# Investigating the effective permeability evolution as a function of hydrate saturation in the hydrate-bearing sands using a kinetic-theory-based pore network model

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1 **Investigating the effective permeability evolution as a function of**

2 **hydrate saturation in the hydrate-bearing sands using a kinetic-**

3 **theory-based pore network model**

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20 **Abstract:**

21 Permeability governs the fluid flow of hydrate-bearing sediment and affects the

22 efficiency of natural gas production from hydrate reservoirs. The permeability in

23 hydrate-bearings sediments is estimated empirically and appears to vary widely for

24 sediments. This study focused on the sandy hydrate-bearing sediments and intended to

25 elucidate the evolution of effective permeability by the mean of pore network modeling.

26 A hydrate kinetics theory-based pore network model (KT-PNM) has been developed,

27 in which the simulation of hydrate formation in porous media is implemented by

28 employing two sub-processes, i.e., hydrate nucleation and hydrate growth. This KT-

29 PNM has been applied to simulate hydrate formation in different pore networks. The

30 permeability reduction exponent ($N$) for sandy hydrate-bearing sediments is determined

31 to fall in the range of $3 - 4$ based on the simulations of seven sandy samples. An

32 empirical equation used for predicting the effective permeability in sandy hydrate-

33 bearing sediments has been further proposed. The developed model and simulations are

34 hoped to provide valuable insights of pore-space effects on hydrate into permeability

35 prediction for studying the fluid seepage in hydrate-bearing sediments and facilitate the

36 numerical simulation of gas production from the hydrate reservoirs.

37 **Keywords**: natural gas hydrate; hydrate formation; pore network modeling; hydrate

38 saturation; effective permeability; permeability reduction exponent

39

## 1. Introduction

Natural gas hydrates (NGHs) are ice-like crystalline solids form under low-temperature and high-pressure conditions when water molecules form a cage-like structure and trap a large number of methane gas molecules within (Boswell and Collett, 2011; Waite et al., 2009). NGHs have been regarded as an important potential source of energy because of their wide distribution in nature, a huge amount of natural gas stored, and high energy density (Boswell et al., 2020; Yin et al., 2019). Aiming at gas recovery from the hydrate-bearing sediments (HBSs), four production methods including the depressurization method, thermal simulation method, chemical inhibitor method, and gas-exchange method (Cui et al., 2018; L. Yang et al., 2019) have been proposed. Among these methods, the depressurization method is considered to be the most economically feasible technique for development of hydrate resources, which was successfully used in the hydrate production tests conducted in the Nankai Trough, Japan in 2013 and 2017 (Tamaki et al., 2017; Yamamoto et al., 2014) and the Shenhu Area of the South China Sea, China in 2017 and 2020 (Li et al., 2018; Ye et al., 2020).

Permeability is a critical parameter governing the fluid flow and affecting the mass and heat transfer processes through HBS (Cai et al., 2020; Dai and Seol, 2014; Ren et al., 2020). In the natural hydrate-bearing system, permeability impacts the methane flux to the ocean (Reagan and Moridis, 2007), methane migration and distribution (Ruppel and Kessler, 2017), hydrate concentration and accumulation (Liu and Flemings, 2007), and the efficiency of gas production from the hydrate reservoirs (Moridis et al., 2011).

61 In addition, permeability can be incorporated into the basin- and reservoir-scale

62 numerical simulations for estimating resource in place and its ultimate gas recovery

63 from hydrate reservoirs (Gupta et al., 2015; Wan et al., 2022; Wu et al., 2021). As in the

64 conventional oil or gas reservoir, the same three types of permeability are defined in

65 HBS including absolute permeability, effective permeability, and relative permeability,

66 but are not referred to as inconsistent as in the former (Dai and Seol, 2014; Kumar et

67 al., 2010; Mahabadi et al., 2016). For clarity, the absolute permeability mentioned in

68 this work defines the ability of a single-phase-fluid to flow without the presence of

69 hydrate; effective permeability means the single-phase-fluid permeability in the

70 presence of solid hydrate phase; and relative permeability describes the ability of one

71 fluid to flow in the presence of one or more other fluids. Experimental results and two-

72 phase flow mechanisms of relative permeability in HBS are rarely revealed in literature

73 (Moridis et al., 2019; Xu et al., 2017). Most recent studies have focused on predictions

74 of effective permeability in HBS by means of theoretical means, experimental

75 measurements, or the combinations, under a respective condition of hydrate formation

76 or dissociation. Predicting effective permeability for hydrate formation is of concern in

77 this work. For this, the term 'permeability' is used exchangeable to effective

78 permeability unless stated otherwise.

79 The analytical or empirical models used for predicting the effective permeability

80 as a function of hydrate saturation include the Tokyo model (Masuda, 1999), Kleinberg

81 model (Kleinberg, 1999), a hybrid model (Delli and Grozic, 2013), a model proposed

82    by Dai and Seol (2014), and several models obtained from fractal calculations (Liu et

83    al., 2019, 2020). In these models, the Tokyo model is most widely used because of its

84    simple formula shown in Eq. (1).

85
$$K_e = (1 - S_h)^N \tag{1}$$

86    The Tokyo model employs the permeability reduction exponent $N$ to relate the

87    normalized effective permeability, the ratio of effective over absolute permeability,

88    denoted as $K_e$ to hydrate saturation $S_h$. $N = 10$ or $N = 15$ is given by Masuda to

89    predict the effective permeability as a function of hydrate saturation, but no rationale is

90    given for these specific choices. Minagawa et al. (2008) proposed a $N$ value range of

91    2.6 – 14 to fit the experimental data of different samples. Other reported values of $N$

92    in the literature range from $N = 3 - 5$ in Kumar et al. (2010), $N = 3.22$ in Mahabadi

93    et al. (2019), $N = 4.4$ in Konno et al. (2010), to $N = 7.7 - 9.4$ in Konno et al. (2013).

94    However, the determination of $N$ still lacks a sound physical foundation and cannot

95    be estimated based on the petrophysical property of the host sediment (Dai and Seol,

96    2014). Physical experiments of permeability measurement are important for validating

97    the above theoretical models and determining the value of $N$ in Tokyo model.

98    However, obtaining the permeability of HBS accurately by means of experiments is

99    challenging under the existing technical conditions. Permeability of natural hydrate-

100    bearing samples is known as hard to be measured under in-situ conditions due to the

101    difficulties in preserving and transporting natural samples (Waite et al., 2008). Most

102    published experiments are completed by using artificially synthesized samples (Lei and

103 Santamarina, 2018; Waite et al., 2009). In the laboratory, the main challenge in

104 measuring the permeability of artificially synthesized samples is maintaining the phase-

105 equilibrium condition of hydrate, which should be able to prevent hydrate dissociation

106 or reformation while preventing the formation of ice converted from water. During the

107 measurements, injection of fluids induces temperature and pressure variations in the

108 surrounding hydrate. Meanwhile, the pore structures of unconsolidated samples might

109 be destroyed by the reaction of hydrate or injection of fluids. Due to these difficulties,

110 the reported permeability data in literature from various experimental methods,

111 specimen types, and testing conditions are widely scattered and hard to implement for

112 further comparative analysis.

