Water retention model for hydrate-bearing sediments considering pore structure evolution

Authors: Lin-Yong Cui, Chao Zhou* and Le-Le Liu

*Corresponding author

Information of the authors:

First author: Dr. Lin-Yong Cui

Postdoctoral fellow, Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong. E-mail: linyong.cui@polyu.edu.hk

Corresponding author: Dr. Chao Zhou

Associate Professor, Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong; Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen, China. E-mail: c.zhou@polyu.edu.hk

Co-author: Dr. Le-Le Liu

Professor, College of Environmental Science and Engineering, Ocean University of China, Qingdao, China. E-mail: lele.liu@ouc.edu.cn

Abstract

The water retention behaviour of hydrate-bearing sediments (HBS) is crucial for evaluating gas production efficiency and sediment response during methane hydrate exploitation from reservoirs. Effects of hydrate on the pore size distribution (PSD) are not explicitly considered in existing models, although the PSD governs the water retention behaviour of HBS. Nuclear magnetic resonance (NMR) data reveal that, with increasing hydrate saturation, the porosity fraction for larger pores decreases significantly, whereas the porosity fraction of smaller pores changes only slightly. Based on these observations, this study proposed a new equation for modelling the PSD evolution with increasing hydrate saturation. Subsequently, by incorporating this PSD evolution equation into the van Genuchten model, a new model was developed to describe the constitutive relationship between water saturation and suction across a wide range of hydrate saturation. Similarly, the proposed PSD evolution equation was applied to other water retention functions, such as those proposed by Fredlund–Xing, to simulate the water retention behaviour of HBS. Model validation against experimental data shows strong agreement between the calculated and measured results. The model successfully captures the key characteristics of water retention in HBS, including variations in air-entry pressure, adsorption/desorption rates, and residual water saturation with hydrate saturation.

Keywords: Hydrate-bearing sediment; water retention curve; hydrate saturation; pore size distribution; residual saturation.

1 Introduction

Methane hydrate-bearing sediments are primarily located in submarine environments, where specific pressure and temperature conditions enable methane hydrates to remain stable. As a promising alternative energy source, methane hydrate has attracted significant global interest due to its clean combustion, extensive distribution and vast estimated reserves (Hassanpouryouzband et al. 2020; Zhang et al. 2024). Common techniques for extracting methane gas from hydrate reservoirs include depressurization, thermal stimulation, chemical inhibitor injection, and CO_2 replacement (Moridis and Reagan 2007). During extraction, hydrate dissociation into methane gas and water alters the saturation of the sediments, resulting in significant changes in their physical and mechanical properties, such as permeability, stiffness, strength, and volumetric deformation (Ng et al. 2022; Ng et al. 2023; Sultaniya et al. 2018). A fundamental element in predicting these dynamics is the water retention curve (WRC), which describes the constitutive relationship between the capillary pressure of the air-water interface and water saturation (Cui et al. 2023b; Dai and Santamarina 2013; Rutqvist et al. 2012; Sun and Cui 2020). Accurately characterizing the WRC is essential for modelling unsaturated fluid flow and sediment response during hydrate exploitation, enabling effective resource recovery and geomechanical risk assessment.

Many mathematical models have been developed to describe the water retention curve (Brooks and Corey 1964; Chang and Zhou 2025; Cui et al. 2025; Cui et al. 2019; Fredlund and Xing 1994; van Genuchten 1980; Zhou and Ng 2014). Among these, the van Genuchten (1980) model and its modifications are often used to simulate the water retention behaviour of HBS (Gamwo and Liu 2010; Moridis and Sloan 2007; Reagan and Moridis 2008). The model is expressed as:

$$S_e = \left[1 + \left(\alpha\psi\right)^n\right]^{-m} \tag{1}$$

where

$$S_e = \frac{\theta_w - \theta_r}{\theta_{sat} - \theta_r} \quad (2)$$

where S_e represents the effective saturation, ψ denotes suction, α is related to the reciprocal of air entry value, and n and m are pore-size distribution parameters. θ_w denotes the actual volumetric water content, while θ_{sat} and θ_r are the saturated and residual volumetric water contents, respectively. In addition, the fixed relationship $n = 1/(1–m)$ is commonly adopted in Eq. (1) to minimise the number of model parameters and to obtain a close-form solution for the relative permeabilities of water k_{rw} and gas k_{rg} (Cui et al. 2023a; Parker et al. 1987; van Genuchten 1980). These permeabilities are expressed as: $k_{rw} = S_e^{1/2}[1 – (1 – S_e^{1/m})^m]^2$ and $k_{rg} = (1 – S_e)^{1/2}(1 – S_e^{1/m})^{2m}$.

The WRC for HBS, differs from that of host sediments without hydrate (Ghezzehei and Kneafsey 2010; Mahabadi et al. 2016a; Mahabadi et al. 2016b; Yan et al. 2023). However, in most numerical simulations, the WRC of HBS is often assumed to remain constant for simplicity, irrespective of hydrate saturation (Hong and Pooladi-Darvish 2005; Kimoto et al. 2007; Moridis and Sloan 2007; Moridis et al. 2011; Reagan and Moridis 2008; Uddin et al. 2011). Two different approaches were adopted in previous studies to address this limitation. The first approach involves establishing empirical correlations between hydrate saturation and parameters a and m in the van Genuchten model, thereby accounting for the influence of hydrate presence on water retention behaviour (Mahabadi et al. 2016a; Zhang et al. 2022). This approach essentially considers HBS with varying hydrate saturation levels as distinct materials. It is effective, but it requires extensive data to calibrate the parameters involved in these empirical correlations accurately. The other approach involves incorporating additional terms related to hydrate saturation into WRC models. Gupta et al. (2015) introduced a hydrate-saturation-dependent scaling factor to account for changes in capillary pressure at different hydrate saturation levels. Yan et al. (2020) proposed a water retention model by making an analogy between the hydrate growth process and the decrease in void ratio:

$$S_e = \frac{1}{\left\{1+\left[1+k\left(\frac{e_0 - e_0 S_h}{1+e_0 S_h}\right)^{\omega}\psi\right]^n\right\}^m} \quad (3)$$

where k, n, m and ω are fitting parameters, e_0 represents the void ratio for a hydrate-free specimen and S_h denotes the degree of hydrate saturation. Eq. (3) represents a modification of the formulation proposed by Gallipoli et al. (2003), in which the influence of hydrate saturation on gas entry pressure (see Fig. 1) is explicitly incorporated. Thus, this equation can simulate HBS with varying hydrate saturation levels using a single set of parameters, treating these materials as the same but at different states of hydrate saturation. However, this approach predicts the same adsorption/desorption rate (i.e., the slope of the tangent line from the inflection point in the WRC presented in Fig. 1) across different hydrate saturation conditions. These predictions are not consistent with common experimental observations (Ghezzehei and Kneafsey 2010; Zhang et al. 2022). In addition, the variation in the residual degree of saturation is not rigorously considered. Therefore, a new model for better capturing the influence of hydrate on the water retention ability of HBS is desired.

Furthermore, the above models do not explicitly consider the influence of hydrate on soil pore structure, which governs the water retention behaviour. In recent years, microstructural analysis has emerged as a powerful tool for pore-scale characterization. NMR enables quantitative analysis of PSD in HBS (Daigle et al. 2014; Ge et al. 2018; Kleinberg et al. 2003a; Kleinberg et al. 2003b; Minagawa et al. 2008; Ren et al. 2022; Yan et al. 2023; Zheng et al. 2020). The transverse relaxation time (T_2) obtained from NMR measurements correlates directly with PSD, where longer relaxation times correspond to large pore sizes, whereas shorter relaxation times reflect smaller pores. This capability provides insights into pore-scale hydrologic processes and a solid basis for improving the modelling water retention behaviour of HBS.

