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Publication Date

2019-12-01

DOI

10.1016/j.apenergy.2019.113861

Peer reviewed

On the Importance of Phase Saturation Heterogeneity in the Analysis of Laboratory Studies of Hydrate Dissociation

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Abstract

Methane hydrates (MHs) have been considered as the future source of energy because of its vast resource volume and high energy density. Energy recovery from MH-bearing sediments has attracted intensifying research activities. Fundamentally, heat transfer, fluid flow through porous media, and the kinetics of hydrate reaction are the three key processes controlling the behavior of MH dissociation and the associated fluid production. Earlier studies have suggested that heterogeneous spatial distribution of S_H is inevitable in MH-bearing samples synthesized in laboratory. In this paper, we extend our study to analyze numerically the simulation results from the two realizations of the samples (homogeneous and heterogeneous) to identify differences in the fluid production and to determine if they are sufficiently different. Additionally, we conduct a sensitivity analysis and a statistical analysis on the key transport and kinetic rate parameters that could affect hydrate dissociation and fluid production in the context of a heterogeneous hydrate-bearing sample, in an effort to provide insights that could lead to improved designs for laboratory experiments and (possibly) field applications. Our results suggest that the approximation of an artificial hydrate-bearing core with heterogeneous phase saturations by an assumption of uniform phase saturation distributions results in practically similar fluid production profile except for the very early stage with maximum 20.0% deviation in the water production. From the sensitivity and statistical analysis, we determine that gas production depends strongly on the kinetic rate constant, K_d^0 and the composite thermal conductivity of the hydrate-bearing sediments, λ_θ ; while, water production is very sensitive to K_d^0 and the absolute permeability of the sandy medium, k . Understanding the effect of phase

heterogeneity and the relative importance of key parameters on the production behavior of hydrate-bearing sediments could provide basis for novel production technologies that lead to enhanced gas production and energy efficiency in the energy recovery process.

Keywords: *Hydrate-bearing sediments; Hydrate dissociation; Heterogeneity; Fluid production; Sensitivity analysis; Controlling mechanism*

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1. Introduction

Methane hydrates (MHs) are solid, nonstoichiometric compounds formed by host H_2O molecules that create lattices lodging the guest CH_4 molecules ($\text{CH}_4 \cdot N_H \text{H}_2\text{O}$) [1]. Pure MHs exist in the sI crystallographic structure, in which hydrogen bonding involving 46 H_2O molecules leads to the creation of two $5^{12}6^2$ large cages and six 5^{12} small cages that encage CH_4 molecules [2]. If all the cages are fully occupied, the ideal hydration number (N_H) for MH is 5.75. However, N_H varies between 5.9 and 7.2 in nature [3, 4] because of the non-ideal (<100%) cage occupancy and the occurrence of different hydrate-forming gas species (C_2H_6 , C_3H_8 , CO_2 and H_2S) in addition to CH_4 (that is the dominant natural hydrate-former). MHs are stable under suitable conditions of low temperature, T and high pressure, P and are widely distributed at permafrost and offshore marine locations in nature. The vast resource volume of CH_4 (~3,000 TCM) in naturally-occurring MH-bearing sediments [5] and their high energy storage capacity ($170 \text{ vCH}_4/\text{vH}_2\text{O}$) make MHs a promising future energy resource [6]. This realization has led to an explosive and intensifying research interest and activities by both the academic and the industry communities over the past two decades [7].

Fundamentally, MH dissociation and fluid production from sandy media involve several coupled physical processes [8]: (a) fluid flow through porous media; (b) heat transfer; (c) phase changes; and (d) kinetic chemical reactions of hydrate dissociation and formation. Depending on the temporal and spatial scale of the hydrate-bearing system, any one (or combinations of more than one) of the above-mentioned processes could be a dominant factor controlling the dissociation process and the associated fluid production [9]. To quantify, analyze and evaluate these dynamic and strongly non-linear coupled processes and the overall behavior of hydrate-bearing sediments (HBS) under production, several empirical [10], analytical [11] and numerical models [12] have been developed.

Yousif et al. [12] first incorporated the kinetic equation of the hydrate dissociation rate into a 1D numerical model in order to predict the gas production from a sandstone core. They were able to match the experimental results by reducing the kinetic rate constant by a factor of 10^{-5} from the base value reported by Kim et al. [10]. In addition, incomplete coupling of heat transfer and the imperfection in estimating the specific surface area involved in the

hydrate reaction limited the applicability of their results. Nazridoust and Ahmadi [13] and several other researchers [14, 15] conducted 2D numerical studies to match the experimental observation of Masuda et al. [16] by varying the conditions of the thermal boundaries and accounting for the effects of gravity, and of the values of the thermophysical parameters and of the kinetic rate parameters. Their studies are based on the assumption of a homogeneous MH-bearing sediment, which is practically impossible to achieve [17]. Liu and Gamwo [18] compared the use of equilibrium and kinetic models for MH dissociation in a 30.0 cm sandstone core sample and recommended the use of a rate-dependent kinetic model for MH dissociation studies. However, without validation against experimental observations, their results (a) could only indicate that the two models can exhibit significant deviations in their predictions, but (b) could not provide evidence of the superiority (in terms of correctness) of either.

Tang et al. [19] obtained an estimate of the order of intrinsic MH dissociation constant from their experimental data of gas production from hydrate-bearing cores, but could not reconcile the discrepancies in the response of T between simulation and observation (possibly because of the assumption of uniform S_H distribution). Recently, Zheng et al. [20, 21] investigated the effects of boundary conditions and petrophysical properties on hydrate dissociation using 1D domains with meshes that were too coarse ($\Delta x = 1\text{m}$) to capture the intense chemical and thermophysical localized processes associated with hydrate dissociation. They determined that the location of the dissociation front over time could be described by a power function. Unfortunately, this quantification of the front movement is applicable only to idealized 1D uniform- S_H system but cannot be extended to the multi-dimensional natural [22] or experimental systems [17].

Perhaps the most important contribution of numerical simulators in the study of systems with unknown behavior and lacking analytical solutions (as is the case of hydrate dissociation) is the ability to conduct sensitivity analyses that help determine the dominant factors affecting the system behavior, the relative importance of these factors, and the system response to variations in their values [23]. Additionally, sensitivity analysis can provide valuable insights into the design of appropriate (or even optimal) production strategies (e.g., the optimal number of wells, the best placement of wells and the pressure

drawdown rate) to improve the economics, reduce the risk and quantify the uncertainties [24].

In his 1D study of a constant-pressure production scenario from hydrates, Ji et al. [25] varied several parameters and indicated that the gas production rate is a sensitive function of well pressure, reservoir temperature and permeability. Kowalsky and Moridis [26] compared kinetic and equilibrium reaction models in the simulation of CH₄-hydrate dissociation from a Class-3 hydrate reservoir. Their results indicated that (a) short-term dissociation and production (such as those encountered in laboratory experimental investigations) are best described by a kinetic dissociation model, and that (b) after an initial short period that only lasts a few days at best, the kinetic and the equilibrium reaction models converge and practically coincide in the prediction of long-term production from natural hydrate accumulations. Li et al. [27] employed T+H and conducted a sensitivity analysis of production from Site SH7 in Shenhu Area and concluded that (a) high permeability and high initial reservoir temperature promotes gas production rate, while (b) the temperature of the well has an insignificant effect. Giraldo et al. [28] used CMG STARS to analyze statistically the sensitivity of the cumulative gas production from a hypothetical hydrate deposit to six key parameters. Their results indicated gas production is enhanced by an increasing absolute permeability, a decreasing bottom-hole pressure and an increasing thermal conductivity of the HBS. A wide range of sensitivity studies of gas production from hydrates in both oceanic deposits and in accumulations associated with the permafrost using various versions of TOUGH+Hydrate (T+H) has been conducted by Moridis et al., e.g. Class 1 [29], Class 2 [30, 31], Class 3 [32], and Class 4 [33].

