Performance of theoretical models in predicting permeability of hydrate bearing sands

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ABSTRACT
Depleted natural gas reservoirs offer significant potential for simultaneous recovery of enhanced coalbed methane and carbon sequestration via clathrate hydrate formation. A major factor affecting the clathrate hydrate formation and that of methane dissociation is the variation of permeability of the porous media in the presence of gas hydrates. In the absence of reliable experimental data, several permeability models have been proposed to establish the relationship between gas hydrate saturation and permeability. In this paper, we introduce a quantitative performance measure to evaluate the effectiveness of a permeability model in fitting the experimental data. Secondly, a novel hybrid model based on the weighted combination of pore-filling and grain coating model is proposed. Experimental permeability and hydraulic conductivity measurements of gas hydrate bearing sands at different carbon dioxide and R-11 synthetic hydrate saturations were used to assess the prediction performance of various permeability models.

RÉSUMÉ
Appauvri réservoirs de gaz naturel offrent un potentiel considérable pour la récupération simultanée de méthane de houille et à la séquestration de carbone par la formation d'hydrates clathrates. Un facteur important affectant la formation de clathrate hydrate et celle de la dissociation du méthane est la variation de la perméabilité du milieu poreux en présence d'hydrates de gaz. En l'absence de données expérimentales fiables, plusieurs modèles de perméabilité ont été proposées pour établir la relation entre la saturation des hydrates de gaz et de la perméabilité. Dans cet article, nous introduisons une mesure de performance quantitatifs pour évaluer l'efficacité d'un modèle de perméabilité en ajustant les données expérimentales. Deuxièmement, un modèle hybride roman basé sur la combinaison pondérée d'un pore de remplissage et le modèle enrobage des grains est proposé. Perméabilité expérimentale et mesures de conductivité hydraulique de l'hydrate de gaz sables aurifères au dioxyde de carbone différente et R-11 de synthèse saturations hydrate ont été utilisés pour évaluer les performances de prévision de modèles de perméabilité différents.

1 INTRODUCTION

Geological formations such as depleted natural gas have received considerable interests for being potential carbon dioxide (CO_2) sequestration sites (White et al. 2005). Besides, depleted natural gas reservoirs offer significant potential for simultaneous recovery of enhanced coalbed methane and carbon sequestration via clathrate hydrate formation (White et al. 2005). Storage of CO_2 in clathrate hydrate form is greatly appealing as clathrate hydrate contains 144 m^3/m^3 of CO_2 to H_2O and thereby providing storage of 12 times or more when compared to gaseous form (Shaw 2003).

The thermodynamic preference of clathrate hydrate formation over that of methane has been well established. However, an equally important phenomenon, the flow of CO_2 and subsequent clathrate hydrate formation in the presence of methane gas is poorly understood. A major factor affecting the carbon dioxide hydrate formation and the methane dissociation is the permeability in the presence of gas hydrates. The permeability variation is known to greatly influence the dissociation properties of gas hydrates within the porous media (Hong 2003). While moderate dissociation of gas hydrates is expected with lower permeability, considerable dissociation occurs when hydrate zone has some permeability (Kumar 2010). Nevertheless, permeability variation in the presence of decomposing gas hydrates is not well understood (Kumar 2005). Moreover, measuring the permeability of gas hydrate bearing sediments (GHBS) is particularly difficult due to the transient nature of gas hydrate (Lee 2008).

In the absence of reliable experimental data, various theoretical models have been proposed to characterize the nature of pore scale interactions between gas hydrates and the GHBS (Lee and Collett 2001; Klienberg et al. 2003). The reported theoretical models predict the permeability changes assuming a specific hydrate formation habit (Klienberg et al. 2003). However, these theoretical models show large variations in predicted permeability for a given hydrate saturation due to different hydrate growth habit assumptions.

Recent studies involved acoustic and seismic data to understand the pore-space growth habit of hydrates within GHBS (Berge et al., 1999; Helgerud, 2001; Lee and Collett, 2001). Tohidi et al. (2001) investigated the hydrate formation using the tetrahydrofuron (THF), methane gas, and carbon dioxide in glass micromodels that represented the porous media. Kleinberg et al. (2003) employed nuclear magnetic resonance (NMR) measurements to quantify pore-size control of hydrate bearing formations.