In this study, a new water retention model that explicitly accounts for the influence of hydrate saturation on HBS was developed. Based on microstructural insights from NMR data, which reveal how hydrate presence affects PSD curves, the model employs a horizontal shifting and vertical scaling strategy to transform PSD curves from hydrate-free to hydrate-bearing conditions. This approach is validated against experimentally measured water retention data. The proposed model in this study can be integrated with the method of Mualem (1976) to predict the hydraulic conduction function, which will be of great significance in assessing the flow properties for both the aqueous and gaseous phases (Cui et al. 2024). The findings hold significant implications for evaluating gas production efficiency and predicting sediment response during methane hydrate exploitation from reservoirs.

2 Model development

2.1 Pore size distribution model of hydrate-bearing sediments

Fig. 2 presents the T_2 spectra of two sandstone specimens at various methane hydrate saturation levels S_h from 0 to 75.6%, as obtained from NMR tests (Ge et al. 2018). The hydrate saturation S_h is defined as $S_h = V_h/(V_w + V_g + V_h)$, since the total pore volume V_v of HBS comprises the volumes of water V_w, gas V_g and hydrate V_h. NMR measurements are sensitive only to mobile hydrogen atoms present in liquid water and hydrocarbons. The hydrogen atoms contained within methane hydrate's crystalline lattice structure remain undetectable by NMR instrumentation due to their restricted mobility under standard excitation conditions. Consequently, the solid methane hydrates exhibit no measurable NMR response. This characteristic enables a direct correlation between the observed transverse relaxation time (T_2) and water-filled pore radius r by the equation: $r \approx 2\rho_2 T_2$, where ρ_2 is the transverse surface relaxivity (μm/ms) (Kleinberg et al. 2003a). Furthermore, the parameter ρ_2 can vary between 0.011 to 0.044 μm/ms depending on the type of hydrate-free porous media (Daigle et al. 2014; Kleinberg et al. 2003a). Based on systematic NMR measurements, Liu et al. (2021) further

136 reported that ρ_2 exhibits a dependence on hydrate saturation, showing an initial increase
137 followed by a decrease. For simplicity, a mean value of 0.035 μm/ms was adopted in this study.
138 Accordingly, the corresponding pore radius is calculated and presented in Fig. 2, with the top
139 x-axis indicating the pore diameter. Note that the use of a constant ρ_2 value enables the
140 determination of pore diameters, which should be sufficient for investigating the evolution
141 trend of the PSD. Any simplification of this value would not affect the conclusions of this study.
142 As illustrated by the typical results in Fig. 2, the PSD evolution with varying hydrate
143 saturation is a complex process. Using the PSD curve of the hydrate-free specimen as a
144 reference, increasing hydrate saturation induces at least two key changes: a noticeable
145 downward compression (i.e., a reduction of pore volume) and a leftward shift (i.e., a reduction
146 of pore size) (Ren et al. 2022; Zhang et al. 2022). Moreover, the leftward shift of the PSD is
147 not uniform. The larger the pore diameter, the further the curve shifts to the left on a semi-
148 logarithmic scale, particularly in specimens with higher hydrate levels. These results suggest
149 that gas hydrates can affect larger pores more significantly. Similar observations have been
150 reported by Clennell et al. (1999); Dai and Santamarina (2013); Kwon et al. (2008); Malinverno
151 (2010); Ng et al. (2019), who found that hydrate growth is inhibited in smaller pores size (<
152 100 nm). Consequently, the porosity fractions for larger pores exhibit a sharp decrease with
153 increasing hydrate saturation. In comparison, the porosity fractions of smaller pores only
154 changed slightly during the hydrate formation process (Ge et al. 2018; Zheng et al. 2020).
155 The observations in Fig. 2 highlight the potential for developing a new water retention
156 model by transforming PSD curves from hydrate-free to hydrate-bearing conditions through
157 horizontal shifting and vertical scaling operations. This approach explicitly incorporates the
158 pore-scale phenomena of preferential hydrate formation in larger pores and the associated
159 evolution of PSD. For convenience, two distinct PSD functions $f(\ln r)$ are defined: $f_0(\ln r)$ for
160 the initial hydrate-free state as a reference state and $f_i(\ln r)$ for the hydrate-bearing state, as

illustrated in Fig. 3. The subscript i is used to denote the i^{th} state of hydrate saturation. The PSD function under hydrate-bearing conditions can be derived from the hydrate-free case by applying horizontal shifting and vertical scaling as described by the following equation:

$$f_i\left(\ln r\right) = \eta_i f_0\left[\ln\left(\delta_i r\right)\right] \tag{4}$$

or equivalently,

$$f_0\left(\ln r\right) = \frac{1}{\eta_i} f_i\left[\ln\left(\frac{r}{\delta_i}\right)\right] \tag{5}$$

where η_i represents the vertical scaling factor, and its value is related to pore volumes with and without pore hydrate. On the one hand, the presence of hydrate within the pore space tends to reduce the pore volume. On the other hand, the hydrate formation process may cause an expansion of the soil skeleton. The use of η_i can account for these two competing effects, with the first mechanism often overwhelming the second one. In this study, a constant value of $\eta_i = e_i/e_0$ is used for all pores, where e_i and e_0 represent the void ratio at hydrate-bearing and hydrate-free states, respectively.

The other parameter δ_i (>1) in Eq. (4) and Eq. (5) describes the reduction of pore size and measures the horizontal shift magnitude of the PSD curve relative to the hydrate-free state in the semi-logarithmic coordinate system (Fig. 3). For HBS, the horizontal shifting process can be nonuniform since the reduction of larger pores is more significant than that of smaller pores (Fig. 2). Therefore, a pore size–dependent shifting factor δ_i is introduced here:

$$\delta_i = \left(\frac{r}{r_{ref}}\right)^{\beta_i} \tag{6}$$

where r_{ref} is a reference pore radius for normalization, and β_i is a positive fitting parameter. According to Eq. (6), r_{ref} should be low enough to ensure that δ_i is above 1. However, direct experimental determination of the minimum pore radius in soils is impractical, so we indirectly estimate this value through the Young-Laplace equation:

$$r_{ref} = C/\psi_{ref} \tag{7}$$

where $C = -2\gamma\cos\alpha$, γ is the surface tension of water, α is the contact angle and ψ_{ref} denotes the reference matric suction. The constant value of $C \approx 0.15$ N/m (Brutsaert 1966) was used. Furthermore, a maximum suction value of approximately 10^6 kPa has been widely observed for a variety of soils (Fredlund and Xing 1994; Ross et al. 1991; Rossi and Nimmo 1994), and is therefore adopted as the reference suction ψ_{ref} in this study. This value corresponds to a pore radius that is dimensionally comparable to the radius of a water molecule (Fredlund and Xing 1994).

The other parameter β_i in Eq. (6) governs the significance of PSD shifting and exhibits a direct dependence on hydrate saturation. To determine its value, Eq. (6) can be rearranged as follows:

$$1-\beta_i = 1-\frac{\ln r - \ln\left(r/\delta_i\right)}{\ln r - \ln r_{ref}} = \frac{\ln\left(r/\delta_i\right) - \ln r_{ref}}{\ln r - \ln r_{ref}} \tag{8}$$

Taking natural logarithms on Eq. (8) yields:

$$\ln\left(1-\beta_i\right) = \ln\left[\ln\left(r/\delta_i\right) - \ln r_{ref}\right] - \ln\left[\ln r - \ln r_{ref}\right] \tag{9}$$

In Eq. (9), r and r/δ_i denote the initial pore radius for the hydrate-free specimen and the pore radius at hydrate saturation S_h, respectively, for the same pore group. It is worthwhile to explore the evolution characteristics of $\ln(\ln r - \ln r_{ref})$, as this can provide a method to determine β_i via Eq. (9). Hence, Fig. 4 presents the evolution of $e_0(1-S_h)$ as a function of $\ln(\ln r - \ln r_{ref})$ based on water retention tests conducted on a HBS specimen by Mahabadi et al. (2016a), where e_0 denotes the initial void ratio of the host specimen without hydrate. D_{10} represents the pore radius at which water intrusion accounts for 10% of the total accessible pore volume (calculated as total pore volume minus the volume occupied by residual water). The same definitions apply to D_{50}, D_{70} and D_{90}. It is evident that there is an almost linear relationship between $e_0(1-S_h)$ and

207 $\ln(\ln r - \ln r_{ref})$, with the slope being nearly identical across different pore groups. Thus, the
208 following relationship can be applied:

209 $$\ln\left[\ln\left(r/\delta_i\right) - \ln r_{ref}\right] - \ln\left[\ln r - \ln r_{ref}\right] = -be_0 S_h \tag{10}$$

210 where b is a nonnegative parameter accounting for the slope of the linear curves in Fig. 4.