113     X-ray computed tomography (X-CT) imaging technology offers a route to obtain

114 the pore-structure characteristics of the hydrate-bearing sediment (Lei et al., 2018;

115 Zhang et al., 2021a), which facilitates the permeability prediction based on realistic CT

116 images using numerical simulation method. Based on the high-resolution gray-scale

117 images obtained from CT imaging, pore network modeling (PNM) is able to resemble

118 the geometric and topologic characteristics of pore spaces by considering the pore

119 spaces as geometrical elements composed of pores that are connected through throats

120 (Blunt, 2001; Ma et al., 2014; Y. Yang et al., 2019) and further predict macroscopic

121 transport properties in porous media (Chen et al., 2018; Sun et al., 2021; Wang et al.,

122 2015), which has been one of the most widely used numerical methods in studying the

123 HBS (Ai et al., 2017; Golsanami et al., 2022; Wang et al., 2015, 2020; Zhang et al.,

124  2020). Two simulation strategies for studying the permeability of HBS have been used

125  in the literature. One is to reconstruct a series of pore networks with CT images scanned

126  from the same hydrate-bearing sample with different hydrate saturation, then calculate

127  the permeability of fluids through conventional PNM routes (Ai et al., 2017; Kou et al.,

128  2021; Wang et al., 2015, 2018; Zhang et al., 2020). In this scenario, hydrates are

129  considered as a part of the solid sediment, and the topologic characteristics of the

130  constructed pore networks are closer to the realistic conditions of HBS. However, the

131  accuracy of the simulation results obtained in this approach depends on the quality of

132  CT images (Chen and Espinoza, 2018; Zhang et al., 2021b); and comparative analyses

133  of permeability still need massive CT experimental results. Another strategy is to

134  directly simulate the formation or/and dissociation process of hydrate in the

135  stochastically-generated regular networks or constructed networks with CT images,

136  then calculate the permeability as a function of hydrate saturation. The accuracy of the

137  simulation conducted by this strategy depends on the hypotheses assumed for

138  constraining the hydrate formation/dissociation. Mahabadi et al. (2016) extracted three-

139  dimensional (3-D) pore networks from CT images of sediments recovered from the

140  hydrate deposit at the Mallik site using the maximal ball algorithm (Silin and Patzek,

141  2006). Hydrates with various saturation and morphology were realized by assigning

142  hydrates to fill in randomly chosen pores in patchy formations of different sizes,

143  occupying 4, 64, or 1024 pores. Simulations conducted by Mahabadi et al. were used

144  to study the water retention curve and permeability of HBS influenced by the hydrate

145   saturation and distribution morphology. Dai and Seol (2014) employed a 50×50 two-

146   dimensional (2-D) lattice pore network to study the relationship between effective

147   permeability and hydrate saturation. The hydrate formation process was simulated

148   under the five conditions assumed preferential for hydrate accumulation. Given the

149   simulation results showing the relationships between hydrate saturation and sediment

150   porosity, and hydraulic tortuosity, they proposed a modified Kozeny-Carman model to

151   characterize the effective permeability in HBSs. For accurate permeability prediction

152   in the hydrate-bearing sediment, comparative analyses based on a large number of

153   results under different conditions are essentially necessary. In this case, the second

154   strategy mentioned above is more accessible to implement than the first one for the sake

155   of cost. By comparing these two strategies, we can find that the hydrate formation

156   process in porous media has not been clearly described with solid physical foundations

157   in the previous PNM simulations. The simulation results obtained from the currently

158   used stochastical method may cause deviations of the predicted permeability from the

159   real tests.

160         We developed a PNM based on the hydrate kinetic theory (called KT-PNM) in this

161   work. KT-PNM simulates the hydrate formation in the water-filled pore spaces by

162   implementing the hydrate nucleation and growth process. And the simulation of single-

163   phase fluid transport in the hydrate-bearing networks is subject to the quasi-static

164   process. This model is applied to realistic pore-space models to analyze the relationship

165   between hydrate saturation and effective permeability. Moreover, this work selectively

166  focuses on sandy HBS since the experimental results of effective permeability in sandy

167  HBS are relatively reliable in literature and the hydrate resources with high quality

168  mainly reside in natural sandy sediments (Li et al., 2021; Waite et al., 2009). The

169  authors believe that the contribution of the present study to the industry is that the

170  proposed approach lays the foundation for bridging the technical gap between the recent

171  theoretical simulation achievements and the real natural conditions of hydrate-bearing

172  sediments. Such an issue is further highlighted when one considers that the worldwide

173  distributed hydrate resources occur in intrinsically different types of sediments, and

174  thus calibrating the theoretical findings to the real reservoir situation is essential for

175  obtaining reliable reservoir engineering results.

176  ## 2.  Hydrate formation PNM based on the kinetic theory

177  ### 2.1 The kinetic process of hydrate formation in porous media

178  Hydrate formation is a time-dependent crystallization process that includes two

179  cohesive stages: hydrate nucleation and hydrate growth, as documented by the former

180  studies (Englezos et al., 1987; Kvamme, 2021; Sloan Jr and Koh, 2007). Hydrate

181  nucleation is the process in which small hydrate crystals (nuclei) grow and disperse in

182  an attempt to achieve the critical size ensuring subsequent growth (Sloan Jr and Koh,

183  2007). The critical size of nucleation for NGH is around 10 nanometers. In natural

184  sediments, hydrate nucleation is influenced by many factors, including the impurities

185  in the pore fluids (e.g., clays, nanobubbles, and microorganisms), temperature, pressure,

186  and previously dissociated hydrate structures. Thus the quantity, occurring location, and

187 induction time for hydrate nucleation are usually considered stochastic with limited

188 predictability (Sloan Jr and Koh, 2007; You et al., 2019). Hydrate growth follows the

189 nucleation referring to the subsequent growth of nucleated hydrate crystals. The stable

190 hydrate nuclei first grow inside the pore space in the coarse-grained sediment. Owing

191 to the Ostwald-ripening effect (Myerson, 2002), dispersed hydrate particles in the pore

192 are concentrated into fewer but larger particles. This process develops but is limited by

193 accessible pore space in sediments and influenced by induced physiochemical

194 processes by this pore confinement. Subsequently, hydrate invades the connected pores

195 and continues to the further growth of hydrate. The process is influenced by the pore

196 size, pore connectivity, and local effective stress (Dai et al., 2012).

197     The formation process of bulk hydrate in the absence of pore space confinement

198 can be modeled using the classic van der Waals-Platteeuw (vdW-P) model (Van der

199 Waals and Platteeuw, 1959) for predicting the thermodynamic formation condition of

200 bulk hydrate. Clarke et al. (1999) extended the vdW-P model to predict the hydrate

201 formation condition in porous media by adding the influence of water activity, a

202 measure of water that is available to react with another material (Azimi et al., 2021).

203 They expressed the water activity ( $a_w$ ) in porous media as a function of pore radius ( $r$ ),

204 contact angle of the mineral surface ( $\theta$ ), surrounding temperature ( $T$ ), interfacial

205 tension between mineral and water ( $\sigma$ ), and the volume of water in the pore ( $V$ ), as

206 shown in Eq. (2). By using the conception of water activity, the influence of

207 sedimentary property on the hydrate formation in the porous media can be described

208    and predicted.

209
$$a_w = EXP\left(-\frac{2\sigma V}{rRT}\cos\theta\right)$$
                                                                    (2)

210    2.2 Model hypotheses and simulation procedure

211        Applications of using water activity in predicting the hydrate formation in porous

212    media have been proved feasible in many previous thermodynamic works (Azimi et al.,

213    2021; Chen et al., 2010). Chen et al. (2010) developed a thermodynamic model to

214    predict the phase equilibrium conditions in the hydrate-bearing porous media. The

215    application of this model was implemented by calculating the water activity caused by

216    the sedimentary geometrical constraints (using Eq. (2)) based on their previously

217    constructed Chen-Guo model (Chen and Guo, 1996). In a recent work, Azimi et al.

218    (2021) employed a similar route of modifying water activity based on the vdW-P model.

219    Both of these models were reported to be capable of predicting the

220    formation/dissociation conditions of simple and mixed-gas hydrate in various porous

221    media. The above two models are applicable for the water-filled conditions in the

222    hydrate-bearing media without gas-water interfaces. No research has applied this route

223    in PNM.

224    2.3 Model hypotheses and simulation procedure

225        Based on the kinetic theory of hydrate formation, a PNM simulator aiming to

226    model the hydrate formation in porous media was developed in this work. In this

227    simulator, the viewpoints of hydrate nucleation and hydrate growth were employed.

228    The water activity of each pore and throat in the pore network is calculated to determine

229    the hydrate growth order in the pore network. To improve the computation efficiency

230    the following hypotheses were adopted.

231    (1) The formation of hydrate in porous media can be independently divided into a

232        nucleation process and a subsequent growth process.