More recently, Kumar et al. (2010) carried out series of permeability measurements at different CO_2 hydrate saturations using glass beads as the porous medium. Ordonez and Grozic (2009) used R-11 synthetic hydrate and measured the hydraulic conductivity of Ottawa sand

samples at various hydrate saturations. Both Kumar et al. (2010) and Ordonez and Grozic (2009) reported grain coating behaviour at low hydrate saturations at 35 and 45 percent respectively. Pore-filling behaviour was observed for higher hydrate saturations.

The effectiveness of a permeability model in predicting the experimental data has been largely carried out in qualitative fashion. Alternatively, quantitative comparison can provide a better means to assess the suitability of a permeability model in fitting the experiment data. Secondly, the existence of grain coating at low hydrate saturation and that of pore-filling at high saturation indicates that these models can be combined in optimal fashion to determine the permeability over a range of hydrate saturations.

In this paper, we introduce a novel quantitative performance measure to assess the effectiveness of a permeability model in fitting the experiment data. Secondly, we propose a novel hybrid model which optimally combines both grain coating and pore-filling model to consistently predict the permeability over the a range of hydrate saturations.

2 PERMEABILITY MODELS

The permeability of GHBS is largely influenced by the gas hydrate formation habit within the porous media. For instance, the permeability of GHBS partially saturated with hydrate depends significantly on where and how the hydrate forms in the pore space. Klinberg et al. (2003) discussed a number of permeability models on the pore scale interaction of hydrates within porous media. These permeability models are summarized in the following sections.

2.1 Parallel Capillary Model

The parallel capillary model is the simplest model, which relates the permeability to the porosity based on the pore geometry. The parallel capillary model is further classified into two types depending on hydrate formation habit. If the hydrate uniformly coats the walls, the relative permeability is given by,

$$k_{rw} = (1 - S_h)^2 \qquad [1]$$

where S_h is the gas hydrate saturation, defined as volume of hydrate per volume of voids. In Eq. [1], the relative permeability is defined as the ratio of permeability at specific hydrate saturation (k) to that of initial permeability (k_0). That is,

$$k_{rw} = \frac{k}{k_0} \qquad [2]$$

On the other hand, if the hydrate occupies the capillary centers, the relative permeability is given by,

$$k_{rw} = 1 - S_h^2 + \frac{2\left(1 - S_h^2\right)}{\log(S_h)} \qquad [3]$$

The parallel capillary model approximates the flow paths by straight parallel cylindrical capillaries. However, it is known that the pore spaces are irregular and much longer than the straight-line capillaries assumption that defines the pressure gradient (Kleinberg et al. 2003).

2.2 Kozeny Models

Kozeny modes can be adopted to better approximate the irregular pore space and flow paths that defines the pressure gradient. The Kozeny grain coating model assumes that hydrates coats the grain surface and hence can be approximated using cylindrical pore model. Accordingly, the relative permeability is given by,

$$k_{rw} = (1 - S_h)^{n+1} \qquad [4]$$

where n is known as the saturation exponent. Spangenberg (2001) defined n as 1.5 for $0 < S_h < 0.8$. For $S_h > 0.8$, any increase in hydrate saturation will have minimal impact on permeability reduction.

On the other hand, the Kozeny pore-filling model assumes that hydrate forms in the pore centers. For instance, the pore surface area increases as hydrate grows in the center of the pore for the cylindrical model. Therefore, the relative permeability is given by,

$$k_{rw} = \frac{(1 - S_h)^{n+2}}{\left(1 + \sqrt{S_h}\right)^2} \qquad [5]$$

In Eq. [5], the saturation exponent is related to hydrate saturation by $n = 0.7S_h + 0.3$ (Spangenberg 2001).

2.3 Reservoir simulator models

Numerical reservoir simulators also attempt to predict the impact of temperature and pressure on the formation of hydrates in GHBS. The permeability models used by well known reservoir simulators are summarized below.