211 Substituting the expression for the evolution characteristics of $\ln(\ln r - \ln r_{ref})$, i.e., Eq. (10),
212 into Eq. (9) yields the expression for parameter β_i:

213 $$\beta_i = 1 - \exp\left(-be_0 S_h\right) \tag{11}$$

214 Applying the expression for the pore size–dependent shifting factor δ_i in Eq. (6) to the
215 PSD evolution function of Eq. (4), one obtains:

216 $$f_i\left(\ln r\right) = \frac{e_i}{e_0} f_0\left[\ln\left(r^{\beta_i+1}/r_{ref}^{\beta_i}\right)\right] \tag{12}$$

217 where $\beta_i = 1 - \exp(-be_0 S_h)$. Eq. (12) represents the PSD evolution with changing the hydrate
218 saturation. If the PSD function $f_0(\ln r)$ for hydrate-free specimens is known, the corresponding
219 PSD function for HBS, $f_i(\ln r)$ can be directly determined through Eq. (12).

220 ***2.2 A new WRC model for hydrate-bearing sediments***

221 We consider a HBS sediment specimen as a homogeneous porous medium with
222 interconnected pores characterized by their radius r. The contribution of all pores with radius
223 $r \rightarrow r + \mathrm{d}r$ to volumetric water content θ_w can be related on a logarithmic scale as follows (Hu
224 et al. 2013):

225 $$f\left(\ln r\right) d\ln r = d\theta_w \tag{13}$$

226 where $f(\ln r)$ is the PSD function. Here, $f(\ln r)d\ln r$ represents the volume of all pores with
227 logarithmic radii in the range $[\ln r, \ln r + \mathrm{d}\ln r]$ per unit volume of the medium. If $r_{\min}$ and $r_{\max}$
228 denote the minimum and the maximum pore radius in the soil, respectively, the volumetric
229 water content can be expressed as:

$$\theta_w(\ln r) = \int_{\ln r_{\min}}^{\ln r} f(\ln r) d\ln r + \theta_r \tag{14}$$

and specifically,

$$\theta_{sat} = \int_{\ln r_{\min}}^{\ln r_{\max}} f(\ln r) d\ln r + \theta_r \tag{15}$$

Note that, in Eqs. (14) and (15), $f(\ln r)$ is a function whose definite integral from $\ln r_{\min}$ to $\ln r_{\max}$ equals $\theta_{sat} - \theta_r$.

In this study, the van Genuchten model (Eq. (1)) is employed to characterize the water retention behaviour of specimens without hydrates. By integrating this model with the PSD evolution equation (Eq.(12)), we can derive the PSD function for HBS. Therefore, by dividing both sides of Eq. (13) by $d(\ln r)$, and applying the chain rule of calculus, the PSD function for hydrate-free state $f_0(\ln r)$ can be expressed as:

$$f_0(\ln r) = r \frac{d\theta_w}{dS_e} \frac{dS_e}{dr} \tag{16}$$

By combining Eqs. (1), (2), (7) and (16), the van Genuchten model implies the PSD function for hydrate-free specimens, $f_0(\ln r)$:

$$f_0(\ln r) = mn(\theta_{sat} - \theta_r) \left[1 + \left(\frac{\alpha C}{r} \right)^n \right]^{-m-1} \left(\frac{\alpha C}{r} \right)^{1/(1-m)} \tag{17}$$

According to the function of PSD evolution with changing the hydrate saturation (Eq. (12)), substituting r in Eq. (17) with $\left(r^{\beta_i+1} / r_{ref}^{\beta_i} \right)$ yields the expression of PSD for HBS, $f_i(\ln r)$:

$$f_i(\ln r) = \eta_i mn(\theta_{sat} - \theta_r) \left[1 + \left(\frac{\alpha C r_{ref}^{\beta_i}}{r^{\beta_i+1}} \right)^n \right]^{-m-1} \left(\frac{\alpha C r_{ref}^{\beta_i}}{r^{\beta_i+1}} \right)^n \tag{18}$$

On the basis of the direct correspondence of pore radius r and suction ψ (Eq. (7)), the PSD function can be transformed into the pore capillary pressure distribution $g(\psi)$ as:

$$g(\psi) = f(\ln r) \frac{d\ln r}{d\psi} = \frac{d\theta_w}{d\psi} \tag{19}$$

Similar to $f(\ln r)d\ln r$, $g(\psi)d\psi$ represents the volume of full pores in which water is retained by capillary pressure ψ to $\psi + d\psi$ per unit volume of the medium. From Eq. (19), it is evident that $g(\psi)$ is identical to the water capacity function. Combining Eqs. (7), (18) and Eq. (19), the water capacity function for HBS, $g_i(\psi)$ can be expressed as:

$$g_i(\psi) = -\eta_i mn(\theta_{sat} - \theta_r)\left[1+\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^n\right]^{-m-1}\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^{n-1}\frac{\alpha\psi^{\beta_i}}{\psi_{ref}^{\beta_i}} \tag{20}$$

Hence, the effective saturation S_e for hydrate-bearing specimen can be represented in terms of water capacity function as follows:

$$S_e = \frac{\int_\infty^\psi g_i(\psi)d\psi}{\int_\infty^0 g_i(\psi)d\psi} \tag{21}$$

By substituting the water capacity function of Eq. (20) into the effective saturation function of Eq. (21), the expression for S_e can be derived as:

$$S_e = \frac{\left[1+\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^n\right]^{-m}\Bigg|_\infty^\psi}{\left[1+\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^n\right]^{-m}\Bigg|_\infty^0} = \left[1+\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^n\right]^{-m} \tag{22}$$

where $\beta_i = 1 - \exp(-be_0S_h)$, and ψ_{ref} is treated as 10^6 kPa.

In Eq. (22), S_e can be expressed in terms of water saturation S_w as $S_e = (S_w - S_r)/(1 - S_r)$, where S_r is the residual saturation, representing the fraction of void volume occupied by residual water. The residual saturation S_r relates to θ_r through the expression: $S_r = V_r/(V_v - V_h) = \theta_r/[\phi(1 - S_h)]$, where V_r and ϕ are the volume of residual water and overall porosity. If the residual water volume V_r remains constant across different hydrate saturation levels, the relationship between the S_r and S_h is: $S_r = S_r^*(1 - S_h)^{-1}$, where S_r^* is the residual saturation for host sediment without hydrate. However, hydrate growth can alter the pore morphology and

connectivity of sediments. Hydrate formation typically initiates at the water-gas interface and progresses inward (Genov et al. 2004; Mori 2001; Taylor et al. 2007). As hydrates continue to grow, they can block pore channels (Pandey et al. 2021), creating isolated fluid spaces that are no longer connected to the main flow paths. This blockage and the resulting reduction in pore connectivity may increase the amount of residual water. Conversely, hydrate formation can cause the expansion of the soil skeleton (Dai et al. 2015), thereby enlarging small pore spaces and potentially reducing the amount of residual water (Yan et al. 2023). Due to the competing mechanisms, S_r^* may either increase or decrease with increasing hydrate saturation. Therefore, the following flexible expression is proposed to reflect these influences:

$$S_r = \frac{S_r^*}{S_r^* + \left(1 - S_r^*\right)\exp\left(-tS_h\right)} \tag{23}$$

where t is a fitting parameter. This equation is capable of simulating both the increase and decrease in S_r due to the presence of hydrate. Moreover, it satisfies the physical boundary conditions that constrain S_r within the interval [0, 1] for any given hydrate saturation level. Fig. 5 compares S_r values calculated from Eq. (23) with experimental data from water retention tests on HBS. For the hydrate saturation ranging from 0 to 0.7, Eq. (23) shows good agreement with the measurements across all five cases.