233    (2) The nucleation of hydrate in pores occurs stochastically. Nucleation fraction ($F_n$)

234        is defined as the ratio of the number of nucleated pores to the total pores in the

235        network.

236    (3) The growth process begins after the nucleation process; the hydrate growth

237        happens following the order of pore-water activity from high to low meanwhile

238        along with the interface between hydrate and water.

239    (4) Assume that hydrates entirely fill the pores once the hydrate nucleates or forms in

240        the pores or throats. This assumption of either 100% or 0% pore occupancy by

241        hydrates reflects Ostwald ripening effect (Lei et al., 2019), which was also adopted

242        in previous works (Dai and Seol, 2014; Mahabadi et al., 2016; Wang et al., 2015).

243    (5) Pores or throats occupied by hydrate are assumed to be immobile. The permeability

244        of the model can be calculated by the conductivity relations between network

245        elements (Blunt, 2001, 2017; Zhao et al., 2022).

246    (6) The influences of the gas-water interface, clay minerals, and other complex

247        controlling factors are neglected in the current vision of the simulator.

248        Simulations of hydrate formation in our simulator are conducted following the

249    workflow as shown in Fig. 1. Herein, (1) Generate pore networks extracted from CT
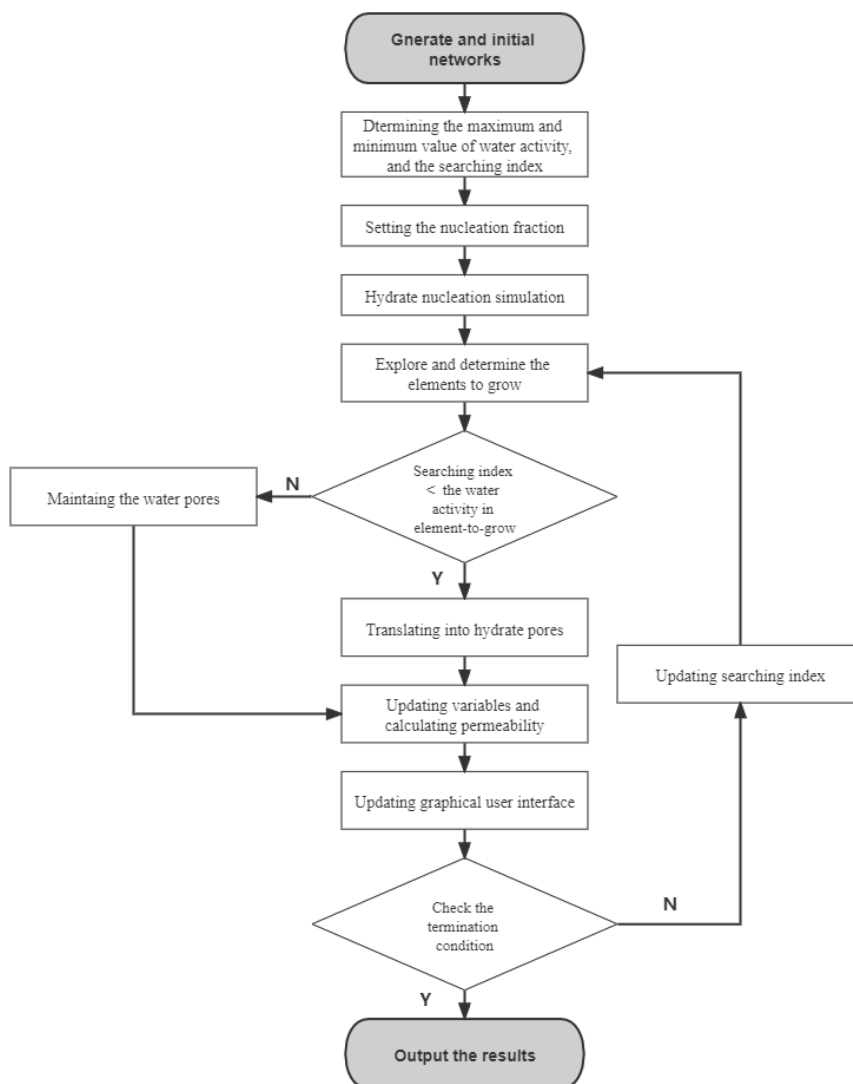
images or generate regular networks using a stochastic method (Blunt, 2001), then initialize the water saturation, wettability conditions (contact angle and interfacial tension) of the network elements (pores and throats), and the terminal hydrate saturation. (2) Explore and determine the maximum and minimum water activity in the pore networks ($A_{w\_max}$ and $A_{w\_min}$); the searching index $Sx$ is initialized to be $A_{w\_max}$. (3) Initiate the nucleation fraction with a value ranging from 0 to 1, and then simulate the hydrate nucleation process using a stochastic algorithm. (4) After the nucleation, explore and determine the network elements that are ready to grow, which count the pores occupied with water neighboring the pores occupied by hydrate. (5) Hydrate growth occurs when $Sx$ is smaller than the water activity of pores in the element-to-grow group. If it occurs, the pore would be translated into pores with hydrate. If not, the pore maintains the condition of water-filling. (6) Update the variables and graphical user interface, then calculate the effective permeability. (7) Check the termination condition whether the hydrate saturation reaches the assigned terminal hydrate saturation. If yes, output the results and terminate the simulation. If no, update the searching index, then make loops for steps (4) to (6) until reaching the terminal hydrate saturation.

Note that the extraction of pore network from CT images was completed using a modified maximal method proposed by Dong and Blunt (2009). The graphical user interface module in our simulator was modified from the open-source PNM code developed by Boujelben (Boujelben et al., 2018). We appreciate the excellent works

271  shared by these scholars.



**Gnerate and initial networks**

Dtermining the maximum and minimum value of water activity, and the searching index

Setting the nucleation fraction

Hydrate nucleation simulation

Explore and determine the elements to grow

Searching index < the water activity in element-to-grow

Maintaing the water pores  N

Y

Translating into hydrate pores

Updating searching index

Updating variables and calculating permeability

Updating graphical user interface

Check the termination condition  N

Y

**Output the results**

272

273  Fig. 1 Workflow for the KT-PNM of hydrate formation and effective permeability

274  calculation

275

276  **3.  Simulation Results and Discussion**

277  3.1  Influence of model dimension

278      Given both the 2D model and 3D model are used in the PNM studies of HBS, here

279  we analyze the influence of model dimension on the correlations between effective

280  permeability and hydrate saturation. Hydrate formation processes are modeled in the

281  regular networks constructed in the forms of 2D and 3D. Basic pore-structure

282  parameters (e.g., pore size distribution range, tortuosity, wettability distribution) are

283  kept the same for these two networks. The nucleation fraction set in the 3D network is

284  0.02 while the parameter set in the 2D networks ranges from 0.02 to 0.18. The effective

285  permeability results of the 3D network and series of 2D networks have been plotted in

286  Fig. 2. In Fig. 2, the geometrical elements colored with blue represent the pores or

287  throats occupied by water, and the elements colored with white represent the pores or

288  throats occupied by hydrate. Normalized effective permeability is given to compare the

289  results, which defines the ratio of effective permeability to the absolute permeability of

290  the sample. It shows that the normalized effective permeability decreases with the

291  increasing hydrate saturation for 2D and 3D networks. The normalized effective

292  permeability in 2D networks is larger than that of the 3D network when the hydrate

293  saturation is lower than a value of ~ 10 %. When the hydrate saturation is larger than

294  this value, the normalized effective permeability in 2D networks decreases rapidly and

295  shows lower values than that of the 3D network. Moreover, the 2D effective

296  permeability decrease to 0 when the hydrate saturation reaches a range of 20 – 30 %

297  while the 3D effective permeability decreases to 0 until the hydrate saturation reaches

298  the value of ~ 60 %. Based on the results in Fig. 2, the permeability reduction exponents

299  fitted with the Tokyo model are within the range of 7 – 9 for 2D networks and 3.5 for

300  the 3D network.