It is obvious that the development of numerical simulators that account for all known (coupled) physical, thermodynamic and chemical processes involved in hydrate dissociation and formation has improved our capability to predict the fluid production from MH-bearing systems. There is a general agreement on the processes and the associated set of differential equations and boundary conditions that need to be included in the simulators and described in studies [34]. A common assumption in the majority of numerical studies (most often necessitated by the absence of supporting laboratory- or geophysical survey-based investigations) is that the initial spatial distributions of the various phases in the MH-

bearing system are always homogeneous. Significant variations of hydrate saturations (S_H between 0 and 100%) have been identified in the geological media in nature from the core samples extracted from Mallik site [35], Shenhu Area [36], Eastern Nankai Trough [37], and the recent Krishna Godavari Basin [22]. Furthermore, a handful of CT-scan and MRI studies on MH formation and dissociation have provided visual evidence that S_H exhibit spatial variations within the HBS [38, 39].

While natural heterogeneity is a universal reality, the degree to which the assumption of homogeneity can significantly affect predictions and the type of systems (laboratory vs. field) in which this is important are currently unknown, although there are limited indications that heterogeneity appears to enhance production from natural hydrate systems [40, 41]. Laboratory studies can provide significant insights into the hydrate behavior in porous media, as well parameters that are applicable to field studies and operations. Previous and current studies by Yin et al. [42, 43] that analyzed numerically earlier laboratory investigations concluded that creation of hydrate-bearing cores with homogeneous phase saturations is virtually impossible. Without expensive in-situ phase visualization techniques (such as CT-scan and MRI) to quantify and account for the phase heterogeneity in the simulations, it is possible that the inevitable assumption of phase homogeneity adopted in most studies would lead to a situation of simulation and history-matching of the hydrate dissociation and fluid production results being a curve-fitting process rather than a valid description of the physical system. Thus, the integrity of such studies, as affected by heterogeneity in the spatial distribution of the various phases (and especially of S_H), is an important issue that has not been investigated at all. For this reason, and given the knowledge gaps that

- (a) hydrate formation in laboratory cores leads to spatial heterogeneity in S_H inevitably [44]
- (b) in the absence of visualization-based evidence and quantification of heterogeneity, most analyses of laboratory studies on hydrate dissociation assume a homogeneous distribution of the various phases in the cores
- (c) lack of understanding on controlling factors on fluid production in the context of a heterogeneous HBS

We extend our numerical analysis to provide a reference and significant guidance for the numerical simulation of a laboratory-synthesized heterogeneous HBS.

The current study builds on the earlier studies of Yin et al. [17, 42, 43], all of which are based on the numerical investigation of the results of the earlier laboratory studies of Chong et al. [45]. The first paper of that series [17] conducted the numerical analysis of hydrate dissociation in, and fluid production from, an artificial hydrate-bearing sandy core, assuming that the process of hydrate formation (using the excess water technique) had resulted in homogeneous phase saturations. The second paper [42] described in detail the excess-water hydrate formation process that preceded the paper of dissociation [42], and determined that heterogeneity in the phase saturations was practically inevitable under the laboratory conditions of the sample creation.

In this paper, we further analyze numerically the simulation results to identify differences in the fluid production from the two realizations of the samples and to determine if they are sufficiently different, in which case significant doubts would be cast on earlier analyses of laboratory results based on the homogeneous phase saturation assumption. Additionally, we conduct a sensitivity analysis of other factors that could affect hydrate dissociation and fluid production in a laboratory context, in an effort to provide insights that could lead to improved designs for laboratory experiments and (possibly) field applications.

The novelties and the main objectives of this study were as follows:

- (a) the first study to determine the difference (if any) in the dissociation and production behaviour of laboratory cores with uniform and heterogeneous phase saturations;
- (b) to assess the sensitivity to, and the relative importance of, key parameters (associated with the various processes involved in hydrate dissociation) on the rate of hydrate dissociation and fluid (both gas and water) production in laboratory cores with inevitably heterogeneous phase saturations;
- (c) to provide important information for the design and optimization of production strategies

2. The Numerical Model and the Simulation Approach

2.1 The T+H numerical model

The simulations are conducted using the T+H code [46, 47], a compositional numerical simulator developed at the Lawrence Berkeley National Laboratory (LBNL) to model the non-isothermal behavior of MH phase change and fluid flow under conditions typical of CH₄-hydrate deposits by solving the coupled equations of mass and energy balance associated with such systems. Fig. S1 in the supporting information summarizes the key equations that were solved in the T+H code at each time step, which include the mass balance equations for each component (CH₄, H₂O and MH in the kinetic model) and the energy balance equation.

The simulation code can model all the known processes involved in the system response of CH₄-hydrates in complex geologic media, including the flow of fluids and heat, the thermophysical properties of reservoir fluids, the thermodynamic changes and phase behavior, and the non-isothermal chemical reaction of CH₄-hydrate formation and/or dissociation, which can be described by an equilibrium model or a kinetic model [46]. T+H uses a fully-implicit numerical scheme, and its formulation accounts for heat and the various mass components that are partitioned among all possible phases: gas (*G*), aqueous (*A*), and hydrate (*H*). It can handle the phase changes, state transitions, strong nonlinearities and steep solution surfaces that are typical of hydrate formation and dissociation problems. A detailed description of the code, its underlying physics and capabilities of the numerical techniques can be found in Moridis [46, 47].

The T+H code is the most widely used code for simulation of the dynamic behavior of methane hydrate in sandy media. Validation and verification of the T+H code has been achieved through comparisons to laboratory and field observations because hydrate reaction in porous media is complex and strongly nonlinear with no analytical solution [48]. In addition, several benchmark problems involving both reservoir-scale (2007 flow test at the Mount Elbert location in the North Slope of Alaska [40]) and core-scale (laboratory tests conducted by Kneafsey and Moridis [49] and Yin et al. [42, 43]) were tested using the T+H code, which showed excellent agreement between the observation and the simulation results.

2.2 Simulation domain and discretization

Fig. 1a presents the schematic of the reactor. Fig. 1b shows the 2D axisymmetric cylindrical simulation domain, which was constructed using the MeshMaker v1.5 application [50]. The detailed description of the mesh system can be found in [42, 43]. We have conducted a mesh-independent study to confirm the robustness of our simulation results. Three different mesh systems with different grid size varying from 1.0 mm to 2.0 mm to 5.0 mm in the simulation domain representing the hydrate-bearing sediments were designed for hydrate dissociation induced by depressurization. The simulated results on both V_G and M_A showed an average deviation less than 2.0%, which suggests the different mesh systems do not have an effect on the kinetic rate of hydrate dissociation and the fluid production. However, when the mesh size was reduced from 2.0 mm to 1.0 mm, the computational time increased significantly by 10 times.