Finally, combining Eqs. (22) and (23), and applying the common assumption of $n = 1/(1-m)$ to Eq. (22), the new WRC function for HBS can be given by:

$$S_w = S_r + \left(1 - S_r\right)\left\{1 + \left[\frac{\alpha\psi^{2-\exp(-be_0S_h)}}{\psi_{ref}^{1-\exp(-be_0S_h)}}\right]^{1/(1-m)}\right\}^{-m} \tag{24}$$

where $S_r = S_r^*/[S_r^* + (1 - S_r^*)\exp(-tS_h)]$. When the hydrate saturation is reduced to 0, the proposed WRC model (i.e., Eq. (24)) reduces to the original form of the van Genuchten model (i.e., Eq. (1)). Fig. 6 presents the evolution of water saturation S_w with variations in suction ψ and hydrate saturation S_h. For a fixed S_h, the curve exhibits a nearly symmetrical "S"–shaped profile, with

the slope approaching zero as suction reaches both its saturated and residual limits. While existing models primarily describe how residual saturation and air-entry pressure vary with hydrate saturation, the proposed model advances this understanding by additionally quantifying hydrate saturation's impact on adsorption/desorption kinetics. For the case considered in Fig. 6, increasing hydrate saturation induces an obvious increase in the residual water saturation and air-entry pressure, accompanied by an increased adsorption/desorption rate.

3 Summary of model parameter and calibration method

In Eq. (24), the proposed WRC model for HBS involves five parameters: S_r^*, t, α, b and m. Under hydrate-free conditions, it reduces to the classical van Genuchten model, with only three parameters: S_r^*, α, and m, which represent the residual saturation, the inverse of the air-entry pressure, and the pore size distribution index, respectively. Under hydrate-bearing conditions, two additional parameters, t and b, are introduced to account for the influence of hydrate saturation on residual saturation and pore size distribution, respectively.

For model calibration, a stepwise parameter calibration procedure is suggested. First, the parameters S_r^*, m and α, are calibrated by fitting Eq. (24) to the water retention data from hydrate-free specimens with $S_h = 0$. Values of these three parameters can be obtained through nonlinear regression to achieve the highest value for the coefficient of determination (R^2). Once these three parameters are determined, they remain constant, while the remaining two parameters, t and b, are subsequently calibrated using water retention data from the same specimen at different hydrate saturation levels.

To validate the model, five water retention datasets from various literature sources were compiled, each with a wide range of hydrate saturation. Table 1 summarizes some of the experimental specifications for the WRC tests. These datasets represent nearly all systematic experimental results on water retention behaviour in hydrate-bearing specimens to date. The

317 specimens in the datasets include sand, clayey silt and recovered sediments, with hydrate types
318 consisting of methane hydrate, THF hydrate and Xe hydrate. Note that for the water retention
319 tests by Ghezzehei and Kneafsey (2010), the initial void ratio e_0 was not reported, so a value
320 of $e_0 = 0.7$ was assumed for model calibration and verification.

321 **4 Results and discussion**

322 ***4.1 Comparison between the measured and calculated WRCs***

323 In this section, comparisons are given between measured and calculated WRCs for the
324 five different specimens. Table 2 summarizes the calibrated parameters for the proposed WRC
325 model (Eq. (24)). The calibrated parameters enabled the model to successfully simulate
326 experimental WRCs across diverse hydrate types (THF hydrate, Xe hydrate and CH_4 hydrate)
327 and hydrate saturation levels ($S_h = 0 \sim 0.7$), as presented in Figs. 7~11. The experimental data
328 points align closely with the WRCs fitted by Eq. (24), with R^2 values exceeding 0.9 in most
329 cases. These results demonstrate that the proposed WRC model, based on the nonuniform
330 shifting-scaling strategy, provides satisfactory predictions for the influence of hydrate presence
331 on the water retention behaviour.

332 Fig. 7 presents the results for the Mallik 5L-38 sediment (Mahabadi et al. 2016a). The
333 host sediment without hydrate has a relatively wider pore size distribution, as indicated by a
334 low m value of 0.52. The value of α, which is approximately the inverse of the gas entry
335 pressure, is found to be 0.19 kPa^{-1}. This value corresponds to the suction level at which the
336 WRC becomes the steepest for the hydrate-free specimen (Fig. 7). The influence of hydrate
337 saturation S_h on α can be represented by rearranging Eq. (24) as follows:

338 $$S_e = \left\{1 + \left[\frac{\alpha^{1/(\beta_i+1)}}{\psi_{ref}^{\beta_i/(\beta_i+1)}}\psi\right]^{(\beta_i+1)/(1-m)}\right\}^{-m} \quad (25)$$

where $\beta_i = 1 - \exp(-be_0 S_h)$. From Eq. (25), it is evident that the inverse of the gas entry pressure is sensitive to the parameter b. For the Mallik 5L-38 sediment, with a calibrated b value of 0.16, an increase in hydrate saturation from 0.4 to 0.7 reduces the inverse of the gas entry pressure from 0.12 kPa^{-1} to 0.09 kPa^{-1}. The other mechanistic parameter t, is 6.67, which results in an increase in residual saturation S_r from 0.07 to 0.35 as S_h increases from 0.4 to 0.7, according to Eq. (23). Fig. 7 shows nearly exact predictions of the WRCs, with only minor deviations occurring at higher suction values for the case of $S_h = 0.7$.

Fig. 8 presents the results obtained for the sand column (Ghezzehei and Kneafsey 2010). For hydrate saturations of 0 and 0.2, the fitted curves nearly coincide. It is important to note that only a limited portion of the WRC was measured in their tests, with suction levels consistently not exceeding 30 kPa across different hydrate saturation levels. Consequently, the fitted value of 6.16×10^{-5} for S_r^* (Table 2) may not be highly accurate. The predicted WRC in Fig. 8 shows minimal variation when S_r^* is adjusted between 2×10^{-5} and 0.1 or when b varies between 1×10^{-4} to 6×10^{-4}. Yet the parameters listed in Table 2 represent the best-fit values for Eq. (24) when matched against the water retention data for hydrate saturation levels ranging from 0.2 to 0.45.

Figs. 9 and 10 present the results for clayey silt specimens (Yan et al. 2023; Zhang et al. 2022). These results are very similar to those of the Mallik 5L-38 sediment specimen. The WRCs for these specimens with varying hydrate saturations are also relatively flat, with m values of 0.47 and 0.61 (Table 2). The model provides good predictions of the observed WRCs.

Fig. 11 presents the results for the fine sand specimen. Unlike the previous cases, the predictions for fine sand (Yan et al. 2023) were found to be less accurate (Fig. 11). The WRCs in Fig. 11 are steeper, resulting in a higher m value of 0.74 (Table 2). However, the general shape of the predicted curve differs from the observed one. It seems that much of the poor predictions can be traced back to the inability of Eq. (24) to capture the experimental WRC

data. For example, the residual water saturation for the host specimen without hydrate S_r^* was estimated to be 0.5 (Table 2), which is unusually high for sandy soils, as they typically exhibit lower residual saturation compared to clayey soils. Additionally, the limited data at lower water contents raises concerns about the accuracy of the fitted S_r^* value. This case underscores the importance of developing independent methods for estimating residual water saturation of HBS to improve model accuracy.

