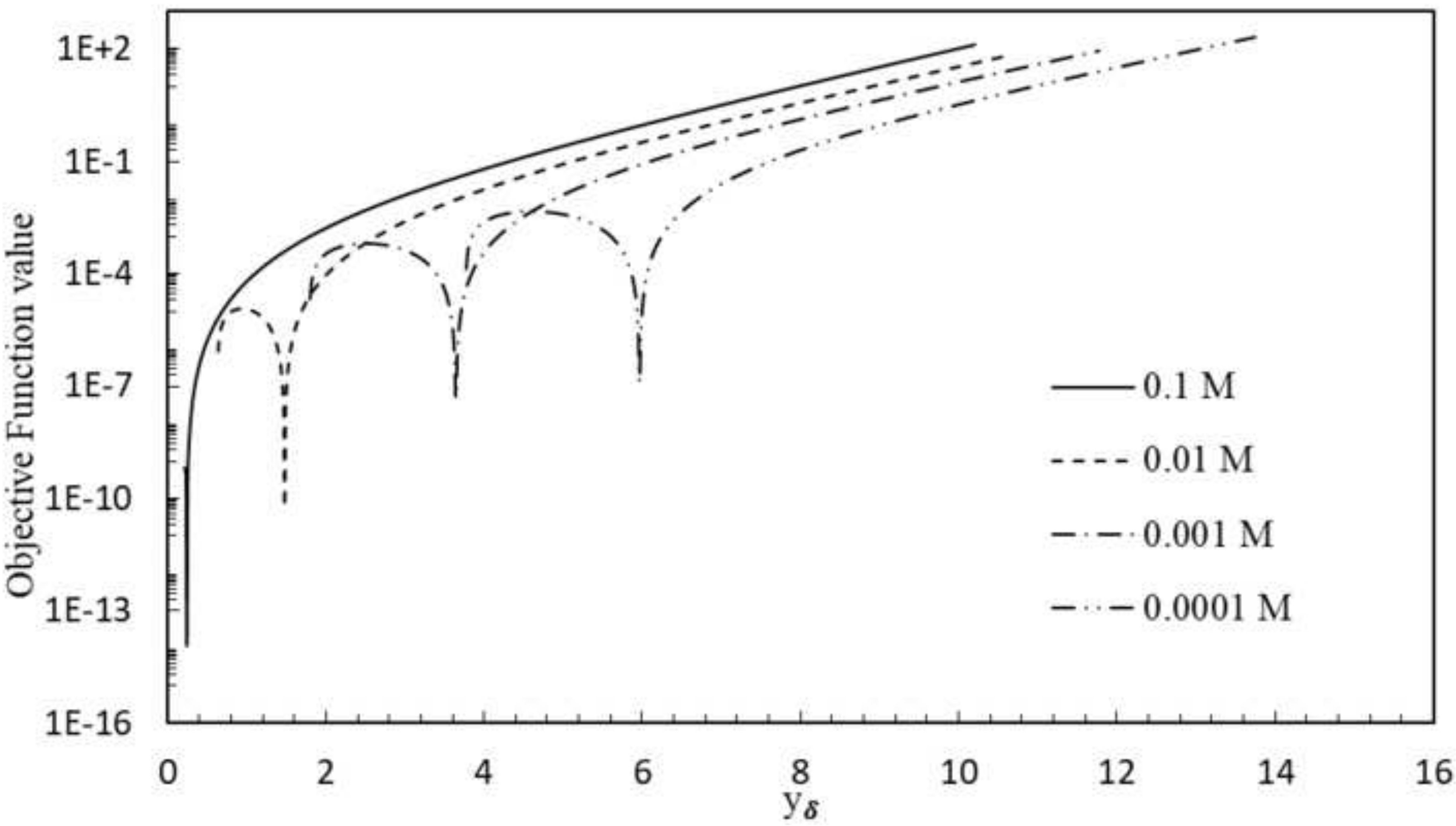


Fig.3b



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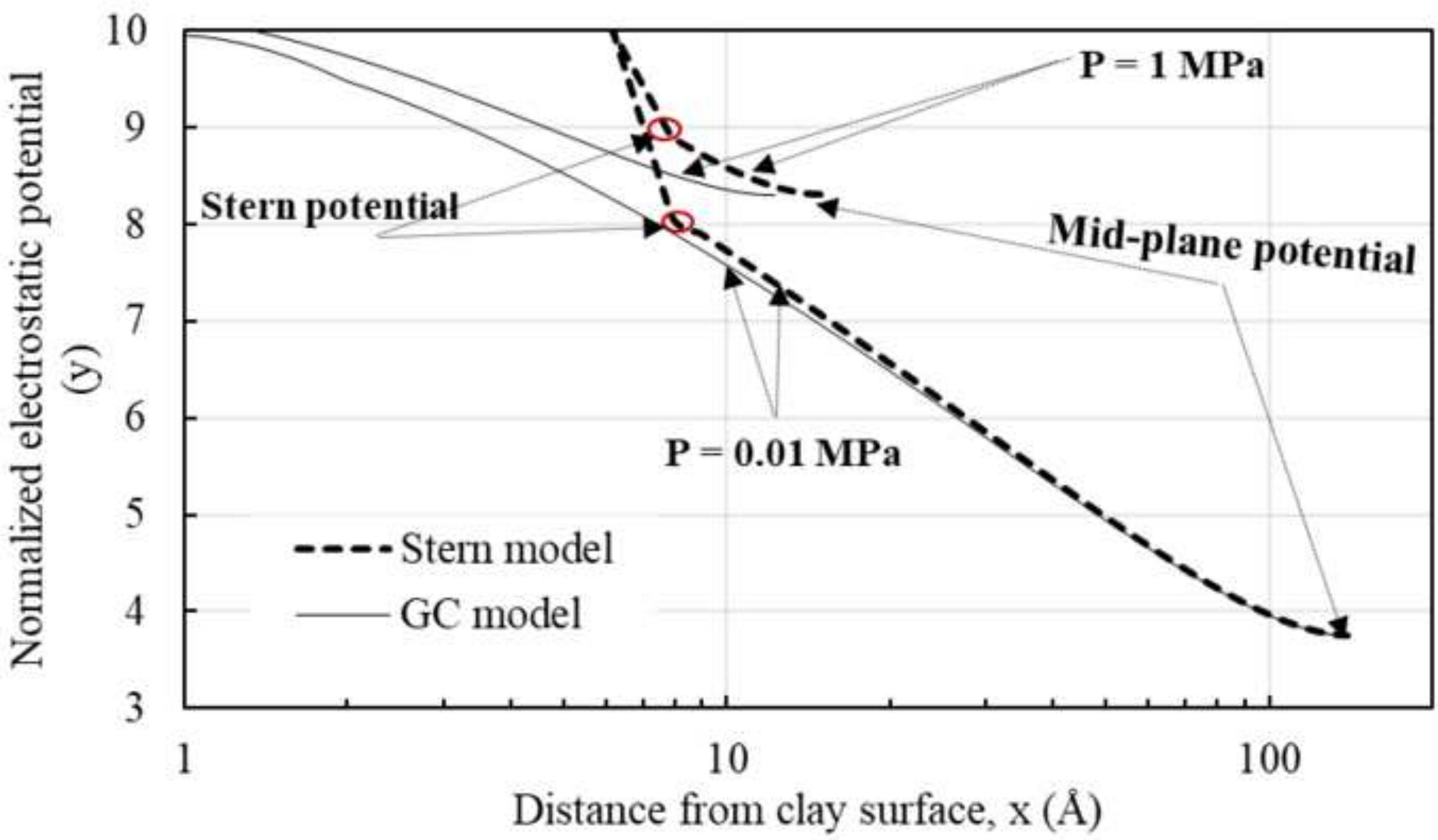