Thus, based on the results from the mesh-independent study and for maximum accuracy, and from the experience gleaned from previous simulation studies [17, 42, 43], a very fine spatial discretization ($\Delta r = 2.0$ mm) was adopted finally in order to capture the steep temperature and phase saturation gradients that are expected during MH dissociation and not to increase the simulation time significantly. For the reasons discussed in detail in these earlier studies, hydrate dissociation in this numerical investigation was described by a kinetic hydrate dissociation reaction model [51]. The total number of grids in the system is 2065, which resulted in a total of 8260 equations to be solved at each time step.

2.3 Thermophysical properties of the sandy medium and boundary conditions

Table 1 (which also appears in [42]) summarizes the thermophysical properties of the fine quartz sand and of the metal parts of the reactor, as well as the parameters for the constitutive models involved in this study. The composite thermal conductivity model of MH-bearing sediment follows the linear composite model of Bejan [52], which accounts for the effect of all three phases. The earlier work of Yin et al. [42, 43] has shown the superiority of this model in the analysis of the experimental studies. In the absence of direct measurements, the parameter values in Table 1 associated with the relative permeability [53] and capillary pressure [54] were obtained from analogs that are representative of sandy materials.

The kinetic equation of hydrate dissociation follows the Kim-Bishnoi [10] and the Clarke and Bishnoi [51] models. Note that to account for the effects of the changing surface area of the reaction and of the geometry of the pore system (which is very different from the one that led to the development of these models), the kinetic reaction rate in the T+H model [46] is adjusted through the introduction of a *surface area adjustment factor* F_A , which in essence modifies the reaction rate constant and has been shown to be time-dependent [42, 43]. The F_A factor in this study were evaluated through the history-matching technique of Thomas et al. [55] that minimizes the deviations between the experimental measurement data and the numerical predictions.

Table 2 lists the boundary conditions of the MH-bearing system of the laboratory experiment, as well as (a) the initial (steady-state) pressure and temperature in the hydrate-bearing core and (b) the stoichiometry-based initial estimates of uniform phase saturations. The initial phase saturations for the case of the sample with heterogeneous initial phase saturations is provided by the earlier study of Yin et al. [42], and is shown in Fig. 2. The time-dependent pressure at the production boundary (i.e., the valve at the top of the experimental apparatus, see Fig. 1) is shown in Fig. 3a, and the associated fluid (aqueous and gas phase) production is shown in Fig. 3b. Both are measured experimentally in the study of Chong et al. [45].

2.4 Simulation cases and key parameters studied

The Reference Case in this study is that with the heterogeneous initial spatial distributions of the various phases (see Fig. 2) and is hereafter referred to as Case RH. The next case (hereafter referred to as Case RU) is that of the core which is assumed to have uniformly distributed phase saturations. The study of these two cases was expected to provide an answer to the key question whether the treatment of heterogeneity in laboratory cores leads to significantly different results from those obtained under the assumption of homogeneity, in which case the validity of a significant body of laboratory investigations could be questioned.

Following this key study, we attempted to determinate through sensitivity analysis and an associated statistical analysis the relative importance of the physical and chemical processes (as quantified by their relevant parameters) that are involved in the hydrate

dissociation in cores under common laboratory conditions, as those in the study of Chong et al. [45]. The results of the study were expected to determine whether these parameters could be controlled in the laboratory, and if this was not possible, to identify the ones that could be determined a-priori through laboratory studies, thus limiting the uncertainty in the analysis and predictions by limiting the number of remaining parameters that needed to be estimated by means of history matching.

After evaluating a large number of possible parameters and dismissing outright the ones that are easily controlled in a laboratory setting (such as the pressure and temperature of the system and its boundaries), the sensitivity and statistical analyses focused on 3 parameters: (1) the intrinsic reaction constant K_d^0 of the dissociation equation, (2) the intrinsic permeability k of the porous medium used in the core, and (3) the composite thermal conductivity k_θ of the hydrate-bearing core.

A review of the available literature reveals tremendous variation in the value of K_d^0 in various studies, from 10^{-12} mol/m² Pa s [56] to 10^5 mol/m² Pa s [57]. This can be partially attributed to the different methodologies for its estimation, some of which often lumped the reaction surface area (A_s) into K_d^0 [43]. In our study, the reaction surface area was automatically estimated by the T+H code and varied with time, and the F_A adjustment factor was the same time-dependent optimized function used in the study of Yin et al. [42] and described by the following equation:

$$F_A = 1.32 \times t^{-0.72} \quad (1)$$

where t is the time in hours. For the sensitivity and statistical analyses, the value of K_d^0 was varied by one order of magnitude up and down from the base value ($= 3.6 \times 10^4$ mol/m² Pa s) reported by Clarke and Bishnoi [51]. These are referred to as Cases KA and KB, respectively.

Permeability (k) is one key transport parameters that governs the fluid flow in reservoir and is a function of grain size and its distribution [58]. The base value of k in our study ($= 3.8$ Darcys) was that determined in the earlier studies of Yin et al. [42, 43] using the mercury porosimetry test. This is a very high permeability that is typical of unconsolidated coarse-grained sandy materials and is near the upper limit of k of natural hydrate

accumulations. Considering that the permeability of natural hydrate-bearing media can be lower (especially in oceanic settings, see [22, 41]) and such media may be the target of laboratory investigations, in addition to the base value we included sensitivity and statistical analyses using reduced k values of 0.38 Darcys and 0.038 Darcys, i.e., one and two orders of magnitude lower than the base case. These are cases PA and PB, respectively.

The composite thermal conductivity k_θ used in this study follows the linear model of Bejan [52], and accounts for the effects of the time-variable phase saturations. k_θ is critically important, as it controls the rate of heat exchange with the environment, which is the main driving force fueling the depressurization-based dissociation in these experiments. The linear model of Bejan estimates k_θ as:

$$\lambda_\theta = \lambda_{dry} + \phi \sum_{\beta=A,G,H} S_\beta \lambda_\beta \quad (2)$$

where S is the saturation, the subscript β denotes the phases involved in the calculations (A : aqueous, G : gas, H : hydrate), λ_β is the thermal conductivity of the β phase, and λ_{dry} is the thermal conductivity of the dry (gas filled) sandy porous medium. The parameter of importance (unrelated to the phase saturations) is λ_{dry} , which is an exclusive property of the sandy porous medium. The base case $\lambda_{dry} = 1.2$ W/mK of quartz sand used in this study had been determined through a history-matching and optimization process in the study of Yin et al. [42]. The additional λ_{dry} values considered in the sensitivity and statistical analyses were 0.3 and 2.5 W/mK (Cases TA and TB, respectively), and represented the limiting cases of λ_{dry} values that corresponded to (a) an extremely porous medium with a very high permeability k , and (b) a very fine-textured medium with low k , respectively.

Table 3 summarizes the 8 simulation cases involved in this study. Every simulation involved variation in the parameter or parameters of interest, with all other simulation parameters remaining as in the reference case, Case RH. The analysis of the study on the effect of heterogeneity focused on comparisons of the results of Cases RH and RU, i.e., the evolution of (i) P and (ii) T at specific locations, as well as (iii) the amount of the cumulative gas and water production. These results were also compared with the direct laboratory measurements, which was the basic criterion for arriving at a definitive answer

to the question of the importance of heterogeneity. Additionally, the mass of water and gas in the reactor (computed numerically, but not measured experimentally) was monitored.

For the analysis of the remaining set of six simulations, we monitored (a) the evolution of P , T at specific locations, the mass change of various phases (H , A and G) in the reactor and the cumulative fluid production (A and G) from the pressure outlet; and (b) the spatial distribution of the key variables P , T , S_H , S_A and S_G at specific time. For the statistical analysis, we conducted a 3-level 3-factor full factorial study based on the parameter values discussed earlier in an effort to elucidate further the controlling mechanism, the interactions between the three key parameters and their relative importance.