4.2 Parameter sensitivity analysis for the new model

In the proposed WRC model (Eq. (24)), the two mechanistic parameters t and b govern hydrate saturation-dependent effects on residual saturation and pore radius, respectively. As shown in Table 2, the calibrated parameters t and b range from -2.26 to 17.85 and 1×10^{-4} to 0.48, respectively, for the five datasets. In this section, a parameter sensitivity analysis is conducted to evaluate how these parameters influence the simulated WRCs. Fig. 12 illustrates the sensitivity of the suction-dependent WRC to the parameters t and b. For this analysis, the intrinsic parameters S_r^*, m and α are fixed at 0.1, 0.5 and 0.07 kPa^{-1}, respectively, while t and b are varied within the ranges $-5 < t < 10$ and $0.5 < b < 2$. Additionally, a sensitivity analysis is also performed on the initial void ratio-dependent water saturation, as shown in Fig. 12(c).

Results presented in Fig. 12(a) show the effect of parameter t on the WRC for hydrate-bearing specimens. Parameter t significantly alters the shape of the WRC. As t increases from -5 to 10, the residual saturation increases rapidly, and the WRC becomes more gradual. The influence of t is particularly pronounced at suction levels higher than the gas entry value. Moreover, as compared to hydrate-free state, both increase (t = -5 and 0) and decrease (t = 5 and 10) of residual water volume may occur at hydrate-bearing state, as shown in Fig. 12(a). As mentioned earlier, hydrate nucleate preferentially in macropores, and their growth can block pore channels, creating isolated pore spaces. This reduction in hydraulic connectivity increases

389 the amount of residual water compared to that of hydrate-free specimen, resulting in increase
390 in the residual water volume V_r. Conversely, the lower density of hydrates relative to pore water
391 may generate expansive stresses during hydrate formation, dilating the sediments matrix,
392 reconnects isolated voids and enhancing drainage efficiency. This process may reduce the
393 amount of residual water, leading to decrease of V_r. Thus, the resultant S_r in hydrate-bearing
394 specimens reflects the balance between these two competing processes. In this study, both
395 increase of V_r (Mahabadi et al. (2016a), Ghezzehei and Kneafsey (2010) and Zhang et al.
396 (2022)) and decrease of V_r (Yan et al. (2023)) are observed.

397 Fig. 12(b) illustrates the effect of parameter b on the WRC. The black dashed represents
398 $b = 0$, corresponds to a condition where only pore volume decreases without a reduction in pore
399 size ($\delta_i = 1$ in Eq. (4)). A nonuniform shifting process begins when b exceeds 0. For the case
400 considered in Fig. 12(b), as b increases from 0.5 to 2, the residual saturation remains constant,
401 but gas entry pressure increases rapidly. Meanwhile, the overall shape of the WRC changes
402 only slightly, showing an approximately horizontal rightward shift. Similar to parameter b,
403 changes in initial void ratio e_0 influence the WRC by shifting it horizontally (Fig. 12(c)),
404 indicating the influence of parameter b and initial void ratio e_0 on the WRC is consistent within
405 the framework of the proposed model.

406 ***4.3 Application of the equation for PSD evolution to other models***

407 While the equation for PSD evolution has been successfully implemented using the van
408 Genuchten (1980) model for HBS, as presented above, its broader applicability across
409 alternative WRC models remains to be verified. To this end, the nonuniform shifting-scaling
410 strategy is applied to two more classical models: the Fredlund and Xing (1994) model and the
411 Brooks and Corey (1964) model. Both models are characterized by their simplicity and
412 efficiency, which make them particularly suitable for testing the broader applicability of the
413 nonuniform shifting-scaling strategy.

414 The Fredlund–Xing and Brooks–Corey functions are respectively written as:

415 $$\theta_w = \theta_r + \frac{\theta_{sat} - \theta_r}{\left\{\ln\left[\exp(1) + (\alpha\psi)^c\right]\right\}^d} \tag{26}$$

416 $$\theta_w = \begin{cases} \theta_r + (\theta_{sat} - \theta_r)(\psi_b/\psi)^\lambda & \psi \geq \psi_b \\ \theta_{sat} & \psi \leq \psi_b \end{cases} \tag{27}$$

417 where α and ψ_b are related to the air entry value. c, d and λ are PSD-related parameters.

418 Following the same nonuniform shifting-scaling strategy used for the van Genuchten
419 model, expressions of WRC based on Fredlund–Xing (see Appendix A) and Brooks–Corey
420 (see Appendix B) are respectively given by:

421 $$S_w = S_r + (1 - S_r)\left\{\ln\left[\exp(1) + \left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^c\right]\right\}^{-d} \tag{28}$$

422 $$S_w = \begin{cases} S_r + (1 - S_r)\left(\frac{\psi_b\psi_{ref}^{\beta_i}}{\psi^{\beta_i+1}}\right)^\lambda & \psi \geq \psi_b^* \\ 1 & \psi \leq \psi_b^* \end{cases} \tag{29}$$

423 where $S_r = S_r^*/[S_r^* + (1 - S_r^*)\exp(-tS_h)]$, $\beta_i = 1 - \exp(-be_0S_h)$ and $\psi_b^* = \left(\psi_b\psi_{ref}^{\beta_i}\right)^{1/(\beta_i+1)}$.

424 The new models based on Fredlund–Xing and Brooks–Corey functions involves six and
425 five parameters, respectively. Following the same calibration procedures as van Genuchten
426 model, Fig. 13 compares experimental data (Mahabadi et al. 2016a) with the model predictions
427 using Eqs. (28) and (29). The calibrated model parameters for Eq. (28) are $S_r^* = 8.26\times10^{-4}$, t
428 $= 9.03$, $\alpha = 0.19$ kP^{-1}, $b = 0.17$, $c = 2.08$ and $d = 1.32$, while those for Eq. (29) are $S_r^* = 4.27\times10^{-4}$, $t = 9.94$, $\psi_b = 2.79$ kPa, $b = 0.17$ and $\lambda = 0.65$.

430 As shown in Fig. 13, both Eqs. (28) and (29) effectively capture the evolution of water
431 saturation as a function of suction for hydrate-bearing specimens across varying hydrate
432 saturations, resulting R^2 of 0.99 and 0.98, respectively. These results further validate the
433 generalizability of the shifting-scaling strategy for modelling the water retention behaviour of

HBS. Furthermore, although all proposed models exhibit satisfactory performance, careful consideration is still required when selecting the most appropriate model for a given application. Compared to the van Genuchten-based model (Eq. (24)), the model based on the Fredlund–Xing function (Eq. (28)) includes one additional parameter. While the new model based on Brooks–Corey function (Eq. (29)) has the same number of parameters as van Genuchten-based model, its piecewise formulation makes the calibration process more challenging, particularly when experimental data are limited. Overall, while all three models demonstrate excellent predictive performance, the van Genuchten-based model is recommended due to its balanced accuracy and computational convenience. Its mathematical smoothness and fewer fitting parameters make it particularly suitable for large-scale simulations or applications where computational resources are limited.

5 Summary and conclusions

NMR observations reveal that increasing hydrate saturation leads to a significant decrease in the porosity fraction associated with larger pores, while causing only minor changes in smaller pores. To quantitatively describe these observations, a new PSD evolution equation was proposed that models the impact of hydrate saturation on the PSD curve through two distinct effects: pore volume reduction and pore size reduction. Moreover, a hydrate-saturation-dependent residual saturation function was introduced to account for pore blockage and the reconnection of isolated voids caused by hydrate formation.

Based on the proposed PSD evolution equation and the van Genuchten model, a new constitutive model was developed to describe the relationship between water saturation and suction across a wide range of hydrate saturations. Model validation against experimental data demonstrates a close match between fitted and observed results. The model effectively captures key features of water retention behaviour in HBS, including variations in air-entry value, residual water saturation, and adsorption/desorption rates with hydrate saturation.

To evaluate the broader applicability of the proposed PSD evolution equation, it was further incorporated into other water retention models, including those of Fredlund–Xing and Brooks–Corey. In both cases, the resulting WRC models successfully reproduced the evolution of water saturation with suction across specimens with varying hydrate saturations, thereby confirming the generalizability of the proposed approach. The results of this study offer new insights into how hydrates influence the water retention process in sediments.