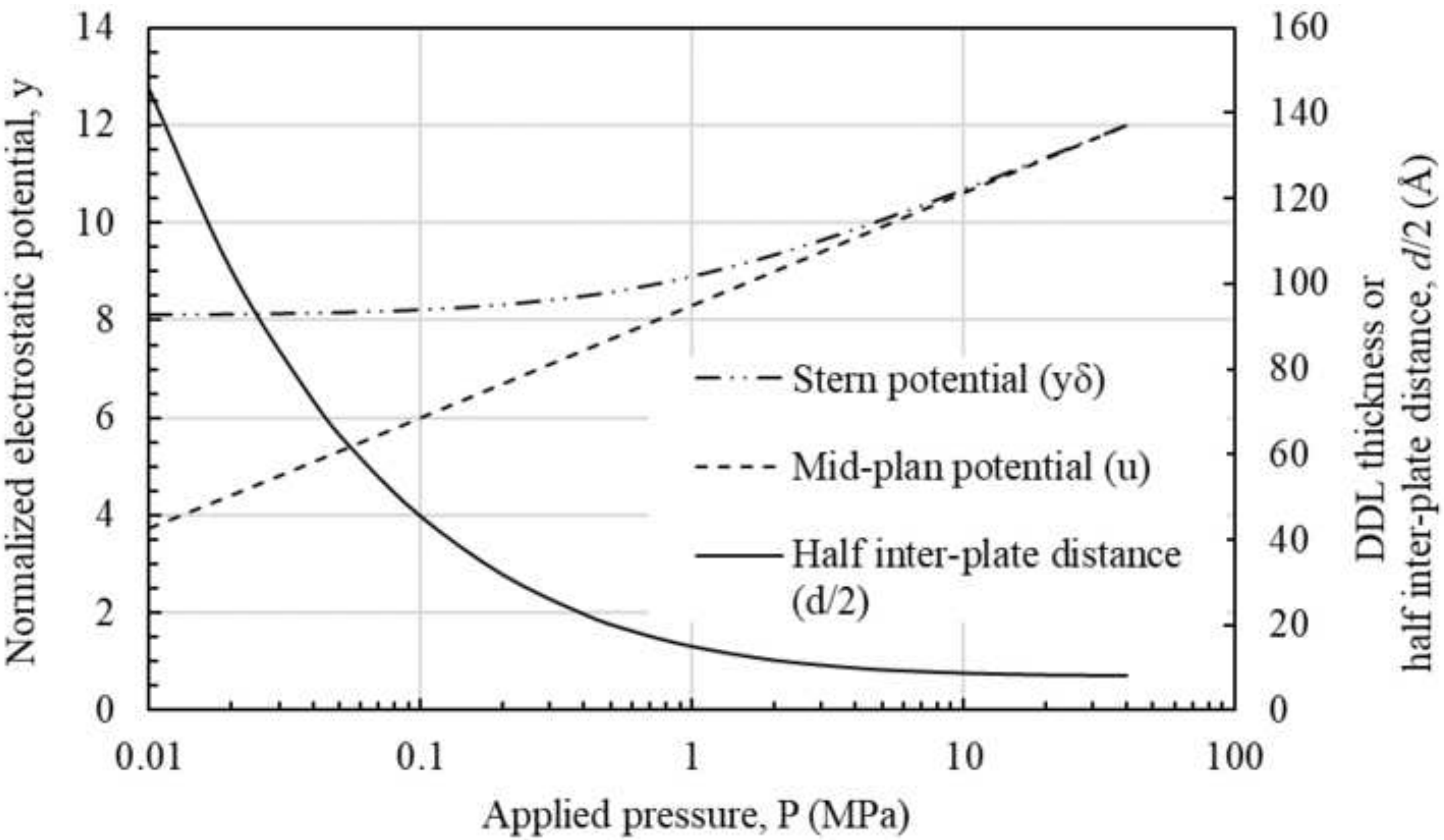

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Fig.5a

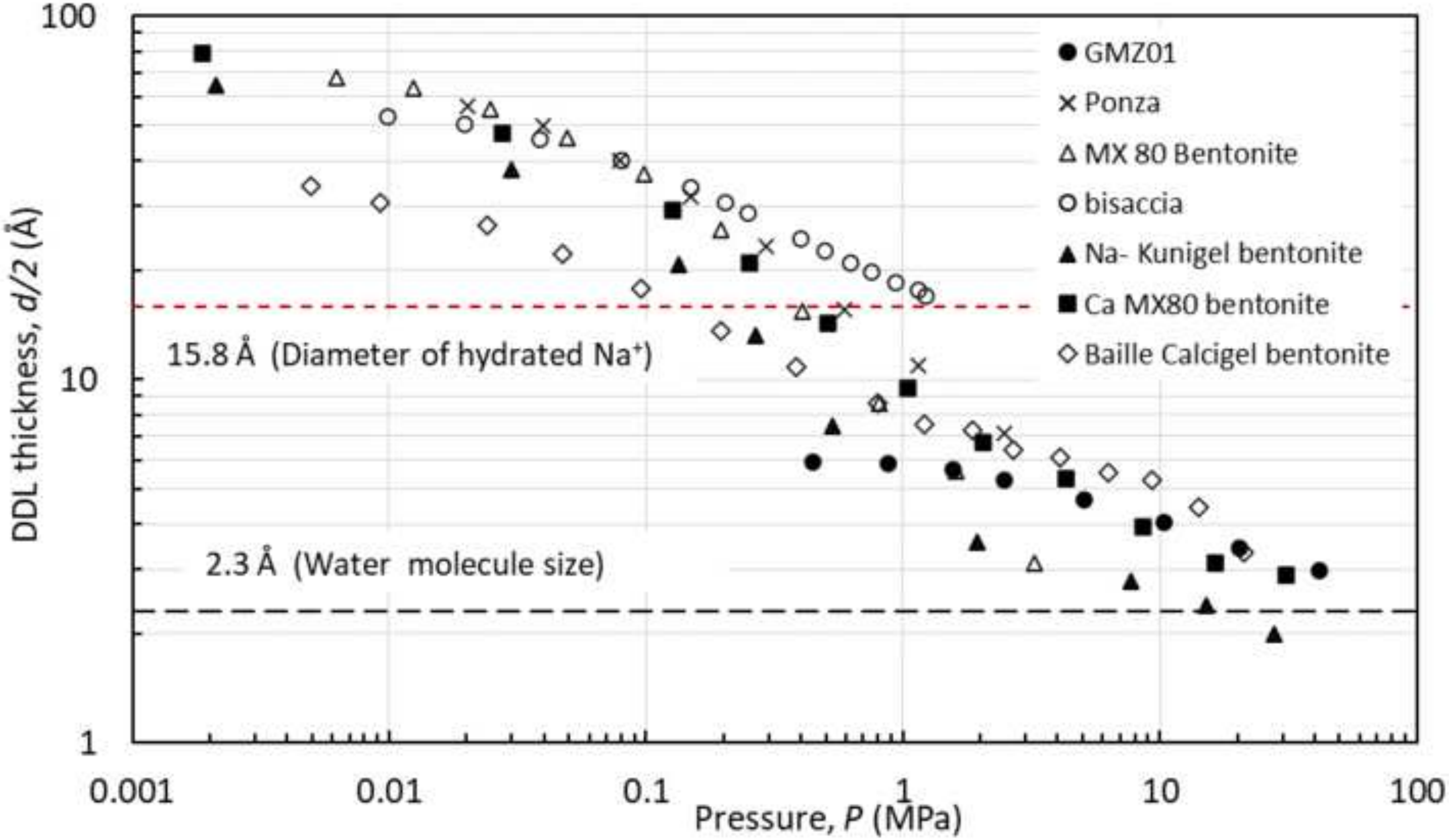