301
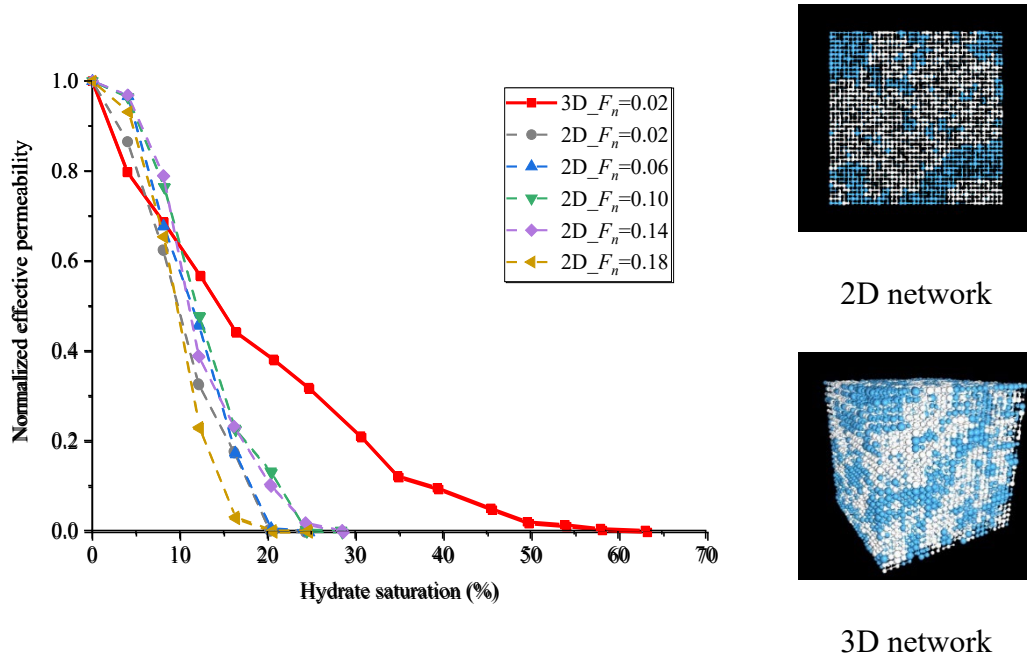


2D network

3D network

Fig. 2 Comparisons of normalized effective permeability between 2D and 3D networks.

The figure on the left shows the normalized effective permeability results; the figures

on the right illustrate the comparisons between 2D and 3D regular networks; the

geometrical elements colored with blue represent the pores or throats occupied by water,

and the elements colored with white represent the pores or throats occupied by hydrate.

307

## 3.2  Influence of nucleation fraction

To visually explain the influence of nucleation fraction on hydrate formation,
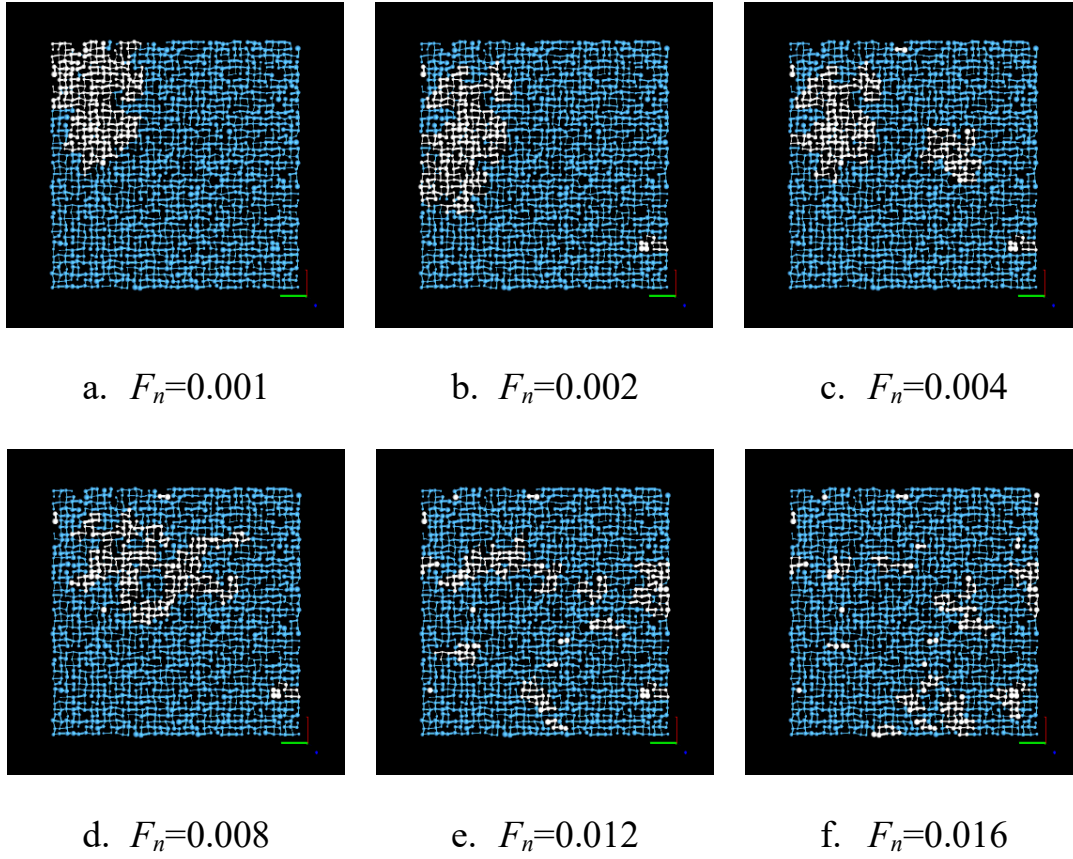
hydrate distributions in regular 2D networks formed with different nucleation fraction

settings have been plotted in Fig. 3. All the results shown in Fig.3 have the same hydrate

saturation of 15 %. The results show that the hydrate distributions formed in the

network would be affected by the nucleation fraction. In the cases with low nucleation

314    fraction (i.e., Figs. 3-a, b, and c), hydrate prefers to accumulate and distribute in partial

315    areas of the network, showing a patchy pattern. In the cases with relatively high

316    nucleation fractions (i.e., Figs. 3-c, d, and e), the formed hydrates preferentially

317    disseminate throughout the network. The effective permeability results calculated from

318    3D regular networks with different nucleation fractions are plotted in Fig. 4. The

319    normalized effective permeability of all the cases decreases from 1 down to 0 when the

320    hydrate increases from 0 to ~ 60 %; the reducing effect of formed hydrate on effective

321    permeability is more pronounced when the hydrate saturation is smaller than 30% than

322    that of the hydrate saturation being within the range of 30 – 60%. Meanwhile, the

323    effective permeability curves of the cases with a higher nucleation fraction decrease

324    faster under low hydrate saturation than the cases with a lower nucleation fraction. It

325    can be deduced that the effective permeability of the sample with disseminate-

326    distributed hydrate is larger than that of patchy-distributed hydrate for the condition of

327    the same hydrate saturation in the same sample. Based on the calculation results in Fig.

328    4, the permeability reduction exponent fitted with the Tokyo model increases from 3 to

329    7 when the nucleation fraction increases from 0.002 to 0.180.