Acknowledgements

The financial support from the Faculty of Construction and Environment of The Hong Kong Polytechnic University (P0046002) is greatly acknowledged. The authors also thank the HKSAR Research Grants Council (RGC) for providing financial support through grant 16207918.

Appendix A: Equation for S_w based on Fredlund and Xing (1994) model

The PSD function for Fredlund and Xing (1994) model given by Eq. (26) can be obtained by combining Eqs. (16), (7) and (26):

$$f\left(\ln r\right)=\left(\theta_{sat}-\theta_{r}\right)mn\left\{\ln\left[\exp\left(1\right)+\left(\frac{\alpha C}{r}\right)^{c}\right]\right\}^{-d-1}\frac{\left(\alpha C/r\right)^{c}}{\exp\left(1\right)+\left(\alpha C/r\right)^{c}} \tag{30}$$

Similarly, Eq. (30) is employed to model the PSD function for the hydrate-free state $f_0(\ln r)$, while the PSD function after the nonuniform shifting-scaling process, $f_i(\ln r)$ can be derived through Eq. (12). Substituting r in Eq. (30) with $\left(r^{\beta_i+1}/r_{ref}^{\beta_i}\right)$ and combing Eq. (12) yields:

$$f_i\left(\ln r\right)=\eta_i\left(\theta_{sat}-\theta_{r}\right)mn\left\{\ln\left[\exp\left(1\right)+\left(\frac{\alpha C r_{ref}^{\beta_i}}{r^{\beta_i+1}}\right)^{c}\right]\right\}^{-d-1}\frac{\left(\alpha C r_{ref}^{\beta_i}/r^{\beta_i+1}\right)^{c}}{\exp\left(1\right)+\left(\alpha C r_{ref}^{\beta_i}/r^{\beta_i+1}\right)^{c}} \tag{31}$$

The water capacity function for the hydrate-bearing state becomes:

$$g_i(\psi) = -\frac{\eta_i(\theta_{sat}-\theta_r)mn}{\psi}\left\{\ln\left[\exp(1)+\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^c\right]\right\}^{-d-1}\frac{\left(\alpha\psi^{\beta_i+1}/\psi_{ref}^{\beta_i}\right)^c}{\exp(1)+\left(\alpha\psi^{\beta_i+1}/\psi_{ref}^{\beta_i}\right)^c} \quad (32)$$

Substituting Eq. (32) into Eq. (21) yields the S_e function:

$$S_e = \frac{\left\{\ln\left[\exp(1)+\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^c\right]\right\}^{-d}\Bigg|_{\infty}^{\psi}}{\left\{\ln\left[\exp(1)+\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^c\right]\right\}^{-d}\Bigg|_{\infty}^{0}} = \left\{\ln\left[\exp(1)+\left(\frac{\alpha\psi^{\beta_i+1}}{\psi_{ref}^{\beta_i}}\right)^c\right]\right\}^{-d} \quad (33)$$

Appendix B: Equation for S_w based on Brooks and Corey (1964) model

The PSD function for Brooks and Corey (1964) model is:

$$f(\ln r) = \begin{cases}\lambda(\theta_{sat}-\theta_r)(r/r_b)^{\lambda} & r \le r_b \\ 0 & r \ge r_b\end{cases} \quad (34)$$

where r_b is the pore radius related to the air entry value ψ_b as: $r_b = C/\psi_b$. We also use the Eq. (34) to determine the $f_0(\ln r)$ function. By substituting r in the Eq. (34) with $\left(r^{\beta_i+1}/r_{ref}^{\beta_i}\right)$, and then substituting the resulting expression back into Eq. (12), we obtain the PSD function for the hydrate-bearing state:

$$f_i(\ln r) = \begin{cases}\eta_i\lambda(\theta_{sat}-\theta_r)\left(\frac{r^{\beta_i+1}}{r_b r_{ref}^{\beta_i}}\right)^{\lambda} & r \le \left(r_b r_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}} \\ 0 & r \ge \left(r_b r_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}}\end{cases} \quad (35)$$

The water capacity function for the hydrate-bearing state can be determined:

$$g_i(\psi) = \begin{cases}-\frac{\eta_i\lambda(\theta_{sat}-\theta_r)}{\psi}\left(\frac{\psi_b\psi_{ref}^{\beta_i}}{\psi^{\beta_i+1}}\right)^{\lambda} & \psi \ge \left(\psi_b\psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}} \\ 0 & \psi \le \left(\psi_b\psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}}\end{cases} \quad (36)$$

Similarly, the S_e in Eq. (21) can be rearranged as:

$$S_e = \begin{cases} \dfrac{\int_{\infty}^{\psi} g_i(\psi)d\psi}{\int_{\infty}^{0} g_i(\psi)d\psi} = \dfrac{\int_{\infty}^{\psi} g_i(\psi)d\psi}{\int_{\infty}^{\left(\psi_b \psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}}} g_i(\psi)d\psi} & \psi \geq \left(\psi_b \psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}} \\ \dfrac{\int_{\infty}^{\psi} g_i(\psi)d\psi}{\int_{\infty}^{0} g_i(\psi)d\psi} = \dfrac{\int_{\infty}^{\left(\psi_b \psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}}} g_i(\psi)d\psi}{\int_{\infty}^{\left(\psi_b \psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}}} g_i(\psi)d\psi} = 1 & \psi \leq \left(\psi_b \psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}} \end{cases} \quad (37)$$

Following the same procedure, we substitute Eq. (36) into Eq. (37) and the integral simplifies to:

$$S_e = \begin{cases} \left(\dfrac{\psi_b \psi_{ref}^{\beta_i}}{\psi^{\beta_i+1}}\right)^{\lambda} & \psi \geq \left(\psi_b \psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}} \\ 1 & \psi \leq \left(\psi_b \psi_{ref}^{\beta_i}\right)^{\frac{1}{\beta_i+1}} \end{cases} \quad (38)$$

References

Brooks, R.H., and Corey, A.T. 1964. Hydraulic properties of porous media. Hydrology, Paper No. 3, Colorado State University, Fort Collins.

Brutsaert, W. 1966. Probability laws for pore-size distributions. Soil science, **101**(2): 85-92. doi:https://doi.org/10.1097/00010694-196602000-00002.

Chang, Z., and Zhou, C. 2025. A new model for water retention and hydraulic conductivity curves of deformable unsaturated soils. Water Resources Research, **61**(5): e2024WR037826. doi:https://doi.org/10.1029/2024WR037826.

Clennell, M.B., Hovland, M., Booth, J.S., Henry, P., and Winters, W.J. 1999. Formation of natural gas hydrates in marine sediments: 1. Conceptual model of gas hydrate growth conditioned by host sediment properties. Journal of Geophysical Research: Solid Earth, **104**(B10): 22985-23003. doi:https://doi.org/10.1029/1999jb900175.