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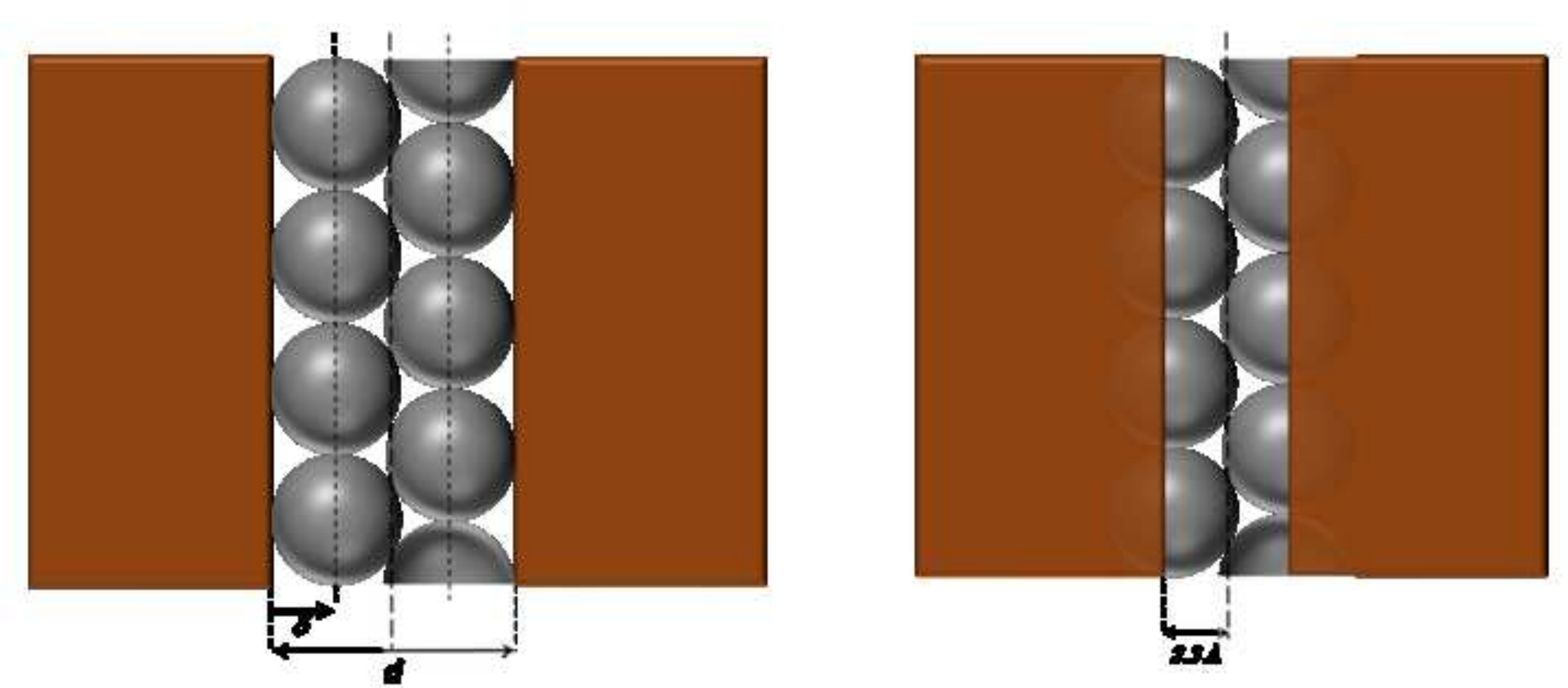
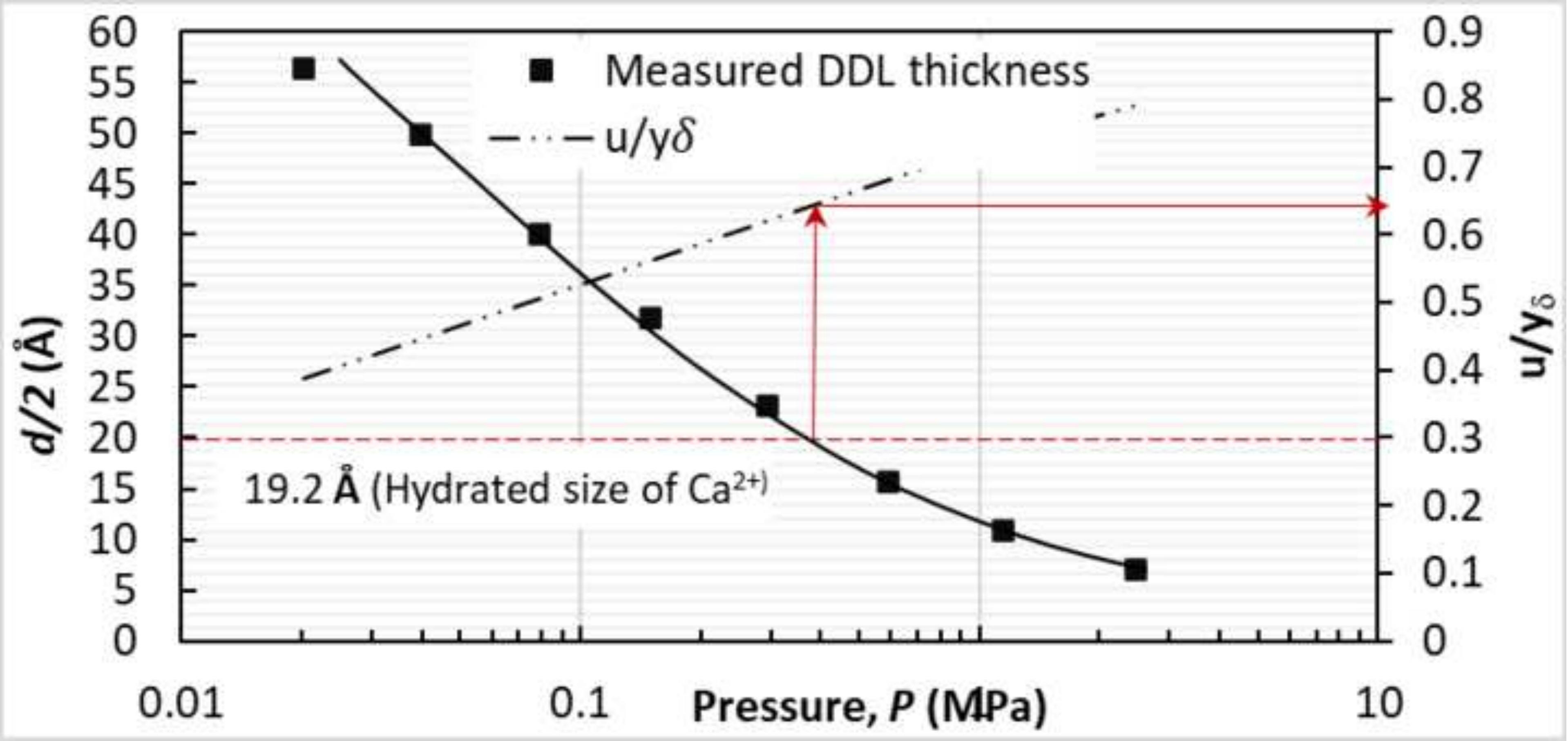
Fig.5b