3. Results and Discussions

3.1 Uniform vs. heterogeneous phase saturation distribution

The results discussed here were obtained from the laboratory observations of Chong et al. [45], as well as from the numerical representation of the same experiments in the simulations of Cases RH and RU. The simulated system involved the reactor in Fig. 1, which initially contains a hydrate-bearing sample created in an earlier experimental process (discussed in [43]). At $t = 0$, a pressure of $P_w = 4.0$ MPa is imposed at the pressure outlet, leading to depressurization and the onset of immediate dissociation because the initial temperature in the reactor (see Fig. 2 and Table 2) is much higher than the equilibrium $T = 4.3$ °C that corresponds to P_w . Two pressure sensors (± 20 kPa) located at the top and bottom outlet of the reactor and twelve temperature monitoring points (± 0.1 °C, locations see Fig. 1a) were installed to acquire the experimental data during hydrate dissociation. It should be noted that the dissociation process does not involve only pure depressurization but a hybrid depressurization and thermal stimulation regime because the water bath surrounding the lower part of the apparatus was kept at $T = 8.0$ °C and becomes a source of heat after the initial sudden drop in P and T in the reactor.

3.1.1 Pressure predictions

Fig. 4a shows the curves describing the evolution of P_{top} and P_{bot} at the locations shown in Fig. 1, (a) as measured in the laboratory experiments of Chong et al. [45], and determined numerically from an optimization process involving history matching of the totality of the

available data from (b) Case RH with heterogeneous initial phase distribution and (c) Case RU with uniformly distributed phase saturation. There is an excellent agreement between the measured data and the results in Case RH, but a measurable difference between these results and those from Case RU.

Thus, the pressure reduction rate is slower in Case RU and lagged that in Case RH. This is attributed to the retardation in the propagation of the pressure change in Case RU that is caused by the assumption of the uniformly high $S_H = 0.40$ and the corresponding severe reduction in the effective permeability k_{eff} near the pressure outlet (see Fig. 1). At the same location, $S_H = 0.10$ in Case RH, and the significantly higher k_{eff} leads to the much faster pressure response evidenced in Fig. 4a.

Note that repeated attempts during the optimization process to have the pressure response in Case RU move closer to the experimental data were not successful because they compromised the agreement of other RU predictions (i.e., T and produced gas and water) with experimental data. This indicates that the problem in the effort to improve the P -match was not caused by weaknesses in the history-matching and the optimization process, but by the (erroneous) assumption of initial phase homogeneity. The obvious conclusions are that (a) the heterogeneous system in Case RH has clearly a superior performance in matching the laboratory data, and that (b) Case RU exhibits significant deviations from the experimental results of the P -evolution, which cannot be further improved by history matching. Consequently, if the *only data* monitored during an experiment are pressures, the assumption of homogeneous phase saturations will lead to unreliable results.

3.1.2 Temperature predictions

It is important to indicate that T -measurements are much less reliable than other monitored variables in laboratory experiments of hydrate dissociation because of some systemic shortcomings. It is not known whether the T probes are in direct contact with the hydrate in the pores (which responds very rapidly to dissociation by lowering the temperature almost instantaneously) or with just grains of the porous medium (in which case the T -response is dominated by the slow conduction and is hampered by the insulating nature of geologic media). Additionally, there is the issue of the retardation of the probe response to T -changes that is a function of the design and the materials involved in its construction.

Finally, there is always the uncertainty of whether the hydrate phase in the pores is continuous or there are localized hydrate-free pockets (in addition to the symmetrical heterogeneity in the phase saturations that was predicted numerically), the existence, location and extent of which is impossible to account for without the benefit of direct visualization. Thus, T -measurements have often a qualitative tinge rather than the authority of a representative quantitative determination.

Fig. 4b shows the evolution of T_{a2} , T_{b2} , T_{a4} and T_{b4} (at the locations shown in Fig. 1) and includes both the laboratory measurements and the numerical predictions (using optimized parameters determined from the history-matching process) from Cases RH and RU. As expected, following an initial short period of T -declines (associated with the fast hydrate dissociation immediately after the pressure is lowered), the temperature at the upper locations (T_{a2} and T_{b2}) was consistently higher than that at the lower section (T_{a4} and T_{b4}) by $\Delta T = 0.5\text{-}1.5\text{ }^{\circ}\text{C}$. This was attributed to the heat influx from the atmospheric boundary into the reactor through the imperfectly insulated upper part of the experimental apparatus, while the lower temperature in the lower part of the reactor is controlled by the cooler water bath. The probes closer to the reactor perimeter (T_{a2} and T_{a4}) responded faster and had a higher T (after the short initial period of intense hydrate dissociation) than the ones closer to the center axis (T_{b2} and T_{b4}) because of the inward direction of heat conduction. A general observation though is that the agreement between observations and numerical predictions based on optimized parameters is not satisfactory in most cases at very early times but is overall good to excellent in the long term when some of the effects discussed in the previous paragraph are attenuated.

The issue though is whether the agreement between the results from the simulations of the Cases RU and RH is satisfactory, thus allowing the far less demanding Case RU with the uniform phase saturations to represent the known and inevitable phase heterogeneity associated with the creation of artificial hydrate samples in laboratory cores. Comparison of the results in the two cases indicate that they are in good agreement, with the temperature predictions in Case RH being consistently higher (but not by much) for reasons probably associated with the locally higher initial hydrate saturations (see Fig. 2) that lead to localized higher composite thermal conductivities and enhanced heat influx.

3.1.3 Fluid production predictions

Fig. 5a shows the cumulative mass production of the aqueous (M_W) and the cumulative volume of the gas phase (V_G) under standard conditions. The match of the experimental data with the predictions from the simulation of Case RH is excellent. The V_G results from the simulation of Case RU with the uniform phase saturations are somewhat lower but still in very good agreement with the Case RH data and the experimental observations. The M_W results from the simulation of Case RU with the uniform phase saturations are consistently lower than those from Case RH and the experimental data, with a maximum deviation of about 20.0 % at about $t = 1.6$ hrs and lower deviations everywhere else (almost zero for $t > 5.0$ hrs). The final mass of water and volume of gas produced in both cases (RH and RU) were practically the same. This tends to indicate that the match of the M_W results between the RU and the RH cases (the latter providing an excellent agreement with the experimental data) ranges from acceptable to very good.

This being the case, it can be argued that, although the simulation of the heterogeneous case is an accurate representation of the ground truth (i.e., the experimental observations, the assumption of a uniform saturation in a standard experimental study of hydrate dissociation (such as the one of Chong et al. [45]) is an acceptable option if the investigation focuses on monitoring the fluid production and the temperature if optimized variables (determined from a history-matching process) are used in the simulation. That having been said, it must be pointed out that the assumption of uniformity in the initial saturations may not lead to a good match with the evolution of experimental pressures, which is likely to result in large deviation in an equilibrium model describing hydrate dissociation.

3.1.4 Predictions of phase masses in the reactor

Fig. 5b presents the evolution of the mass of all phases inside the reactor. The general observation is that numerical predictions from the two cases RH and RU are quite close. This confirms the earlier conclusion that a uniform initial phase saturation in the simulation of Case RU is an acceptable substitute for the more accurate description of heterogeneity in Case RH if only fluid production is the focus of study.