512 Cui, L.Y., Zhou, C., and Ye, W.M. 2025. Modified hydraulic conductivity equations of
513 bentonite-based materials under saturated and unsaturated conditions. Canadian
514 Geotechnical Journal, **0**(ja): null. doi:10.1139/cgj-2024-0703.
515 Cui, L.Y., Ye, W.M., Wang, Q., Chen, Y.G., and Cui, Y.J. 2023a. A model for describing
516 advective and diffusive gas transport through initially saturated bentonite with
517 consideration of temperature. Engineering Geology, **323**: 107215.
518 doi:https://doi.org/10.1016/j.enggeo.2023.107215.
519 Cui, L.Y., Ye, W.M., Wang, Q., Chen, Y.G., Chen, B., and Cui, Y.J. 2019. Investigation on
520 gas migration in saturated bentonite using the residual capillary pressure technique with
521 consideration of temperature. Process Safety and Environmental Protection, **125**: 269-278.
522 doi:https://doi.org/10.1016/j.psep.2019.03.036.
523 Cui, L.Y., Masum, S.A., Ye, W.M., Thomas, H.R., Zhou, C., and Hu, H.Q. 2024. Numerical
524 investigation of gas migration behaviour in saturated bentonite with consideration of
525 temperature. Acta Geotechnica, **19**(5): 2381-2393. doi:https://doi.org/10.1007/s11440-
526 024-02272-5.
527 Cui, L.Y., Ye, W.M., Ji, Y.H., Xu, L., Ye, G.L., Ye, B., Chen, B., Cui, Y.J., and Zhang, F.
528 2023b. A new apparatus for investigating gas transport property in geomaterials with
529 ultralow permeability. Construction and Building Materials, **385**: 131523.
530 doi:https://doi.org/10.1016/j.conbuildmat.2023.131523.
531 Dai, S., and Santamarina, J.C. 2013. Water retention curve for hydrate-bearing sediments.
532 Geophysical Research Letters, **40**(21): 5637-5641.
533 doi:https://doi.org/10.1002/2013GL057884.
534 Dai, S., Cha, J.H., Rosenbaum, E.J., Zhang, W., and Seol, Y. 2015. Thermal conductivity
535 measurements in unsaturated hydrate-bearing sediments. Geophysical Research Letters,
536 **42**(15): 6295-6305. doi:https://doi.org/10.1002/2015GL064492.

Daigle, H., Thomas, B., Rowe, H., and Nieto, M. 2014. Nuclear magnetic resonance characterization of shallow marine sediments from the Nankai Trough, Integrated Ocean Drilling Program Expedition 333. Journal of Geophysical Research: Solid Earth, **119**(4): 2631-2650. doi:https://doi.org/10.1002/2013JB010784.

Fredlund, D.G., and Xing, A.Q. 1994. Equations for the soil-water characteristic curve. Canadian Geotechnical Journal, **31**(4): 521-532. doi:https://doi.org/10.1139/t94-061.

Gallipoli, D., Wheeler, S.J., and Karstunen, M. 2003. Modelling the variation of degree of saturation in a deformable unsaturated soil. Géotechnique, **53**(1): 105-112. doi:https://doi.org/10.1680/geot.2003.53.1.105.

Gamwo, I.K., and Liu, Y. 2010. Mathematical modeling and numerical simulation of methane production in a hydrate reservoir. Industrial & Engineering Chemistry Research, **49**(11): 5231-5245. doi:https://doi.org/10.1021/ie901452v.

Ge, X., Liu, J., Fan, Y., Xing, D., Deng, S., and Cai, J. 2018. Laboratory investigation into the formation and dissociation process of gas hydrate by low-field NMR technique. Journal of Geophysical Research: Solid Earth, **123**(5): 3339-3346. doi:https://doi.org/10.1029/2017JB014705.

Genov, G., Kuhs, W.F., Staykova, D.K., Goreshnik, E., and Salamatin, A.N. 2004. Experimental studies on the formation of porous gas hydrates. American Mineralogist, **89**(8-9): 1228-1239. doi:https://doi.org/10.2138/am-2004-8-910.

Ghezzehei, T.A., and Kneafsey, T.J. 2010. Measurements of the capillary pressure-saturation relationship of methane hydrate bearing sediments. *In* Offshore Technology Conference, Houston, Texas, USA.

Gupta, S., Helmig, R., and Wohlmuth, B. 2015. Non-isothermal, multi-phase, multi-component flows through deformable methane hydrate reservoirs. Computational Geosciences, **19**(5): 1063-1088. doi:https://doi.org/10.1007/s10596-015-9520-9.

562 Hassanpouryouzband, A., Joonaki, E., Vasheghani Farahani, M., Takeya, S., Ruppel, C., Yang,
563 J., English, N.J., Schicks, J.M., Edlmann, K., Mehrabian, H., Aman, Z.M., and Tohidi, B.
564 2020. Gas hydrates in sustainable chemistry. Chemical Society Reviews, **49**(15): 5225-
565 5309. doi:https://doi.org/10.1039/C8CS00989A.
566 Hong, H., and Pooladi-Darvish, M. 2005. Simulation of depressurization for gas production
567 from gas hydrate reservoirs. Journal of Canadian Petroleum Technology, **44**(11).
568 doi:https://doi.org/10.2118/05-11-03.
569 Hu, R., Chen, Y.F., Liu, H.H., and Zhou, C.B. 2013. A water retention curve and unsaturated
570 hydraulic conductivity model for deformable soils: consideration of the change in pore-
571 size distribution. Géotechnique, **63**(16): 1389-1405.
572 doi:https://doi.org/10.1680/geot.12.P.182.
573 Kimoto, S., Oka, F., Fushita, T., and Fujiwaki, M. 2007. A chemo-thermo-mechanically
574 coupled numerical simulation of the subsurface ground deformations due to methane
575 hydrate dissociation. Computers and Geotechnics, **34**(4): 216-228.
576 doi:https://doi.org/10.1016/j.compgeo.2007.02.006.
577 Kleinberg, R.L., Flaum, C., Griffin, D.D., Brewer, P.G., Malby, G.E., Peltzer, E.T., and
578 Yesinowski, J.P. 2003a. Deep sea NMR: Methane hydrate growth habit in porous media
579 and its relationship to hydraulic permeability, deposit accumulation, and submarine slope
580 stability. Journal of Geophysical Research: Solid Earth, **108**(B10).
581 doi:https://doi.org/10.1029/2003JB002389.
582 Kleinberg, R.L., Flaum, C., Straley, C., Brewer, P.G., Malby, G.E., Peltzer III, E.T., Friederich,
583 G., and Yesinowski, J.P. 2003b. Seafloor nuclear magnetic resonance assay of methane
584 hydrate in sediment and rock. Journal of Geophysical Research: Solid Earth, **108**(B3).
585 doi:https://doi.org/10.1029/2001JB000919.

586 Kwon, T.H., Cho, G.C., and Santamarina, J.C. 2008. Gas hydrate dissociation in sediments:
587 Pressure-temperature evolution. Geochemistry, Geophysics, Geosystems, **9**(3).
588 doi:https://doi.org/10.1029/2007gc001920.
589 Liu, L., Zhang, Z., Liu, C., Wu, N., Ning, F., Zhang, Y., Meng, Q., and Li, C. 2021. Nuclear
590 magnetic resonance transverse surface relaxivity in quartzitic sands containing gas
591 hydrate. Energy & Fuels, **35**(7): 6144-6152.
592 doi:https://doi.org/10.1021/acs.energyfuels.1c00225.
593 Mahabadi, N., Zheng, X., and Jang, J. 2016a. The effect of hydrate saturation on water retention
594 curves in hydrate-bearing sediments. Geophysical Research Letters, **43**(9): 4279-4287.
595 doi:https://doi.org/10.1002/2016GL068656.
596 Mahabadi, N., Dai, S., Seol, Y., Sup Yun, T., and Jang, J. 2016b. The water retention curve
597 and relative permeability for gas production from hydrate-bearing sediments: pore-
598 network model simulation. Geochemistry, Geophysics, Geosystems, **17**(8): 3099-3110.
599 doi:https://doi.org/10.1002/2016GC006372.
600 Malinverno, A. 2010. Marine gas hydrates in thin sand layers that soak up microbial methane.
601 Earth and Planetary Science Letters, **292**(3-4): 399-408.
602 doi:https://doi.org/10.1016/j.epsl.2010.02.008.
603 Minagawa, H., Nishikawa, Y., Ikeda, I., Miyazaki, K., Takahara, N., Sakamoto, Y., Komai, T.,
604 and Narita, H. 2008. Characterization of sand sediment by pore size distribution and
605 permeability using proton nuclear magnetic resonance measurement. Journal of
606 Geophysical Research: Solid Earth, **113**(B7). doi:https://doi.org/10.1029/2007jb005403.
607 Mori, Y.H. 2001. Estimating the thickness of hydrate films from their lateral growth rates:
608 application of a simplified heat transfer model. Journal of Crystal Growth, **223**(1): 206-
609 212. doi:https://doi.org/10.1016/S0022-0248(01)00614-5.