330

331

a.  $F_n$=0.001          b.  $F_n$=0.002          c.  $F_n$=0.004



d.  $F_n$=0.008          e.  $F_n$=0.012          f.  $F_n$=0.016

332   Fig. 3 The distribution of formed hydrates in 2D regular networks in different

333   nucleation fraction settings
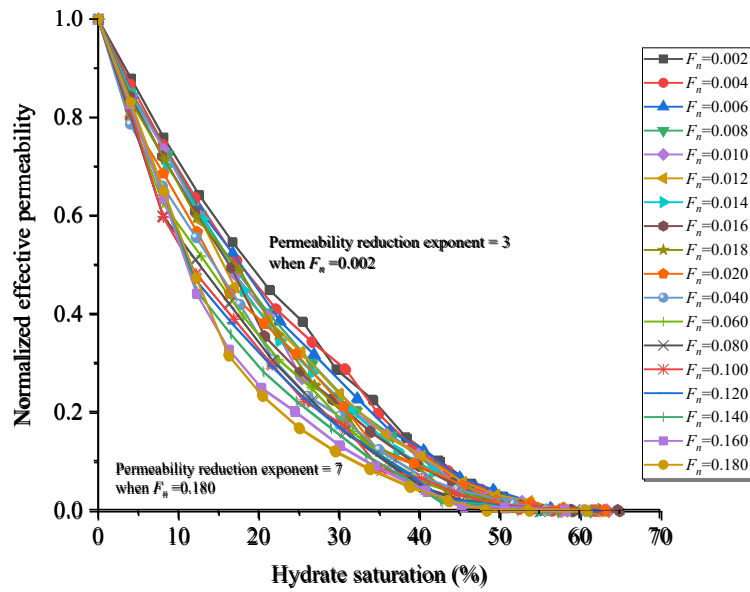


334

335   Fig. 4 Calculated normalized effective permeability of 3D regular networks in different

336  nucleation fraction settings. The permeability reduction exponent fitted with the Tokyo

337  model is 3 when the nucleation fraction is 0.002. And the fitted permeability reduction

338  exponent is 7 when the nucleation fraction is 0.180.

339

340  ## 3.3 Influence of hydrate growth type during formation

341    Three types of hydrate growth, including low $A_w$ priority, high $A_w$ priority, and

342  evenly growth, are simulated in this work. The case of low $A_w$ priority means that the

343  hydrate contacting the hydrate-water interface preferentially grows into the neighboring

344  water-pores with lower water activity. The case of high $A_w$ priority means the opposite

345  condition of higher water activity. The case of evenly growth indicates that the hydrate

346  around the hydrate-water interface would evenly grow into the neighboring water-pores

347  with the same priority. Fig. 5 shows the effective permeability results of 3D networks

348  influenced by the hydrate growth type along with the illustrating views of these three

349  growth types in a 2D network. Seen from the 2D illustrating views, hydrates mainly

350  form in the smaller pores under the condition of low $A_w$ priority and form in the larger

351  pores under the condition of high $A_w$ priority; under the condition of evenly growth, the

352  formed hydrates are distributed among the pores in the form of regular clusters. When

353  the hydrate saturation is smaller than ~15 %, the results of calculated effective

354  permeability show slight differences for the three cases. When is the hydrate saturation

355  is in the range of 15 – 60 %, the effective permeability of the case with high $A_w$ priority

356  is larger than that of low $A_w$ priority; the effective permeability of evenly growth type

357    shows lower values than those of the above two cases.

358



Low $A_w$ priority
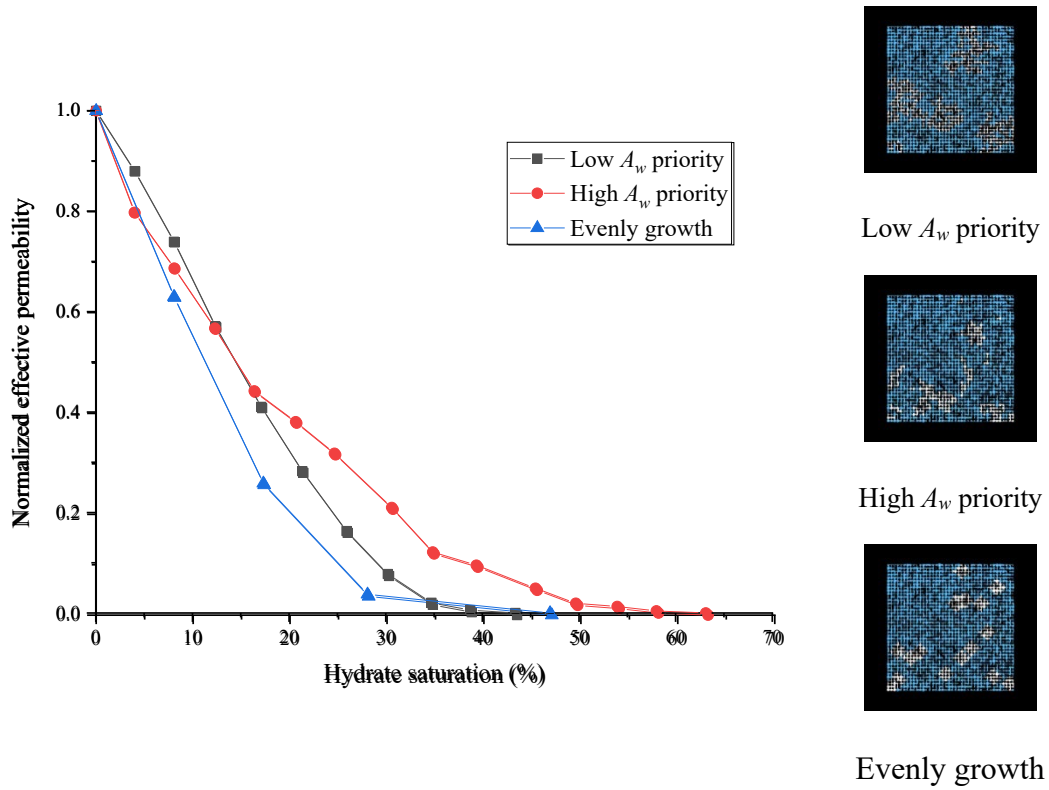
High $A_w$ priority

Evenly growth

359    Fig. 5 The effective permeability results of cases with three hydrate growth types in 3D

360    networks (left) and their illustrating views in 2D networks (right). High $A_w$ priority and

361    low $A_w$ priority mean the hydrate preferentially grows into the neighboring water-pores

362    with higher and lower water activity, respectively. And the evenly growth indicates that

363    the hydrate would evenly grow into the neighboring water-pores.

364

365    3.4   Simulation results in sandy samples

366       All the simulation cases listed in Sections 3.1 – 3.3 are completed in regular

367    networks, further simulations based on the networks extracted from CT images of sandy

368    samples are documented in the following.

### 3.4.1  CT scanning and image processing

Seven sandy samples were selected to obtain CT gray-scale images and generate pore networks for the hydrate formation simulation. These sandy samples were synthesized by compacting quartz sands with different grain sizes into an aluminum vessel. CT scans of these samples were conducted using a Phoenix, v|tome|x version CT scanner in Qingdao Institution of Marine Geology. The size of the representative effective volume (REV) cropped for image processing and further simulation is $400 \times 400 \times 400$ pixel[3]. Other parameters including the image resolution have been listed in Table 1. 2D CT gray-scale slices of used samples are given in Fig. 6.

The obtained 2D grayscale images were reconstructed to 16-bit three-dimensional (3D) grayscale images using a software package "Datos|rec" developed by Phoenix Contact company. Subsequent image noise reduction, image filtering, and phase segmentation were completed using the software Avizo 9.7 developed by Thermo Fisher Scientific. The image filtering method employed in the processing was the non-local means algorithm (Liu et al., 2008). And the phase segmentation between the sand phase and fluid phase was completed using the interactive thresholding method based on the grayscale differences between phases. To further analyze the distribution characteristics of sand grains, the segmented sand phase is separated into sand grains based on the topological relations of gray areas (Fig. 7). The grain size distributions of the samples calculated from image data are plotted in Fig. 8. It shows that the grain radii of used samples are distinctively distributed in the range of $0 - 800$ μm; the grain

390 radius of samples generally increases from Sample #1 to Sample #7. The grain-size

391 distribution of the used samples is consistent with the natural sandy HBSs (Ito et al.,

392 2015; Kraemer et al., 2000; Minagawa et al., 2012; Winters et al., 2011; Yamamoto et

393 al., 2014).