Masuda et al. (1997) proposed the University of Tokyo model by generalizing the parallel capillary model defined in Eq. [1] as,

$$k_{rw} = (1 - S_h)^N \qquad [6]$$

In Eq. [6], the saturation exponent N, was selected by taking the preferential accumulation of hydrate in pores into account. Masuda et al. (2002) used $N = 10, 15$ in their work. Moridis et al. (1998) proposed the Lawrence Berkley National Laboratory (LBNL) model for permeability prediction in EOSHYDR/TOUGH2 reservoir simulator. The LBNL model is based on van Genuchten (1980) and Parker et al. (1987):

$$k_{rw} = \sqrt{\overline{S_w}}\left[1 - \left(1 - \overline{S_w}^{\frac{1}{m}}\right)^m\right]^2 \quad [7]$$

with

$$\overline{S_w} = \frac{S_w - S_r}{1 - S_r} \quad [8]$$

where S_r is the irreducible water saturation. Moridis et al. (1998) used $S_r = 0.1$ and $m = 0.46$.

3 QUANTITATIVE PERFORMANCE MEASURE

The effectiveness of a permeability model is determined by comparing the predicted permeability with the permeability measurements from experiment data. To this end, the accuracy of permeability models has been largely carried out in qualitative fashion. Therefore, it is highly desirable to quantify the performance of the permeability in predicting permeability.

In this paper, we propose a novel method to quantify the prediction performance of a permeability model by computing the Normalized mean squared error (NMSE). The NMSE between the permeability measurements and that predicted by a theoretical model is given by,

$$NMSE = \left[\frac{1}{K}\sum_{k=1}^{K}\left(k_{rw}^{mod}(k) - k_{rw}^{exp}(k)\right)^2\right] \Big/ \left[\frac{1}{K}\sum_{k=1}^{K} k_{rw}^{exp}(k)^2\right] \quad [9]$$

where k_{rw}^{mod} is the relative permeability values predicted by the theoretical model, k_{rw}^{exp} is the experimental relative permeability values, and K denotes the number of permeability measurements. Note that NMSE measure signifies the efficacy of a model in fitting the experimental permeability measurements. From Eq. [9], we can infer that lower NMSE is associated with better prediction.

4 HYBRID MODEL

Recent studies have indicated the applicability of grain coating model at low hydrate saturations and that of pore-filling model at high hydrate saturations (Tohidi et al. 2002; Kumar et al. 2010). For instance, Tohidi et al. (2002) and Clennell et al. (1999) noticed the permeability model switched from that of grain coating to pore-filling at a hydrate saturation of 40 percent and above. Kumar et al. (2010) and Ordonez and Grozic (2009) reported similar findings although at different gas hydrate saturations of 35 and 45 percent respectively.

Given the previous research, it can be inferred that both grain coating and pore-filling process plays a dominant role depending on the magnitude of gas hydrate saturation. Accordingly, the relative permeability can be predicted using the combination of both grain coating and pore-filling model. For instance, the grain coating and the pore-filling model can be combined in a weighted form to obtain the relative permeability as,

$$k_{rw} = \alpha k_{rw}^{PF} + \beta k_{rw}^{GC} \quad [10]$$

where k_{rw}^{GC} and k_{rw}^{PF} are the Kozeny grain coating and pore-filling models given by Eq. [4] and [5] respectively. α and β are the pore-filling and grain coating weighting parameters. The weighting parameters can be defined as,

$$\alpha = S_h^N$$
$$\beta = (1 - S_h)^M \quad [11]$$

In Eq. [11], the parameters N and M are the exponents that governs the change of α and β with respect to hydrate saturation. To simplify, the exponents N and M can be set similar (i.e. $N = M$). Figure 1 shows weighting parameters as a function for hydrate saturation assuming $N = M$. Letting $N = 1$, we see that α and β varies linearly with respect to gas hydrate saturation. Hence, increasing S_h offers more weightage to pore-filling model than grain coating model and vice-versa.