3.1.5 Spatial distributions of P , T , S_H , S_A and S_G

Fig. 6 presents the spatial distributions of P , T and various phase saturations at $t = 10.0$ min and 100.0 min for Case RU and RH. The spatial distributions of P for both cases are practically the same because of the large permeability of the system. The spatial distributions of T show some, but far from drastic, differences which are associated with the differences in the phase saturations (which are substantial). Thus, the S_H distribution in Case RH exhibits a concave ‘U’ shape with varying $S_H = 0$ near the top pressure outlet and $S_H = 0.45$ near the bottom boundary (see Fig. 6c). On the contrary, S_H in Case RU maintains almost symmetric as cylindrical shape, with lower S_H values along the outer surface of the core (where dissociation is at a maximum) and higher S_H toward the center. This pattern persists for the duration of the simulation. The same substantial differences in their spatial distributions and their patterns between cases RH and RU are observed in the aqueous and gas saturations, with the RH results showing substantial heterogeneities. A remarkable observation gleaned from these figures is that, contrary to expectations, similar temperatures and fluid production results are obtained despite drastic differences in the spatial saturations of the various phases.

3.1.6 Energy efficiency ratio

To further evaluate the potential of gas production from hydrate-bearing sediments induced by depressurization from the energy perspective, we computed the energy consumption for the base case (Case RH) by monitoring the heat inflow from the reactor boundary (top surface, bottom surface and the circumferential surface) into the reactor over time. The heat inflow was integrated over time to estimate the total energy input and then for the evaluation of the overall energy efficiency ratio (EER). EER was used to evaluate the economic-viability of the hydrate recovery technology in a number of hydrate dissociation experiments [11, 12] and field production tests [59]. EER is defined as the ratio of the energy content of the produced CH_4 (Q_R) to the total heat input (Q_I) to the system of MHBS as shown:

$$EER = \frac{Q_R}{Q_I} = \frac{V_G(t) \times Q_C}{\int_0^t Q_S(t)} \quad (3)$$

where V_G is the cumulative volume of produced CH_4 , Q_C is the lower heating value of CH_4 ($3.58 \times 10^7 \text{ J/m}^3$) and Q_S represents the heat inflow from the reactor metal boundary to the HBS at time, t .

Fig. 7 presents the evolution of the cumulative energy released, Q_R and the cumulative energy input into the system, Q_I and the estimated EER over time for Case RH. It is observed that Q_R increased with the same trend as V_G (see Fig. 3), and Q_I increased at a much slower rate initially and yielded an initial peak of $\text{EER} = 430$ at $t = 0.01 \text{ hr}$. This is attributed to the relatively slow rate of the heat conduction upon depressurization, and the specific heat in the MHBS system mainly fuels the initial fast hydrate dissociation. This is also corroborated by the initial sharp temperature decrease as observed in Fig. 4b.

After the initial peak, EER of the system kept decreasing rapidly over time because of the increasing rate of heat inflow from surrounding to the reactor and accounts for the hydrate dissociation. After $t = 1.0 \text{ hr}$, EER decreased at a much attenuated rate towards the end of the dissociation process, which indicated that the system is practically generating a constant energy return for the energy input. The evolution of EER over time also confirms that the energy used for hydrate dissociation transits from initial specific heat of the MHBS to the later heat inflow from the surrounding (that is the circulating water bath and the ambient air). At the end of the dissociation process, the cumulative energy input plateaued to $Q_I = 63.2 \text{ kJ}$. Given the produced V_G is 20.4 L with a total energy released of 730.7 kJ , the estimated EER in Case RH yielded 11.6 . This value is larger than 1 and slightly higher than the EER values ($6.2\text{--}11.4$) reported by Selim and Sloan [11], which shows very promising energy efficiency of the depressurization test in this study.

3.2 Sensitivity variation: kinetic rate constant (K_d^0)

The second part of the study involved a sensitivity and statistical analysis of the fluid production behavior of this typical experimental system, in an effort to (a) assess the effect of variations in key transport parameters on the dissociation behavior, and (b) to determine the relative importance of these parameters. This information is useful in the design of laboratory experiments, as it provides a guide as to the inputs in which the investigation will need to focus in order to minimize uncertainties and enhance the reliability of the results. As discussed earlier, the parameters in which we focused are (a) the intrinsic kinetic

rate constant of hydrate dissociation K_d^0 , the intrinsic permeability k , and (c) the thermal conductivity of the sandy porous medium, λ_{dry} . Note that all simulations in this part of the study are conducted using the heterogeneous initial phase distribution, which has been shown to accurately represent the laboratory observations [42].

3.2.1 Evolution of P and T

To simulate the effect of the kinetic rate constant K_d^0 , we reduced it by a factor of 10 (Case KA) and increased by a factor of 10 (Case KB) from the base value $K_d^0 = 3.6 \times 10^4 \text{ mol/m}^2 \text{ Pa s}$ [51], while maintaining the same function of F_A used in Case RH. Fig. 8a shows that the evolution of P_{top} and P_{bot} is practically the same in all three cases. The evolution of T_{a4} and T_{b4} , however, showed drastic difference among the three cases (Fig. 8b), with the lowest temperatures associated with the highest K_d^0 . This was expected because a higher K_d^0 is associated with faster and more intense dissociation, leading to lower temperatures because of the strong endothermic nature of the dissociation reaction. Actually, Case KB (with the highest K_d^0) is the only one in which T_{min} reaches the equilibrium $T_{eq} = 4.2 \text{ }^\circ\text{C}$ at $P = 4.0 \text{ MPa}$, which indicated that the enthalpy of the intense dissociation ($\Delta H = 56.9 \text{ kJ/mol}$ [60]) significantly exceeded the influx of heat from the surroundings. In all other cases, T_{min} exceeded T_{eq} , indicating the effect of significant heat influxes that could not be countered by the cooling caused by slower dissociation. As expected, the temperature was always lower close to the core boundaries because these were the locations (as opposed to near the core center) where hydrate saturation was higher, and the dissociation was at more intense rate.

3.2.2 Evolution of fluid production and mass in the reactor

The cumulative amounts of both the produced V_G and M_W increased with an increasing K_d^0 (see Fig. 8c). The differences were very significant. The largest K_d^0 (Case KB) led to a $V_G = 23.5 \text{ L}$ that was about 1.2 times larger than in the reference Case RH and about 8 times larger than in Case KA with the lowest K_d^0 . The effect was much less pronounced in the value of M_W in the three cases because of the aqueous-rich environment for hydrate-bearing sediments.

The sum of the aqueous and gas masses that (a) were produced through the pressure outlet and (b) remain in the reactor at the end of the experiment is the same in Cases RH and KB

because of the exhaustion of the finite mass of hydrate initially in the reactor, but differs in Case KA because the low K_d^0 is insufficient to cause exhaustion (complete dissociation) of the hydrate in the time-frame of the experiment (Fig. 8d). The final gas mass in the reactor in Case KB is lower than that in Case RH because less gas has been produced (lower V_G) for the low K_d^0 (Fig 7c). Conversely, the water mass remaining in the reactor in Case KB was larger than that in Case RH because the latter had a larger M_W (Fig. 8c). Case KA has the lowest mass of water and gas in the reactor because of the incomplete dissociation of hydrate.