394



| Sample #1 | Sample #2 | Sample #3 | Sample #4 |

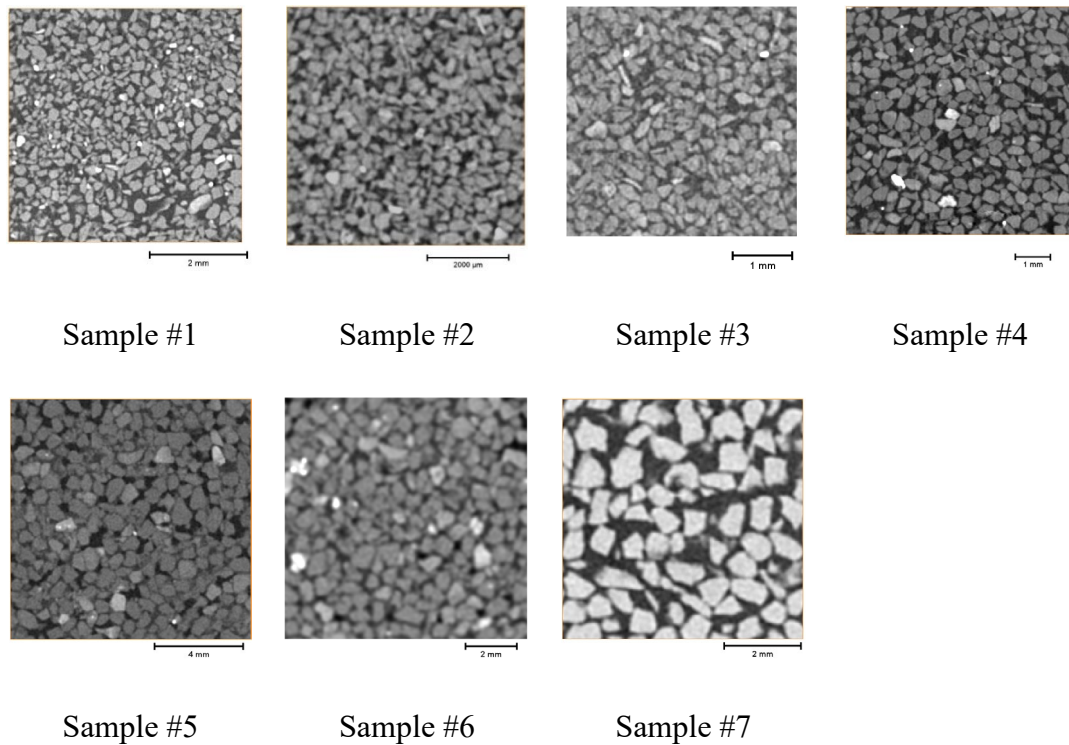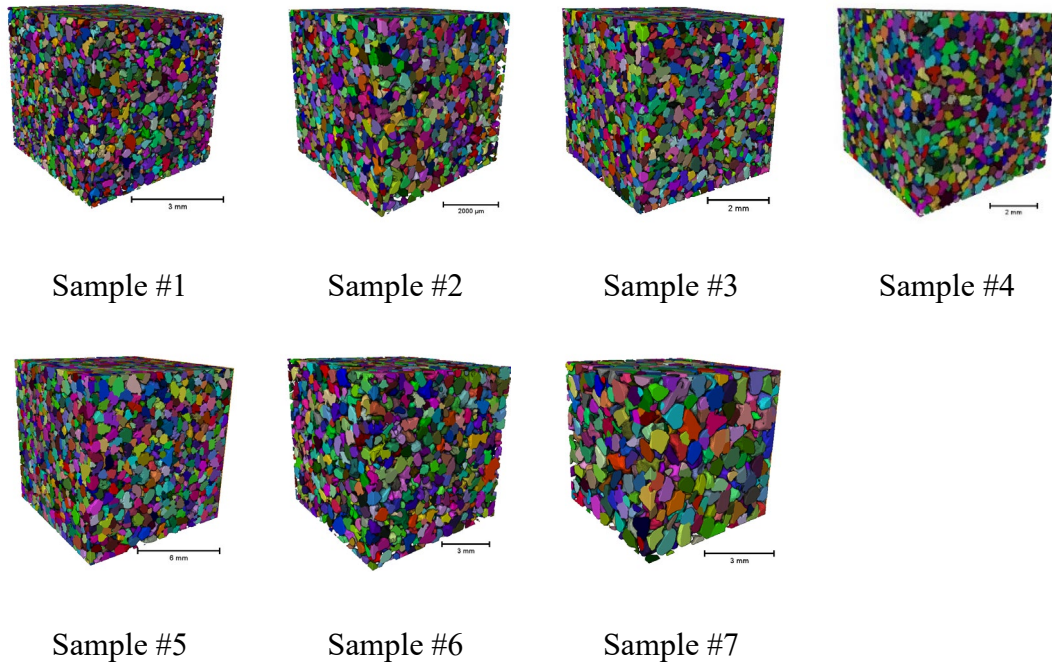| Sample #5 | Sample #6 | Sample #7 |

395 Fig. 6 Slices of gray-scale CT images for the seven sandy samples. The gray area with

396 a clear boundary in the images is sands; the dark area may include the gas phase and

397 water phase; the size of these present CT slices is $400 \times 400 \times 1$ pixel$^3$; the resolution of

398 each slice and other parameters can be found in Table 1.

399

| Sample #1 | Sample #2 | Sample #3 | Sample #4 |

| Sample #5 | Sample #6 | Sample #7 |

400     Fig. 7 3D presentation of separated sand grains extracted from CT images for seven

401     sandy samples. Adjacent grains in each sample are colored with different colors.

402
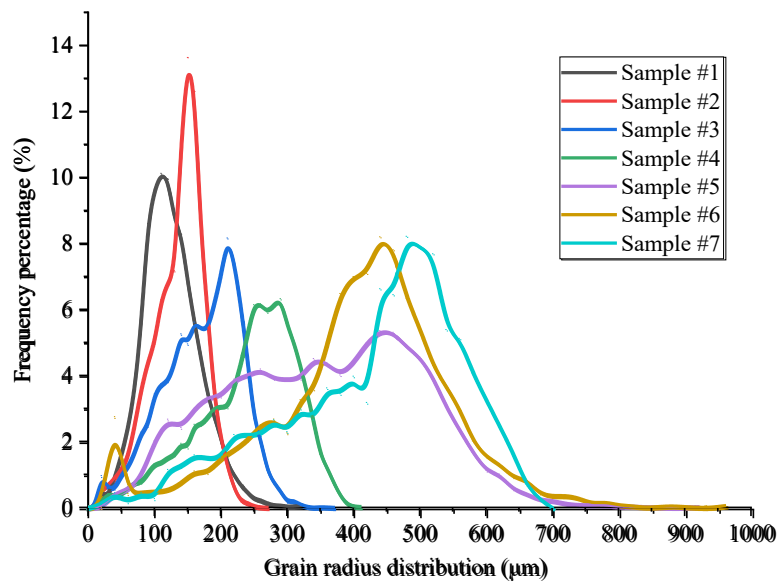


403

404     Fig. 8 Grain radius distribution of the simulated samples. Frequency percentage on the

405     Y coordinate axis means the quantity percentage of grains with a certain radius against

406     the number of total grains.

407

408 Table 1 Properties of the simulated samples calculated from CT images

| Sample NO. | Porosity (%) | Geometric tortuosity | Image resolution (μm) | Max grain radius (μm) | Mean grain radius (μm) | Max pore radius (μm) | Mean pore radius (μm) |
|---|---|---|---|---|---|---|---|
| Sample# 1 | 45.6 | 1.26 | 12.0 | 280 | 121 | 210 | 73 |
| Sample# 2 | 39.1 | 1.32 | 13.5 | 230 | 130 | 210 | 80 |
| Sample# 3 | 34.9 | 1.44 | 12.5 | 300 | 167 | 290 | 101 |
| Sample# 4 | 34.5 | 1.47 | 16.0 | 390 | 236 | 310 | 105 |
| Sample# 5 | 34.3 | 1.46 | 37.3 | 680 | 347 | 460 | 158 |
| Sample# 6 | 38.8 | 1.49 | 23.7 | 720 | 397 | 540 | 220 |
| Sample# 7 | 42.2 | 1.44 | 15.8 | 660 | 420 | 550 | 240 |

409

410 3.4.2 Hydrate saturation vs. normalized effective permeability

411 The hydrate formation processes in the seven sandy samples are simulated using

412 the developed KT-PNM. These simulations are implemented in the 3D dimension

413 following the hydrate growth type of high $A_w$ priority. For the reason that the nucleation

414 fraction cannot be predicted or measured, this parameter is assumed to be a constant

415 value of 0.02 for seven cases by comparing the simulation results of hydrate distribution

416 with CT images from the literature (Lei et al., 2018, 2019). Fig. 9 shows the graphical

417 results of simulations under the same condition of hydrate saturation being 60 % for 7

418 samples. And Fig. 10 illustrates the effective permeability results as a function of

419 hydrate saturation. It can be observed that both the hydrate distribution in the networks

420 and the effective permeability curves show noticeable differences for various samples.