(i) Separation distance beyond which stern layer starts compressing

(ii) Minimum separation distance after penetration of the cations into the siloxane cavities

Pasted Layer



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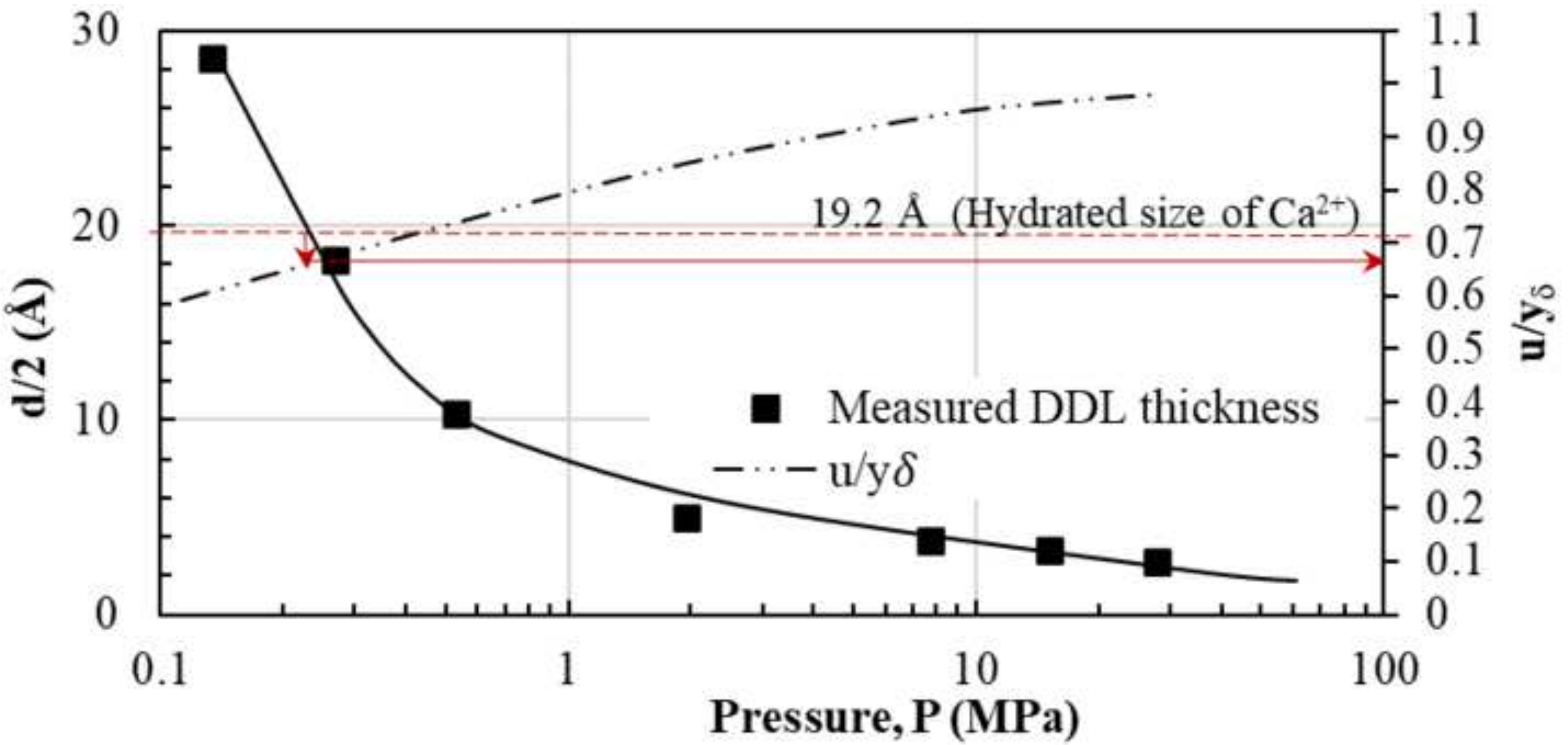