3.2.3 Spatial distributions of P , T , S_H , S_A and S_G

The spatial distributions of these variable for the reference Case RH have been discussed in [42], and are included in the leftmost column of Fig. 9 for reference purposes. Fig. 9a shows a uniform distribution of $P = 4.0$ MPa in all three cases at $t = 1.0$ hr. The remaining distributions show the effects of slower and faster dissociation and are entirely consistent with expectations. The spatial distribution of T in Fig. 9b shows an enlarged cold region ($T_{min} = 5.0$ °C, much colder than in the reference Case RH) in the center of the reactor in Case KB, but the temperature decline is much lower in Case KA with the lowest K_d^0 . The volume of $S_H > 0$ is the smallest in Case KB and the largest in Case KA (where the largest S_H levels are encountered) in Fig. 9c for the reasons already discussed. The aqueous S_A and gas S_G saturations distributions reflect the difference in the dissociation rates of the three cases. The intense dissociation in Case KB results in the higher S_A and S_G , as well as the largest amounts of water and gas in the reactor, while the opposite occurs in Case KA because of limited dissociation. These visual observations are consistent with the information provided by Figs. 8d and 8e.

3.3 Sensitivity variation: absolute permeability (k)

3.3.1 Evolution of P and T

In T+H [46], adjusting k affects the estimation of the reaction surface area and the hydrate particle radius because of the empirical Kozeny-Carman equations used for the estimation of these parameters when applying the kinetic model of Clarke and Bishnoi [46]. Thus, to ensure that the same hydrate surface area was used in the sensitivity study, the hydrate particle radius was kept the same ($r_h = 24.2$ μm) as in the reference Case RH.

Fig. 10a shows the evolution of P_{top} and P_{bot} over time in the 3 difference permeability cases, i.e., Case FA (when $k = 0.38$ Darcys), Case FB (when $k = 0.038$ Darcys) and the reference Case RH (in which $k = 3.8$ Darcys). Note that the permeabilities in cases FA and FB represent much finer media and not necessarily sands (in which a $k = 0.038$ Darcys is highly unlikely).

Unlike the case of K_d^0 , a reduction in k has a profound effect on the pressure behavior. An increasing permeability is associated with an earlier reduction in P because of the limited resistance to flow through fluid removal from the pressure outlet and the consequent faster depressurization. Additionally, a higher k results in a sharper decline in P . Thus, the time for P to reach its final plateau increases from 2.4 min in Case RH (with the highest k) to 12.0 min in Case FA to 180.0 min in Case FB). The effect of the lower k is at its extreme in T_{bot} of Case FB because of the larger distance of the sensor from the pressure outlet and the very low in the intervening space. Actually, the effect is so significant that the pressure at a location next to the outlet (decreasing with k) is below the dissociation pressure because the low permeability locally maximizes the level of depressurization in the vicinity of the outlet while not permitting warmer fluids from deeper in the core to reach that point.

Fig. 10b shows the evolution of T_{a4} and T_{b4} over time. There is very little difference between the results of the two highest- k cases (RH and FA), which appears to indicate that the both exceed a threshold above which T does not change with varying k . Following an initial decline caused by the effect of the intense initial hydrate dissociation, T increases because of heat influx through the boundaries through a process discussed earlier in this paper and in the work of Yin et al. [42]. The picture is different for Case FB, which is slower to react because the low k (the lowest of the 3 cases) does not allow depressurization to be felt deeper in the core where the T -sensors are located, thus delaying dissociation and the initial reduction in T . The temperatures in the 3 cases eventually (after about 1.0 hr) converge under the combination effect of water bath and ambient atmosphere temperature.

3.3.2 Evolution of fluid production and mass in the reactor

Fig. 10c shows a diverging behavior between the evolutions of the cumulative mass of produced water M_W and the cumulative volume V_G of the produced gas (through the pressure outlet) as k varies: an increasing k is associated with an increasing M_W but also

with a decreasing V_G . The reason for this behavior is that the aqueous phase dominates early in the process because the initial state of the system involves only the solid hydrate and the liquid water, resulting in the highest possible level of relative permeability to water. Conversely, gas evolves later upon the initiation of dissociation and its relative permeability has to increase from zero (initially) to a higher level. Consequently, gas production is delayed not only because of the advantageous initial effective permeability of the aqueous phase, but also because the lower permeability does not allow easy movement toward the pressure outlet.

A corollary of this observation is that the relative amounts of aqueous and gas phases remaining in the reactor follow the opposite pattern for the reasons discussed above: an increasing k is expected to be associated with a lower mass of water and a higher mass of gas in the reactor. This is confirmed by the results in Fig. 10d. Because of complete dissociation in all 3 cases, larger amounts of produced fluids will leave lesser amounts in the reactor. The assumption of a permeability threshold (above which k seems to have a very limited effect on T and the hydrate mass in the reactor during laboratory experiments of dissociation) appears to be valid because of the coincidence of the curves describing the evolution of hydrates in the higher- k Cases RH and FA. The lowest- k Case FB shows a delay in the hydrate saturation, indicating that the lower k lowers the dissociation rate.

3.3.3 Spatial distributions of P , T , S_H , S_A and S_G

Fig. 11 compares the spatial distribution of key variables for $k = 3.8$ (Case RH, left column, as presented earlier in Yin et al. [42]), $k = 0.38$ Darcys (Case FA, middle column) and $k = 0.038$ Darcys (Case FB, right column) at $t = 1.0$ hr. The patterns of the various parameters are the same in all three cases, with smaller differences between the distributions in Cases RH and FA, and larger differences (mainly in the phase saturations, with S_H being higher) between Case FB and the other two cases. Review of the visualization results of the phase distributions confirm the conclusions and insights gleaned from Figure 9, i.e., an increasing k is associated with an increasing amount of gas and a decreasing amount of water in the reactor. It should be noted that such intervention of fluid production is commonly expected in a core-scale experiment, where the effect of boundary is significant; whereas in a

reservoir-scale production scenario, such behavior is rare and can only be expected towards the full depletion of the hydrate reservoir.

3.4 Sensitivity variation: thermal conductivity of sandy medium (λ_{dry})

3.4.1 Evolution of P and T

The evolution of P_{top} and P_{bot} in Cases RH ($\lambda_{dry} = 1.2$ w/mK), TA (lower $\lambda_{dry} = 0.3$ W/mK) and TB (higher $\lambda_{dry} = 2.5$, much higher than values reported for sandy sediments) in Fig. 12a shows the insignificant to negligible effect of λ_{dry} on the pressure behavior. It appears that the pressure behavior in this type of laboratory experiments is controlled exclusively by k (Fig. 10a), as the variations in K_d^0 (Fig. 8a) and λ_{dry} (Fig. 12a) do not seem to have any measurable impact. Conversely, λ_{dry} plays an important role in the evolution of temperatures, which Fig. 12b shows to be consistent with expectations: an increasing λ_{dry} results in a higher composite thermal conductivity and enhances heat influx through the boundaries, thus leading to higher temperatures and earlier attenuation of the T -disturbance (decline) caused by the intense hydrate dissociation at early times. A decreasing λ_{dry} is associated with decreasing temperatures that persist for long time, thus delaying heat influx from the boundaries and causing a slower recovery from the temperature low level associated with the initial intense hydrate dissociation when depressurization is at its maximum.