421 We have made correlation analyses between the normalized effective permeability

422 results and the pore-structure parameters, including maximum or minimum pore radius,

423 mean pore radius, pore tortuosity, and porosity. No clear correlations can be determined.

424 However, we found that the permeability reduction exponents fitted with the Tokyo

425 model in all the simulated samples are in a limited range of 3 − 4. Possible reasons

426 causing the similar permeability reduction exponents for seven samples are analyzed as

427 follows. Firstly, all the effective permeability results in Fig. 10 have been normalized,

428 which means the position of the curves plotted is little affected by the mean pore size

429 of the samples. The changes in curves show the influences of pore structures and

430 hydrate distribution on the normalized effective permeability. And the growth of

431 hydrate in the pore spaces can be influenced by the hydrate nucleation properties,

432 connectivity of pores, and the pore size distribution, as documented in Section 2. In

433 Figs. 6 − 7, most of the pores in all the sandy samples are well connected and the PSD

434 curves of the seven samples are all close to the normal distribution curve. In this case,

435 the changes of normalized effective permeability as a function of hydrate saturation

436 would be similar in trend. The permeability reduction exponent range of 3 − 4 in the

437 Tokyo model permits a good match between the normalized effective permeability and

438 hydrate saturation for sandy samples would be reasonable.

439

Sample #1  Sample #2  Sample #3  Sample #4

Sample #5  Sample #6  Sample #7
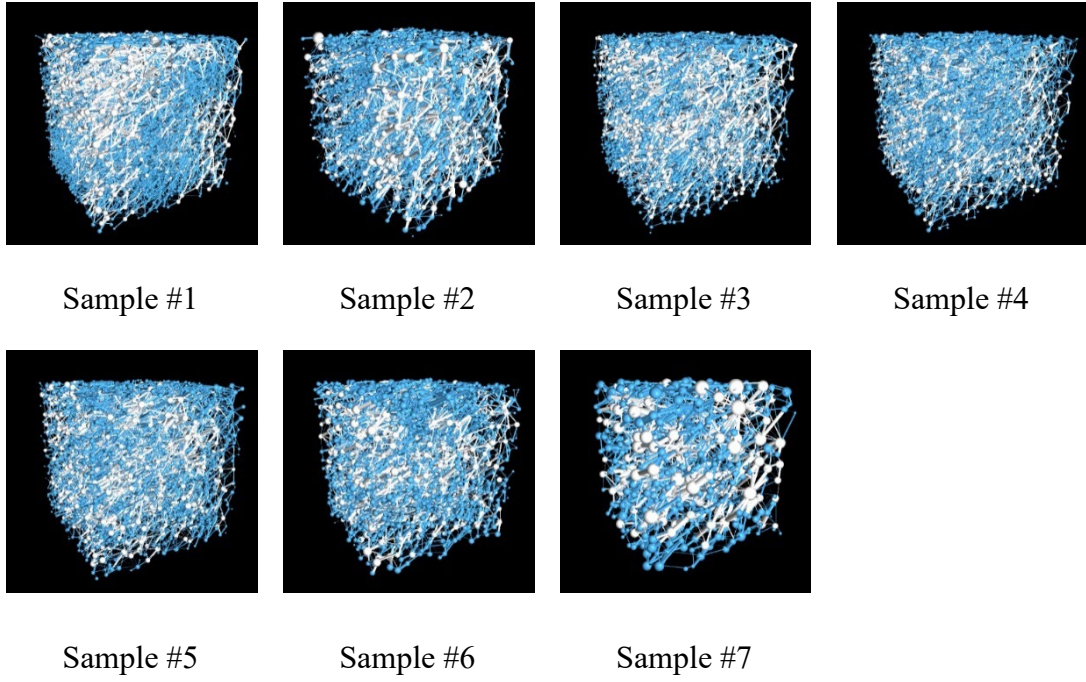
440   Fig. 9 Hydrate distributions obtained from KT-PNM for the seven sandy samples. White

441   areas represent the network elements occupied with hydrate. And blue areas mean the

442   network elements occupied by the water phase.
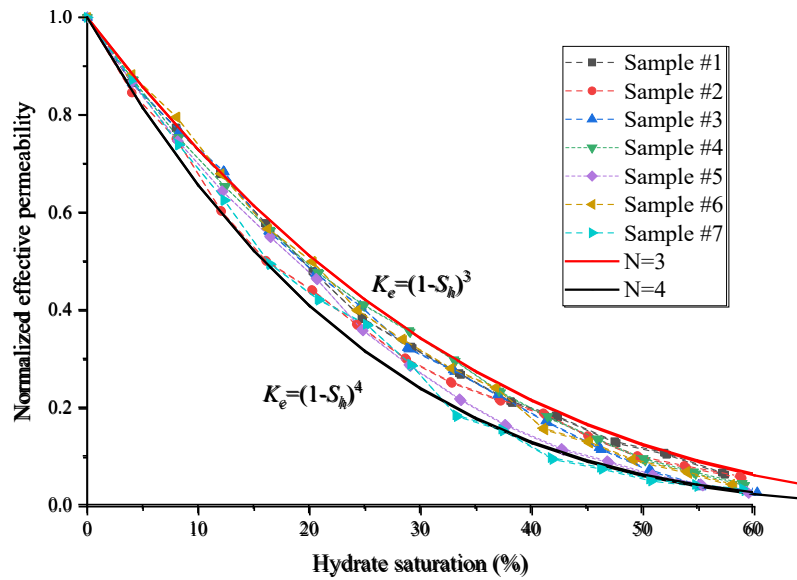


443

444   Fig. 10 The relationships between normalized effective permeability and hydrate

445   saturation calculated from KT-PNM for seven sandy samples

446

447    To validate the obtained parameter values of permeability reduction exponent, we

448    compared the simulation results with the experimental results of sandy samples in the

449    literature (Fig. 11-a). The red and black lines in the figure represent the normalized

450    effective permeability curves with the permeability reduction exponent equals 3 and 4,

451    correspondingly. It reveals that the experimental normalized effective permeability data

452    are basically located in the areas closed by the exponent lines. Considering the

453    differences in the experimental methods and sample property, the results concluded

454    from numerical simulations can be considered to agree well with the experiments.

455    However, note that the drawn conclusion of permeability reduction exponent can hardly

456    apply to the predictions of effective permeability in silty HBS or sandy HBS containing

457    clay minerals. The permeability in these media behaves differently from the hydrate

458    saturation compared to the sandy sediments (Fig. 11-b). Sample property and testing

459    methods supporting the experimental data plotted in Fig. 11 are listed in Table 2.