610 Moridis, G.J., and Reagan, M.T. Gas production from oceanic class 2 hydrate accumulations.
611 *In* Offshore Technology Conference. Houston, Texas, U.S.A. 2007, OTC-18866-MS.
612 Moridis, G.J., and Sloan, E.D. 2007. Gas production potential of disperse low-saturation
613 hydrate accumulations in oceanic sediments. Energy Conversion and Management, **48**(6):
614 1834-1849. doi:https://doi.org/10.1016/j.enconman.2007.01.023.
615 Moridis, G.J., Silpngarmlert, S., Reagan, M.T., Collett, T., and Zhang, K. 2011. Gas production
616 from a cold, stratigraphically-bounded gas hydrate deposit at the Mount Elbert Gas
617 Hydrate Stratigraphic Test Well, Alaska North Slope: Implications of uncertainties.
618 Marine and Petroleum Geology, **28**(2): 517-534.
619 doi:https://doi.org/10.1016/j.marpetgeo.2010.01.005.
620 Mualem, Y. 1976. A new model for predicting the hydraulic conductivity of unsaturated porous
621 media. Water Resources Research, **12**(3): 513-522.
622 doi:https://doi.org/10.1029/WR012i003p00513.
623 Ng, C.W.W., Baghbanrezvan, S., Kadlicek, T., and Zhou, C. 2019. A state-dependent
624 constitutive model for methane hydrate-bearing sediments inside the stability region.
625 Géotechnique, **70**(12): 1094-1108. doi:https://doi.org/10.1680/jgeot.18.P.143.
626 Ng, C.W.W., Baghbanrezvan, S., Lau, S.Y., Sanchez, M., and Zhou, C. 2022. Effects of
627 hydrate dissociation on vertical casing–sediment interaction in carbon dioxide hydrate–
628 bearing sand: novel in-flight centrifuge modeling. Journal of Geotechnical and
629 Geoenvironmental Engineering, **148**(3): 04021199.
630 doi:https://doi.org/10.1061/(ASCE)GT.1943-5606.0002732.
631 Ng, C.W.W., Lau, S.Y., Zhang, Q., Zhang, S., So, P.S., and Sánchez, M. 2023. A state-
632 dependent constitutive model for gas hydrate-bearing sediment incorporating phase
633 change. Gas Science and Engineering, **119**: 205102.
634 doi:https://doi.org/10.1016/j.jgsce.2023.205102.

635 Pandey, J.S., Strand, Ø., von Solms, N., Ersland, G., and Almenningen, S. 2021. Direct
636 visualization of CH_4/CO_2 hydrate phase transitions in sandstone pores. Crystal Growth &
637 Design, **21**(5): 2793-2806. doi:https://doi.org/10.1021/acs.cgd.0c01714.
638 Parker, J., Lenhard, R., and Kuppusamy, T. 1987. A parametric model for constitutive
639 properties governing multiphase flow in porous media. Water Resources Research, **23**(4):
640 618-624. doi:https://doi.org/10.1029/WR023i004p00618.
641 Reagan, M.T., and Moridis, G.J. 2008. Dynamic response of oceanic hydrate deposits to ocean
642 temperature change. Journal of Geophysical Research: Oceans, **113**(C12).
643 doi:https://doi.org/10.1029/2008JC004938.
644 Ren, J., Yin, Z., Li, Q., Wu, F., Chen, D., and Li, S. 2022. Pore-scale investigation of CH_4
645 hydrate kinetics in clayey-silty sediments by low-field NMR. Energy & Fuels, **36**(24):
646 14874-14887. doi:https://doi.org/10.1021/acs.energyfuels.2c03255.
647 Ross, P.J., Williams, J., and Bristow, K.L. 1991. Equation for extending water-retention curves
648 to dryness. Soil Science Society of America Journal, **55**(4): 923-927.
649 doi:https://doi.org/10.2136/sssaj1991.03615995005500040004x.
650 Rossi, C., and Nimmo, J.R. 1994. Modeling of soil water retention from saturation to oven
651 dryness. Water Resources Research, **30**(3): 701-708.
652 doi:https://doi.org/10.1029/93WR03238.
653 Rutqvist, J., Moridis, G.J., Grover, T., Silpngarmlert, S., Collett, T.S., and Holdich, S.A. 2012.
654 Coupled multiphase fluid flow and wellbore stability analysis associated with gas
655 production from oceanic hydrate-bearing sediments. Journal of Petroleum Science and
656 Engineering, **92-93**: 65-81. doi:https://doi.org/10.1016/j.petrol.2012.06.004.
657 Sultaniya, A., Priest, J.A., and Clayton, C.R.I. 2018. Impact of formation and dissociation
658 conditions on stiffness of a hydrate-bearing sand. Canadian Geotechnical Journal, **55**(7):
659 988-998. doi:https://doi.org/10.1139/cgj-2017-0241.

660 Sun, W.J., and Cui, Y.J. 2020. Determining the soil-water retention curve using mercury
661 intrusion porosimetry test in consideration of soil volume change. Journal of Rock
662 Mechanics and Geotechnical Engineering, **12**(5): 1070-1079.
663 doi:https://doi.org/10.1016/j.jrmge.2019.12.022.
664 Taylor, C.J., Miller, K.T., Koh, C.A., and Sloan, E.D. 2007. Macroscopic investigation of
665 hydrate film growth at the hydrocarbon/water interface. Chemical Engineering Science,
666 **62**(23): 6524-6533. doi:https://doi.org/10.1016/j.ces.2007.07.038.
667 Uddin, M., Wright, F., and Coombe, D.A. 2011. Numerical study of gas evolution and transport
668 behaviours in natural gas-hydrate reservoirs. Journal of Canadian Petroleum Technology,
669 **50**(01): 70-89. doi:https://doi.org/10.2118/137439-PA.
670 van Genuchten, M.T. 1980. A closed-form equation for predicting the hydraulic conductivity
671 of unsaturated soils. Soil Science Society of America Journal, **44**(5): 892-898.
672 doi:https://doi.org/10.2136/sssaj1980.03615995004400050002x.
673 Yan, R., L. Hayley, J., and Priest, J.A. 2020. Modeling water retention curve of hydrate-bearing
674 sediment. International Journal of Geomechanics, **20**(2).
675 doi:https://doi.org/10.1061/(ASCE)GM.1943-5622.0001585.
676 Yan, R., Xu, Y., and Yan, M. 2023. Soil-water characteristic curve and permeability of hydrate-
677 bearing soils. Chinese Journal of Geotechnical Engineering, **45**(5): 921-930.
678 Zhang, Y., Liu, L., Li, J., Chen, Q., Li, C., Sun, J., and Liu, C. 2024. The pore-structure
679 characteristics of foraminiferal shells and their relations with natural gas hydrate
680 formation in the marine sediments. Gas Science and Engineering, **124**: 205257.
681 doi:https://doi.org/10.1016/j.jgsce.2024.205257.
682 Zhang, Z., Ning, F., Lu, W., Zhou, J., Liu, L., Ji, Y., Wei, C., and Liu, C. 2022. Analysis of the
683 effect of hydrate on water retention curves in gas hydrate-bearing sediments using gas

drainage combined with NMR. Journal of Natural Gas Science and Engineering, **108**. doi:https://doi.org/10.1016/j.jngse.2022.104833.

Zheng, J., Yang, L., Ma, S., Zhao, Y., and Yang, M. 2020. Quantitative analysis of CO_2 hydrate formation in porous media by proton NMR. AIChE Journal, **66**(2): e16820. doi:https://doi.org/10.1002/aic.16820.

Zhou, C., and Ng, C.W.W. 2014. A new and simple stress-dependent water retention model for unsaturated soil. Computers and Geotechnics, **62**: 216-222. doi:https://doi.org/10.1016/j.compgeo.2014.07.012.