3.4.2 Evolution of fluid production and mass in the reactor

The effect of an increasing λ_{dry} on the cumulative amounts of water (M_W) and gas (V_G) produced through the pressure outlet in the three Cases RH, TA and TB is shown in Fig. 12c and conforms to expectations: for a given K_d^0 and k , a higher λ_{dry} leads to higher amounts of M_W and V_G . Unlike the observations in Figure 9d that demonstrated the effect of k , Figure 12d shows that an increasing λ_{dry} results in increasing amounts of gas and water in the reactor. The reason for this behavior is the higher rate of dissociation related to λ_{dry} , as the resulting higher composite thermal conductivity provides larger amounts of heat to fuel dissociation. This is evident from the evolution of the hydrate mass in the reactor, which shows that a faster decline corresponds to a higher λ_{dry} .

3.4.3 Spatial distributions of P , T , S_H , S_A and S_G

The visual observations of the spatial distributions of key variables at $t = 1.0$ hr in the three cases RH, TA and TB are shown in Fig. 13 and confirm the observations from Fig. 12 (in which the leftmost column reflects results obtained in the earlier study of Yin et al. [42]). The lowest λ_{dry} in Case TA is associated with the largest temperature drop because of the slowest influx of heat from the boundaries, and this is clearly reflected in the b2 panel in Fig. 13. The decreased rate of hydrate dissociation results in the larger amounts of hydrate and the lower amounts of water and gas in panels c1, d1 and e1, respectively. The situation is the opposite along the third column of panels that correspond to the highest λ_{dry} in Case TB: the amount of hydrates is the lowest in the three cases, while the amounts of water and gas in the reactor are the highest (see panels c3, d3 and e3, respectively).

3.5. The 3^3 full factorial design of experiment

To further elucidate the controlling mechanism and the interactions between the three key parameters (namely k , K_d^0 , and λ_{dry}) and their effects on the produced amounts of gas V_G and water M_W , we designed a 3-level 3-factor full factorial Design of Experiment (DOE). The three factors are denoted as 1st Factor (K_d^0), 2nd Factor (k) and 3rd Factor (λ_{dry}), and the three levels of each factors are denoted as 0 (low value), 1 (intermediate value), and 2 (high value). Thus, there are $3 \times 3 \times 3 = 27$ combinations in total. A statistical software (Minitab 19 [61]) was used to analyze the simulated data for statistical significance. Table 4 summarizes the values of the parameters used in the 27 combinations, together with the simulated predictions of V_G and M_W at $t = 1.0$ hr. The reason for the selection of only the $t = 1.0$ hr results is because this is the time at which the simulation for the high K_d^0 value stops when dissociation is complete and there are no further changes in the system. Analysis of variance (ANOVA) and F -test were carried out to test the differences in the means (for variables or groups) for statistical significance. Table 5 summarizes the ANOVA results for this study. The modelled sum of squares (SS_{Model}) is 1613.43 for V_G and 24324.7 for M_W and both account for over 99.0 percent of the total variability in the fluid production.

Figs. 13a and 13b present the normal probability plot of the errors on V_G and M_W , and suggest that there is a good normal distribution of the errors. The residuals that are

independent of the observations ensure the reliability of the fitted model and the ANOVA analysis [62]. Figs. 14a and 14b show the main effects of the varying factors on V_G and M_W . K_d^0 appears to be the most important variable and has the largest slope, indicating that any change in its level greatly affects the response variables. Increasing both K_d^0 and λ_{dry} have a positive effect on the production rate of V_G and M_W . However, increasing k enhances the production rate of M_W at all levels, but its effect on the production rate of V_G is not linear: a high value of k resulted in a decrease in the production rate of V_G for the reasons discussed in Section 3.3.2.

Figs. 15a and 15b show the Pareto chart of the effects on V_G and M_W and include the absolute values of the standardized effects, from the largest effect to the smallest effect. The factors that cross the reference line at 2.31 (t -value with a 95% confidence level) are statistically significant at the 0.05 level. The Pareto chart suggests five main effects of the variations in the three factors on both V_G and M_W but they follow different order. In terms of V_G , the main effects follow the order of $K_d^0 > \lambda_{dry} > K_d^0 + \lambda_{dry} > k > K_d^0 + k$. In terms of M_W , they follow the order of $K_d^0 = k > \lambda_{dry} > K_d^0 + \lambda_{dry} > K_d^0 + k$.

To conclude, K_d^0 appears to be the most significant parameter controlling the levels of V_G and M_W . λ_{dry} contributes significantly to the produced gas amount V_G and k dominates the produced water mass M_W . These findings provide a comprehensive understanding of the relative importance of the different groups of parameters and, because composite variations of more than one factors do not appear to be as significant, provide support to our earlier analysis in the sensitivity study that involved varying parameters one factor at a time.

4. Conclusions

The present study was designed to determine (a) the importance of heterogeneity in the prediction of hydrate behavior, and (b) the relative importance of key transport and kinetic rate parameters on fluid (gas and water) production from a non-uniform hydrate-bearing sample experiencing depressurization-induced dissociation by means of sensitivity and statistical analysis. The results of this study suggest the following conclusions:

1. In the absence of experimental methods that can quantify the phase saturations in experimental cores through visualization, numerical simulation provides an

- alternative that can describe the inevitable heterogeneity in the samples [42]. In numerical studies analysing the system behaviour and fluid production, the approximation of an artificial (laboratory-made) hydrate-bearing core with heterogeneous phase saturations by an assumption of uniform phase saturation distributions is valid except for the very early stages of the dissociation process.
2. While accounting for the initial phase heterogeneity yields results that can very accurately match laboratory measurements after an optimization (history-matching process), the determination of these initial phase saturation distributions is a demanding and cumbersome process, requiring faithful numerical representation of all the stages in the sample preparation (see Yin et al. [43]) and history-matching of the results in each one of these stages. Under the standard experimental conditions described in this paper, the assumption of initial homogeneity in the phase saturations is a much simpler and easier stoichiometry-based process, yielding results (cumulative amounts of produced gas V_G and water M_W , and temperatures in the core) that range from an acceptable to an excellent match of those from the heterogeneous study, especially in the long run. The maximum deviations in these parameters do not exceed 20.0 % early in the dissociation process and decrease monotonically with time. However, the agreement of the pressure evolutions in the two approaches is consistently unsatisfactory, which is attributed to the high permeability reduction in the uniform sample.
 3. The sensitivity analysis yielded results that confirmed to expectations: under the laboratory conditions in this study, an increasing K_d^0 increases the cumulative amounts of produced gas V_G and water M_W because of faster dissociation rate, as does an increasing λ_{dry} because of faster heat influx from the boundaries to sustain the endothermic dissociation reaction. A more complicated situation occurs with an increasing permeability k : water production increases because of the advantageous initial relative permeability to the aqueous phase, but gas production decreases because of the initial adverse regime of relative permeability to gas caused by the enhanced aqueous flow.
 4. The statistical analysis indicated that the relative importance of the three factors (K_d^0 , k and λ_{dry}) follows the order $K_d^0 > k > \lambda_{dry}$, each differing from the next one in

the descending order by about one order of magnitude. This provides insights into sound laboratory practices that can improve the conclusions reached by laboratory studies. K_d^θ ranging very widely [13, 42, 51], it appears that a sensible approach is to first determine experimentally and accurately k and λ_{dry} , and with the minimization of the associated uncertainties, to focus on the determination of an accurate K_d^θ estimate through a history-matching and optimization process of the laboratory data.