460
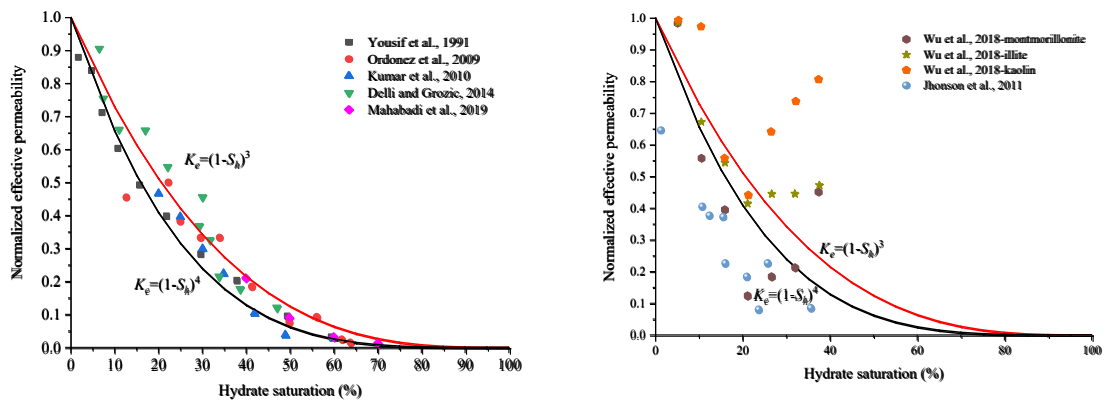


(a) Simulation results vs. experimental    (b) Simulation results vs. experimental

results of sandy samples                    results of silty samples

461    Fig. 11 Comparison of normalized effective permeability as a function of hydrate

462    saturation between KT-PNM simulations and the experimental results from the

463    literature

464

465    Table 2 Summary of permeability tests in the hydrate-bearing sediments obtained from

466    literature

| Literature | Sample property | Hydrate synthesizing method | Permeability measuring method |
|---|---|---|---|
| Yousif et al. (1991) | Berea sandstone with a porosity of 18.8 % | Methane hydrate, excess-gas method | Gas-flow method |
| Ordonez et al. (2009) | Ottawa sand | R-11 ($CCl_3F$) hydrate | Water-flow method |
| Kumar et al. (2010) | Glass beads with a diameter range of 88.9 – 149.8 μm | $CO_2$ hydrate, excess-gas method | Gas-flow method |
| Delli and Grozic (2014) | Ottawa 20/30 silica sand with a grain size distribution of 600 – 800 μm | $CO_2$ hydrate, excess-gas method | Water-flow method |
| Mahabadi et al. (2019) | Three different groups of sands | THF hydrate | Water-flow method |
| Jhonson et al. | Unconsolidated samples from the | Methane hydrate, | Brine-flow |

| (2011) | Mount Elbert site on the Alaska North Slope (ANS) | excess-gas method | method |
| Wu et al. (2018) | Montmorillonite with median diameter 8.27 μm; kaolin with median diameter 6.91 μm; illite with median diameter 3.53 μm | Methane hydrate, ice-seed method | Gas-flow method |

467

### 3.4.3   Hydrate saturation vs. effective permeability

469   To predict the evolution of effective permeability as a function of hydrate

470   saturation, Eq. (3) was deduced by coupling the Kozeny-Carman equation with the

471   Tokyo model.

472
$$K_e = m \frac{\phi^3 r_g^{\,2}}{\tau}(1 - S_h)^n \,, \tag{3}$$

473   where $\phi$ is the porosity of the sample, $r_g$ is the mean grain radius, $\tau$ is the mean

474   tortuosity of pore spaces, $m$ and $n$ indicates the pore-structure parameter affecting

475   the fluid flow and permeability reduction exponent as introduced in the Tokyo model.

476   For sandy media, $m$ was determined to be 0.6 after fitting with the simulation results

477   and $n$ was determined to be 3.5 taking a mean value of the range $3 - 4$. The equation

478   for predicting the effective permeability as a function of hydrate saturation in sandy

479   media can be expressed as Eq. (4).

480
$$K_e = 0.6 \frac{\phi^3 r^2}{\tau}(1 - S_h)^{3.5} \tag{4}$$

481   A comparison between effective permeability results calculated from Eq. (4) and

482   experimental results from previous literature is plotted in Fig. 12. It should be noted

483    that effective permeability results of hydrate-bearing sandy samples were rarely

484    reported in previous works. As a result, only two sets of experimental results (Kumar

485    et al., 2010; Pan et al., 2010) are plotted in Fig. 12. From the comparison, the model

486    calculation results show good agreement with the experiments. However, this

487    agreement merely proved the reliability of Eq. (4) in predicting the effective

488    permeability of sandy HBS to a certain degree. Further validation with more

489    experimental results is still necessary for future studies. There is still one more issue

490    that should be explained. Most of the reported experimental results, including all these

491    in Fig. 11 and Fig. 12, were actually conducted in different experimental conditions.

492    These differences, as listed in Table 2, may include the property of sandy samples, type

493    of guest-molecular materials, hydrate synthesizing method, and permeability measuring

494    method. Any of these differences would affect the accuracy of the obtained results. In

495    this case, physical experiment of permeability measurement with higher accuracy

496    would be helpful for improving the prediction of PNM in HBS.
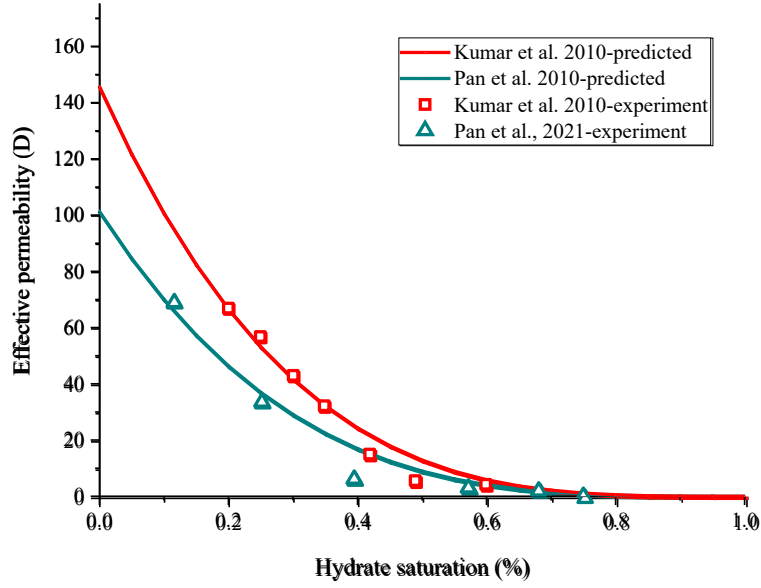
497

Fig. 12 Comparison of effective permeability as a function of hydrate saturation

between equation calculation and experimental results from literature

498

## 4. Conclusions

500      In this work, we developed a KT-PNM to simulate the hydrate formation and

501 analyze the changes in effective permeability as a function of hydrate saturation in

502 sandy HBS. In the developed KT-PNM, the hydrate nucleation and hydrate growth

503 conceptions in the hydrate formation kinetic theory are physically embedded.

504 Simulation results of regular networks show that the 2D PNM leads to an

505 underestimated permeability or overestimated permeability reduction exponent

506 compared to the 3D PNM, thus failing to provide accurate predictions of permeability

507 in HBS. The amount of nucleation pores determines the distribution of formed hydrates

508 in the pore network and further impacts the evolution of effective permeability with

509 hydrate saturation. Under the same condition of hydrate saturation, the reduction effect

of disseminate-distributed hydrates formed with higher nucleation fraction is stronger than that of patchy-distributed hydrates formed with lower nucleation fraction. Simulation results of extracted networks from seven sandy samples show that the changes in the normalized effective permeability as a function of hydrate saturation are similar for different sandy samples. The permeability reduction exponent for sandy HBS fitted with the Tokyo model is determined to be within a range of 3 – 4 based on the simulations. This result further permits the modification of the Kozeny-Carman equation and the Tokyo model to predict the effective permeability in sandy HBS:

$$K_e = 0.6 \frac{\phi^3 r_g^2}{\tau} (1 - S_h)^{3.5}$$ . This equation shows the combined effects of the pore-structure features of sediment and hydrate formation on effective permeability, of which the prediction results agree well with the reported experiments.

The developed KT-PNM proposed in this work is not merely appliable for sandy HBS. The route of model development can be extended to other types of HBSs if adequate experimental data are available for verification. Moreover, the model and simulation results in this work are relevant to the research of kinetics, thermodynamics, property analysis, and hydrate production numerical simulation related to hydrate formed in the hydrate-bearing sediment.

## Declaration of competing interest

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

**Data availability statements**

All the CT data supporting the simulations in this work can be downloaded from the Mendeley repository (https://data.mendeley.com/datasets/v3b9wxp2tf/1).

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