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Fig.6c

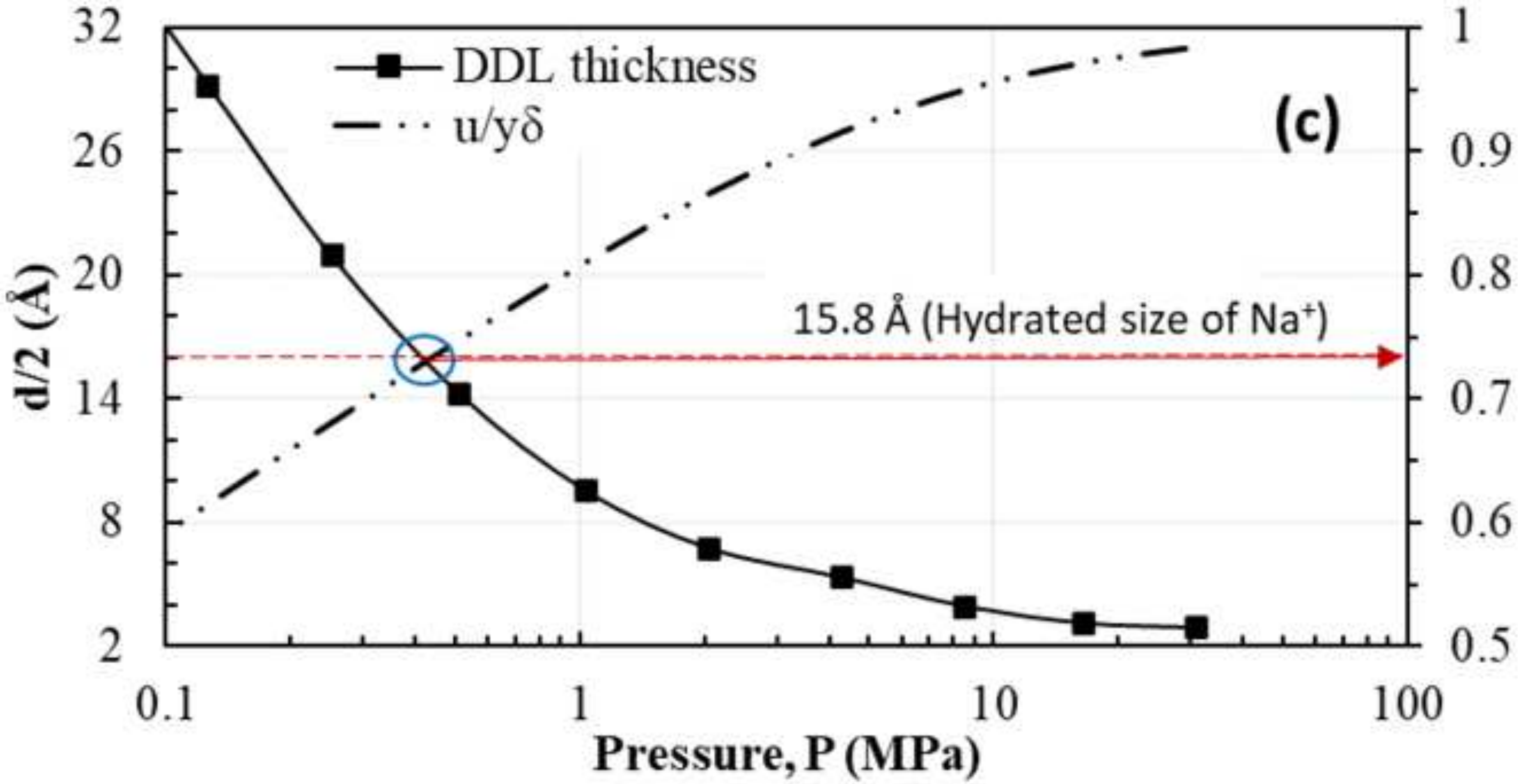
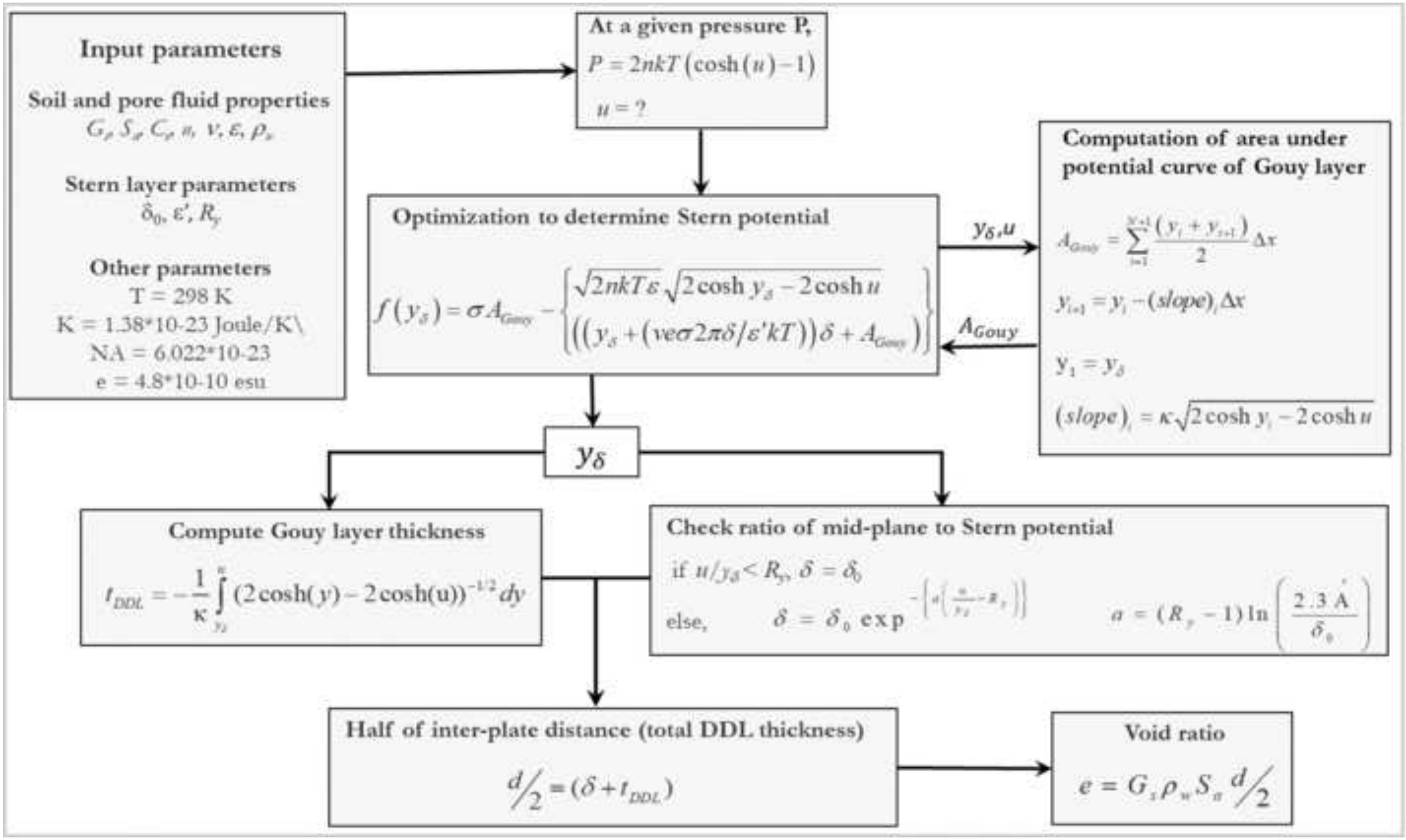