Nomenclature

ANOVA	analysis of variance
CT	computer tomography
F_A	surface area adjustment factor (dimensionless)
ΔH	enthalpy of hydrate dissociation reaction (kJ/mol)
k	absolute permeability (Darcys)
λ_{dry}	thermal conductivity of sand at dry condition (W/m K)
λ_θ	composite thermal conductivity (W/m K)
λ_β	thermal conductivity of the β phases (W/m K)
K_d^0	kinetic rate constant (mol/m ² Pa s)
MH	methane hydrates
MRI	magnetic resonance imaging
M_W	cumulative production of the aqueous mass (g)
N_H	hydration number
P	pressure (MPa)
P_{top}	pressure at top line (MPa)
P_{bot}	pressure at bottom line (MPa)
Q_C	low heating value of CH ₄ (J/m ³)
Q_I	cumulative heat inflow from reactor boundary to MHBS (J)
Q_R	cumulative heat released from produced CH ₄ (J)
Q_S	heat flow from reactor boundary to MHBS (W)
S_H	saturation of hydrate phase
S_A	saturation of aqueous phase
S_G	saturation of gas phase
T	time (hr)
T	temperature (°C)
T_{eq}	equilibrium temperature of methane hydrate (°C)
T+H	TOUGH+Hydrate code
ΔT	temperature difference (°C)
V_G	cumulative production of the gas phase volume (L)

Acknowledgement

The financial support from the National University of Singapore (R-261-508-001-646 and R-261-508-001-733) is greatly appreciated. Zhenyuan Yin would like to thank the LRSPL and EDB for the industrial postgraduate program (IPP) scholarship.

Tables

Table 1: Thermophysical parameters and constitutive models used in Case RH.

Parameter	Value
Hydration number (N_H)	6.0
Absolute permeability (k)	$k_r = k_z = 3.83 \times 10^{-12} \text{ m}^2$
Porosity of sandy medium (ϕ)	0.448
Absolute permeability of pressure outlet (k_w)	$k_r = 0$ and $k_z = 5.0 \times 10^{-9} \text{ m}^2$
Porosity of pressure outlet (ϕ_w)	1.0
Density of quartz sand (ρ_s)	2650 kg/m ³
Density of SS316 (ρ_{ss})	8000 kg/m ³
Thermal conductivity of sand (λ_{dry})	1.20 W/m K
Specific heat of quartz sand (C_R)	800 J/kg K
Thermal conductivity of SS316 (λ_S)	16.0 W/m K
Specific heat of SS316 (C_S)	500 J/kg K
Thermal conductivity of water (λ_{water})	0.60 W/m K
Thermal conductivity of air (λ_{air})	0.024 W/m K
Thermal conductivity of MH (λ_h)	0.45 W/m K
Composite thermal conductivity model (k_θ) [46]	$\lambda_\theta = \lambda_{dry} + \phi(\lambda_A S_A + \lambda_H S_H + \lambda_G S_G)$
Relative permeability model (Stone's model [53])	$k_{rA} = \left(\frac{S_A - S_{irA}}{1 - S_{irA}} \right)^{n_A}$
	$k_{rG} = \left(\frac{S_G - S_{irG}}{1 - S_{irG}} \right)^{n_G}$
n_A	5.0
n_G	3.5
S_{irA}	0.05
S_{irG}	0.01
Capillary pressure model (vG model [63])	$P_{cap} = -P_0[(S^*)^{-1/m} - 1]^{1-m}$
	$S^* = \frac{S_A - S_{irA}}{S_{mxA} - S_{irA}}$
S_{irA}	0.049
M	0.50
P_0	$5 \times 10^3 \text{ Pa}$
S_{mxA}	1.00
Hydrate reaction kinetic model (Kim et al. [10])	$n_H = F_A K_0 A_S \exp\left(\frac{-\Delta E}{RT}\right)(f_{eq} - f_g)$
Hydration reaction constant (K_0)	$3.6 \times 10^4 \text{ mol/m}^2 \text{ Pa s}$
Activation energy (ΔE)	81.0 kJ/mol
Reaction surface area (A_S)	Moridis [46]
Hydrate particle radius (r_h)	24.2 μm
Surface area adjustment factor (F_A)	$F_A = 1.32 \times t^{-0.72}$ (Yin et al. [17])

Table 2: Initial and boundary conditions of the MH-bearing sample.

Initial and Boundary Condition	Value
Gas composition	100% CH ₄
Initial pressure	6.2 MPa
Initial average temperature	8.4 °C
Bottom-hole pressure (P_w)	Time-dependent (Fig. 3a)
Initial average hydrate saturation (S_H) – RU Case	0.40
Initial average aqueous saturation (S_A) – RU Case	0.58
Initial average gas saturation (S_G) – RU Case	0.02
Circulating-water boundary temperature (T_{bath})	8.0 °C
Ambient air boundary temperature (T_{air})	22.0 °C

Table 3. List of simulation cases with various parameters studied.

Case No.		λ_{θ} (W/m K)	k (Darcy)	K_d^{θ} (mol/m ² Pa s)	Mechanism to be studied
1	Case RH	Linear Composite Model $\lambda_{dry} = 1.2$	3.8	3.60×10^4	Base case - Heterogeneous
2	Case RU	Same as Case RH			Uniformity/Homogeneity
3	Case KA			3.60×10^3	Kinetic rate effects
4	Case KB			3.60×10^5	
5	Case PA		0.38		Permeability effects
6	Case PB		0.038		
7	Case TA	Linear Composite Model $\lambda_{dry} = 0.3$			Thermal effects
8	Case TB	Linear Composite Model $\lambda_{dry} = 2.5$			

Table 4. Summary of V_G and M_W at $t = 1.0$ hr for all 27 combinations in the 3^3 design of experiment.

1 st Factor: Kinetic rate constant, K_d^0 (mol/m ² Pa s)	Response Variable	2 nd Factor: Absolute permeability, k (D)								
		0.038			0.38			3.8		
		3 rd Factor: Thermal conductivity of sand, λ_{dry} (W/m K)								
		0.3	1.2	2.5	0.3	1.2	2.5	0.3	1.2	2.5
3.60×10 ³	V_G (L)	1.35	1.53	1.60	1.72	1.99	2.10	0.90	1.20	1.34
	M_W (g)	53.97	55.15	55.58	57.07	58.41	59.00	78.25	78.99	79.27
3.60×10 ⁴	V_G (L)	7.95	9.99	11.07	9.78	12.60	14.12	9.49	12.52	14.16
	M_W (g)	73.35	76.98	78.72	77.19	81.72	84.00	90.43	93.64	95.48
3.60×10 ⁵	V_G (L)	14.39	19.16	21.76	16.26	21.48	23.53	15.94	21.26	23.20
	M_W (g)	117.01	126.01	130.81	121.21	130.43	134.05	136.30	143.84	147.49

Table 5. Analysis of variance on V_G and M_W from the 3^3 full factorial design of experiment.

Source of Variation	Degrees of Freedom	Sum of Squares (V_G)	F_0	P -Value	Sum of Squares (M_W)	F_0	P -Value
Model	18	1613.43	1437.82	<0.001	24324.7	9118.50	<0.001
K_d^0	2	1483.62	11899.22	<0.001	22021.8	74396.93	<0.001
k	2	13.27	106.44	<0.001	1927.3	6502.28	<0.001
λ_{dry}	2	71.48	573.27	<0.001	205.8	694.16	<0.001
$K_d^0 + k$	4	6.57	26.36	<0.001	70.0	118.02	<0.001
$K_d^0 + \lambda_{dry}$	4	38.16	153.04	<0.001	97.9	165.21	<0.001
$k + \lambda_{dry}$	4	0.34	1.35	0.33	2.0	3.36	0.07
Error	8	0.50			1.2		
Total	26	1613.93			24325.9		

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