DDL thickness
u/yδ
(c)
15.8 Å (Hydrated size of Na⁺)
d/2 (Å)
32
26
20
14
8
2
u/y_δ
1
0.9
0.8
0.7
0.6
0.5
0.1
1
10
100
Pressure, P (MPa)

Fig.7



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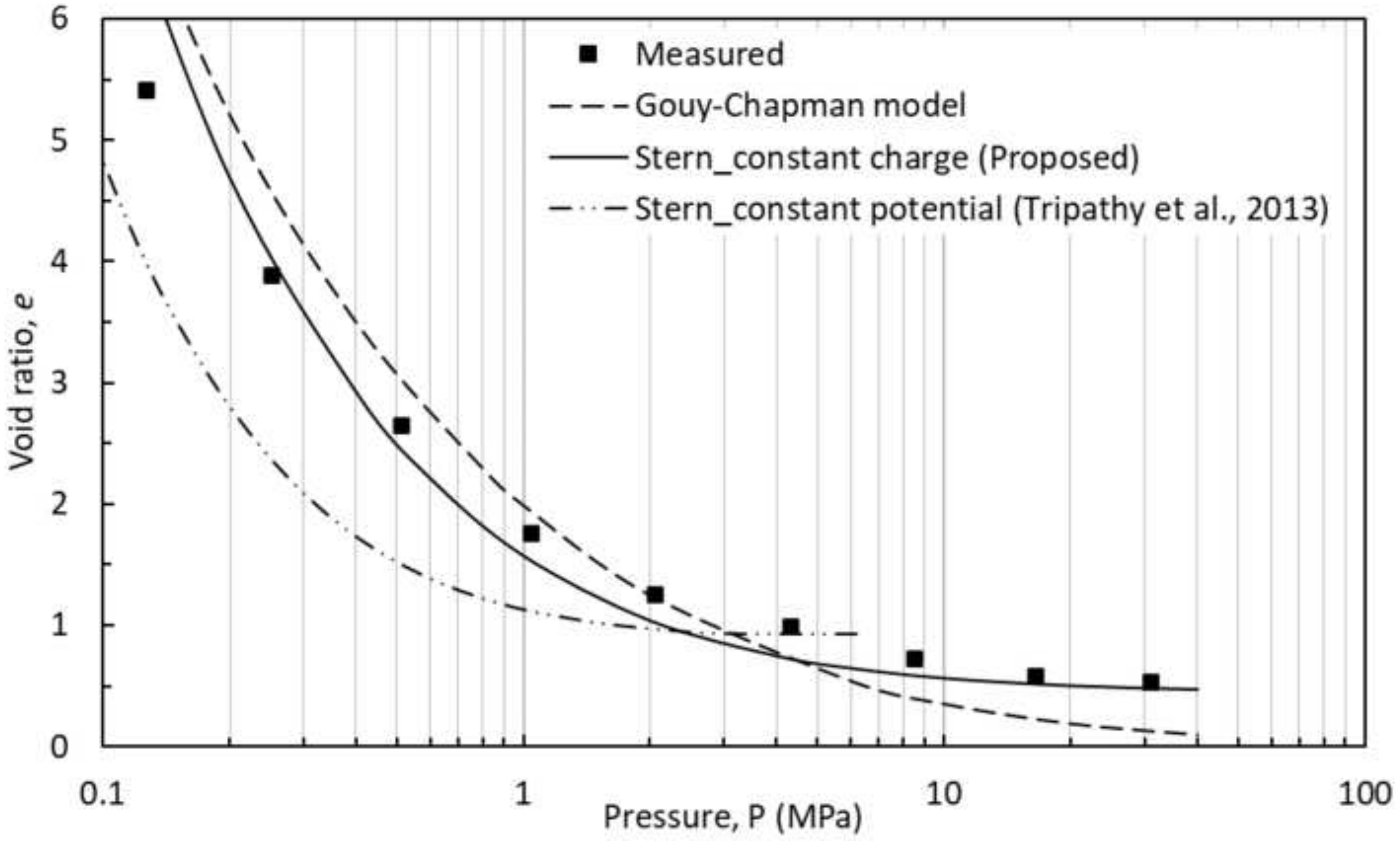
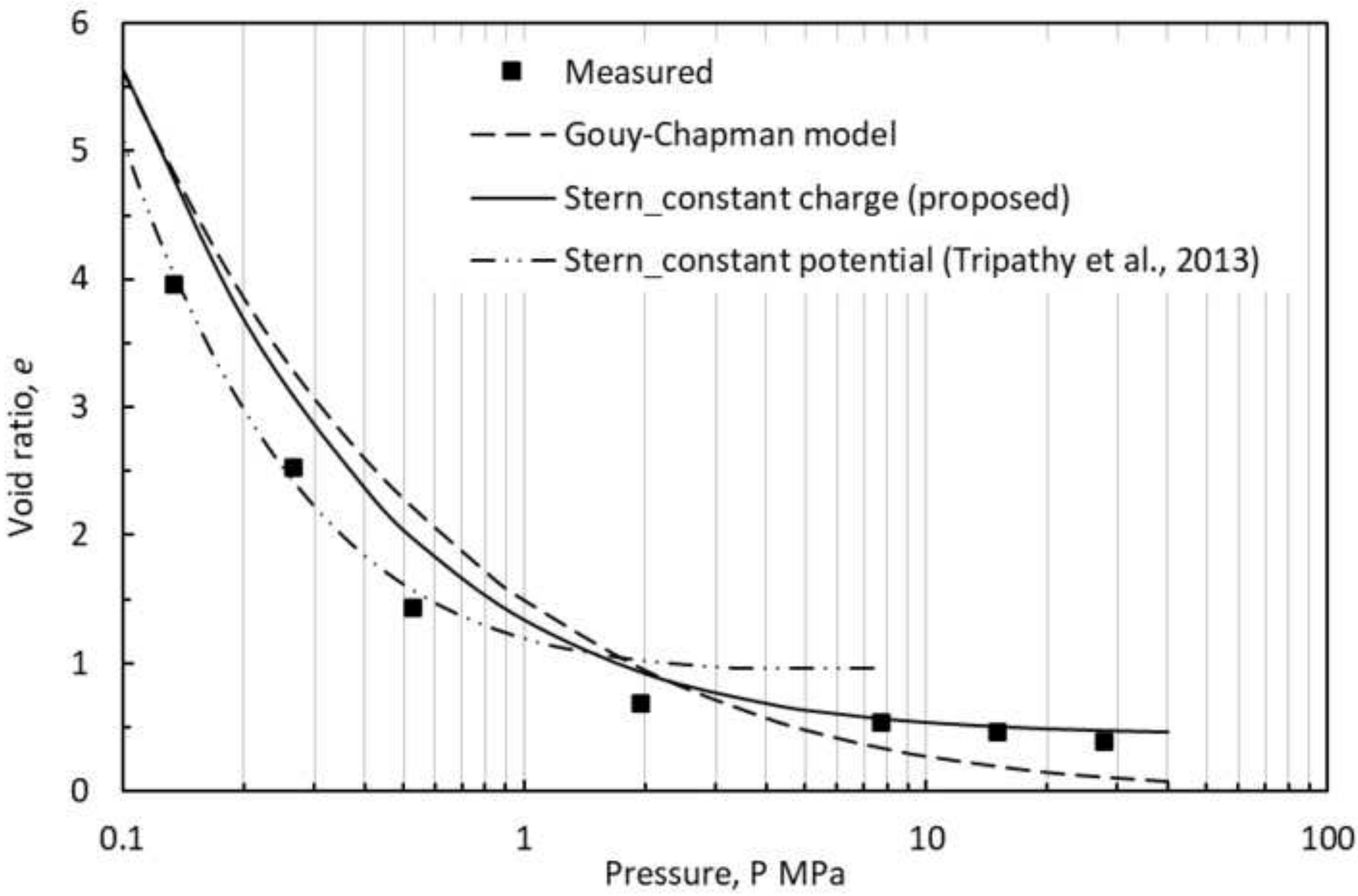

Measured
Gouy-Chapman model
Stern_constant charge (Proposed)
Stern_constant potential (Tripathy et al., 2013)
Void ratio, e
Pressure, P (MPa)
0
1
2
3
4
5
6
0.1
1
10
100


Measured
Gouy-Chapman model
Stern_constant charge (proposed)
Stern_constant potential (Tripathy et al., 2013)
Void ratio, e
Pressure, P MPa
0
1
2
3
4
5
6
0.1
1
10
100

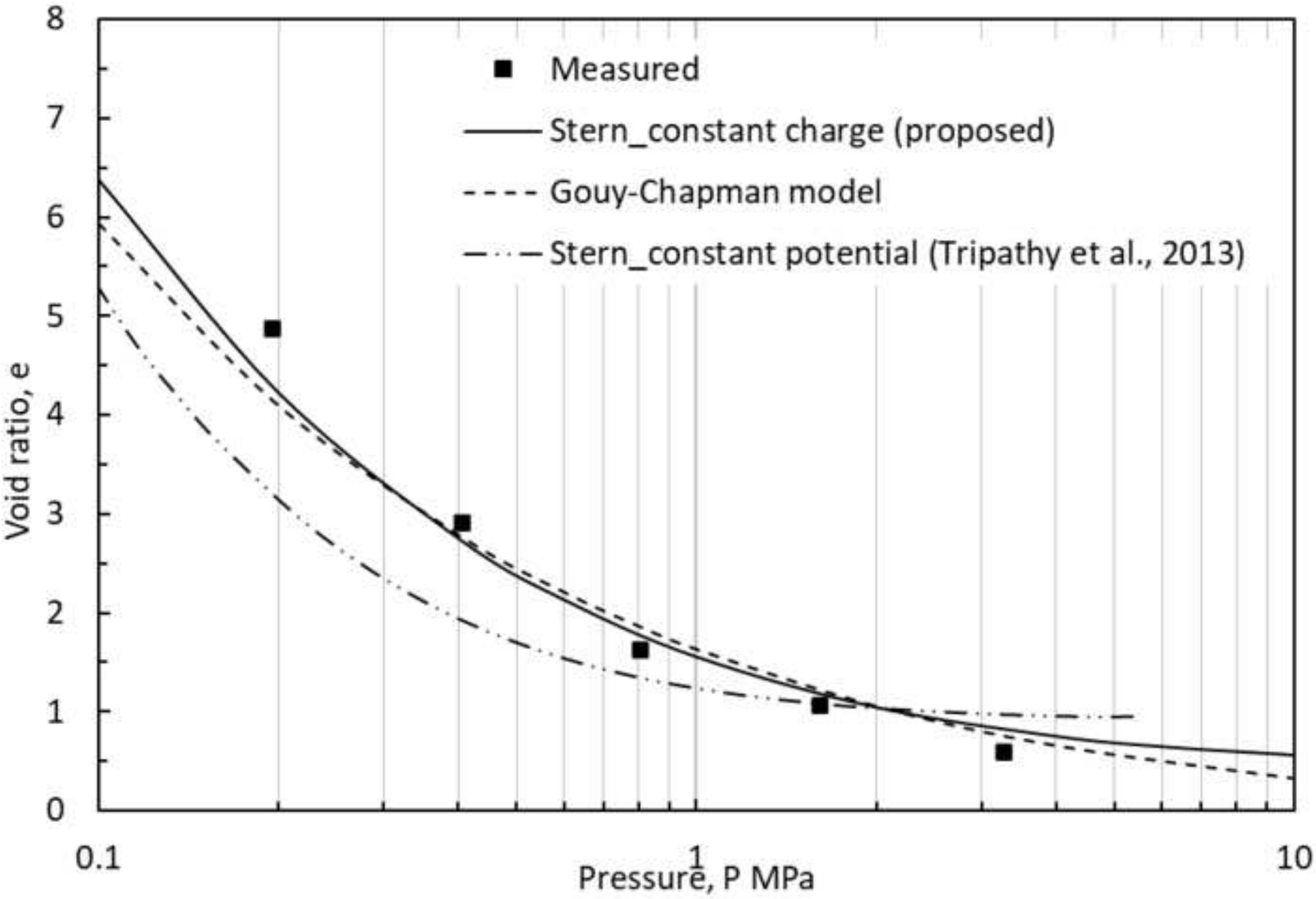


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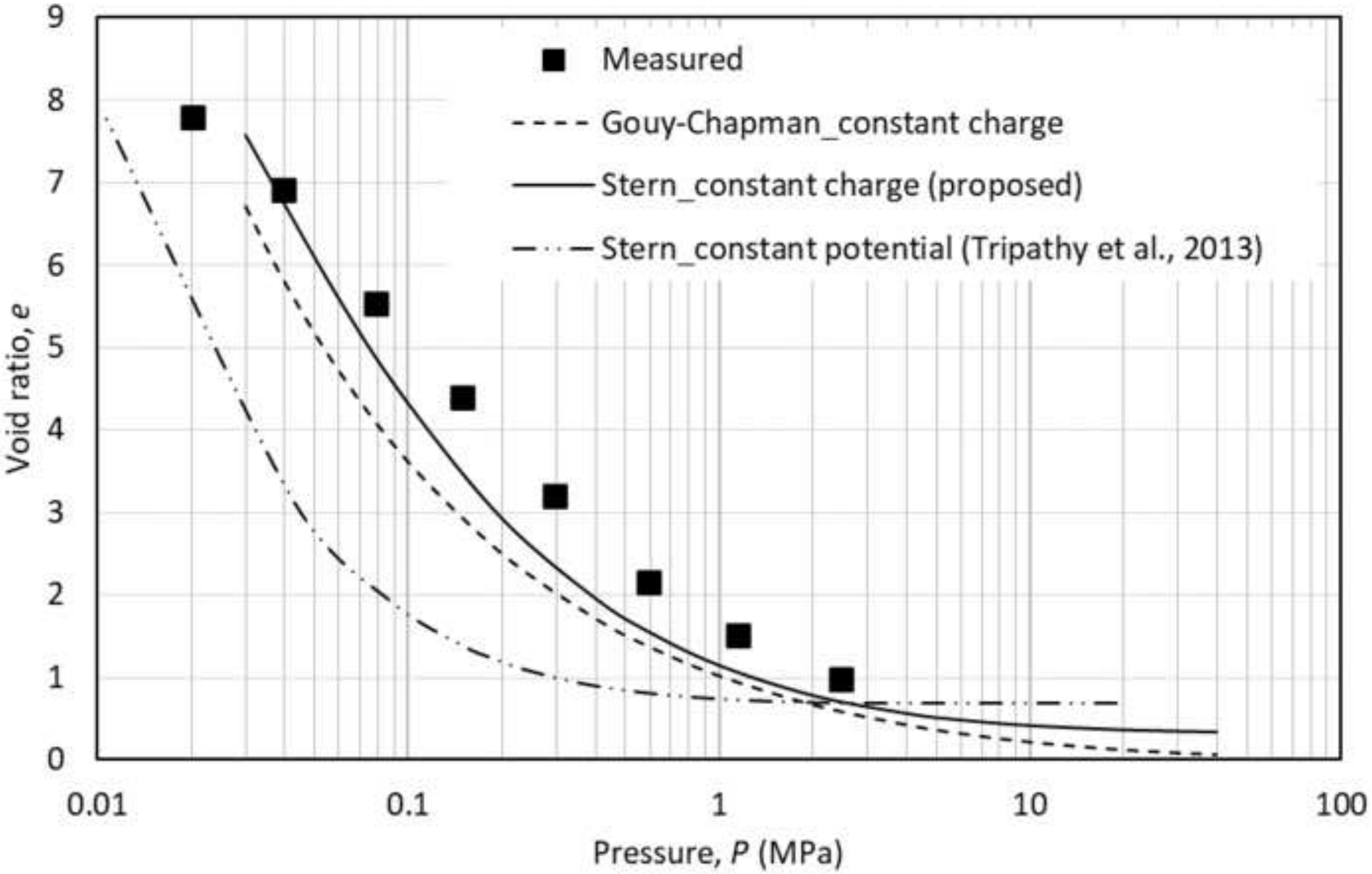
Fig.8d



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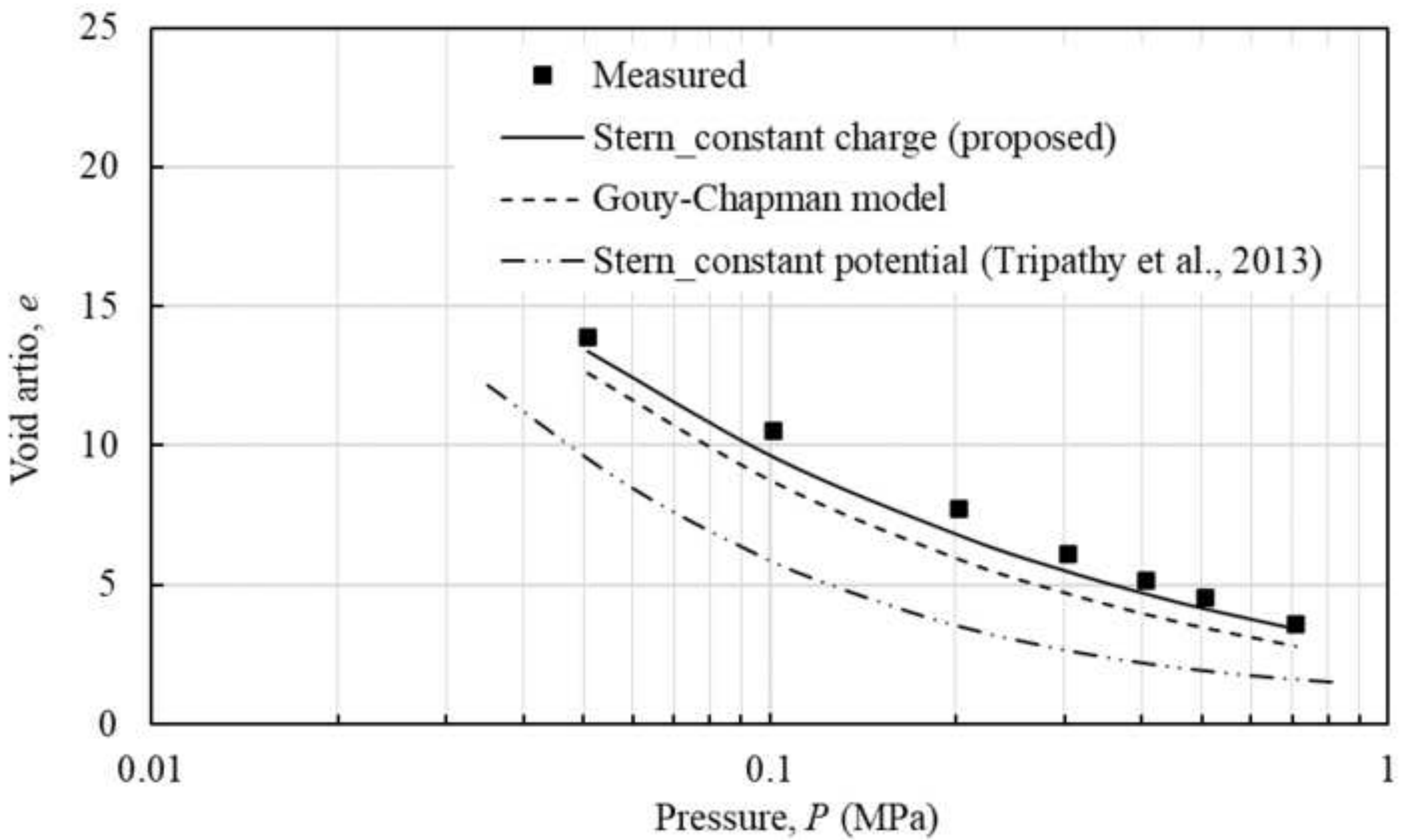

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