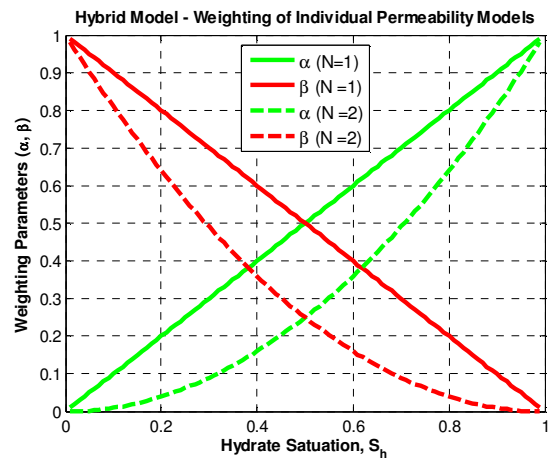


Figure 1 Weighting parameters α and β as a function of hydrate saturation for $N = M$ (Red: Grain coating, Green: Pore-filling)

On the other hand, the hybrid model can also be based on $N \neq M$. In this case, the change of α is no longer complimentary to that of β. In this paper, the selection of N and M were based on minimizing the NMSE between the permeabilities predicted by the hybrid model and that of experiment. For optimal N and M, the error between the predicted and measured permeability will be minimum to allow for better prediction performance.

5 RESULTS AND DISCUSSION

5.1 Experimental Data

Experimental permeabilities for CO_2 hydrate (Kumar et al. 2010) and hydraulic conductivities for R-11 synthetic

hydrate (Ordonez and Grozic 2009) were used to evaluate the predictive performance of various theoretical models.

Kumar et al. (2010) experimentally measured the permeability to CO_2 at varying hydrate saturations in a porous medium made of packed glass beads. While the equilibrium pressure of 2.0 MPa at 4 ^oC is required for CO_2 hydrate formation, the experiment maintained a pressure of 2.76 MPa to allow for sufficient hydrate formation.

On the other hand, Ordonez and Grozic (2009) measured the variation of hydraulic conductivity of Ottawa sand samples at different R-11 synthetic hydrate saturations. Tricholrofluoromethane (CCL_3 F) also known as R-11 synthetic hydrate has an advantage as it can be formed at atmospheric pressures. Moreover, the density properties are similar among methane/CO_2 and that of R-11 hydrate. Hence, the R-11 synthetic hydrate can be used as a realistic proxy of methane/CO_2 hydrates.

While Kumar et al. (2010) measured relative permeability, Ordonez and Grozic (2009) measured relative hydraulic conductivity. It should be noted that hydraulic conductivity is the measure of the ability of porous media to the flow of the water, whereas permeability is part of this and is a property of the porous media only.

5.2 Hybrid Model Results

As discussed in Section 4, the hybrid model determines the relative permeability via weighted combination of permeabilities obtained from Kozeny pore-filling and grain coating models. In Eq [11], the weighting parameters and hence N and M were optimized using the NMSE measure. For example, the N and M that yielded the least NMSE was selected as the optimal parameters.

Case 1: N = M

In this scenario, the parameters N and M were assumed to be same. The value of N was incremented from 0 to 15 in steps of 0.05 and the corresponding NMSE value was obtained between the permeabilities predicted by hybrid model using Eq. [10] and that of experiment. Figure 2 shows the NMSE obtained for hybrid model with different values of N. The optimal value of N was found to be 1.31 for CO_2 hydrate and 1.11 for R-11 synthetic hydrate. As discussed earlier, for $N \approx 1$, the relative permeability for hybrid model is obtained as a linear combination of Kozeny grain coating and pore-filling model. Secondly, the optimized value of N are in close agreement for CO_2 hydrate and that of R-11 synthetic hydrate. Thus, it indicates the suitability of R-11 hydrate to be used as a realistic proxy of CO_2 hydrate.

Case 2: N ≠ M

In this scenario, the parameters N and M were set to be different. Once again N and M was varied in steps of 0.05 over a range 0 and 3. Figure 3 shows the NMSE obtained for hybrid model with different values of N and M. The optimal values for N and M were obtained as 0.36 and 2.41 for CO_2 hydrate and 1.81 and 0.81 for R-11 hydrate.

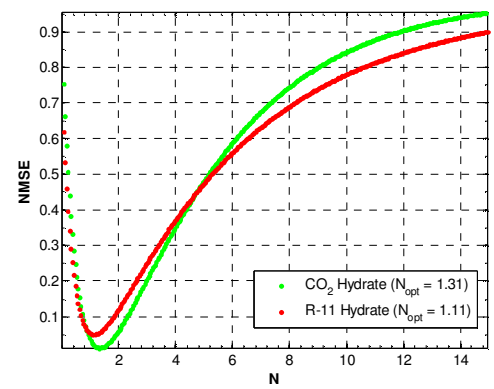
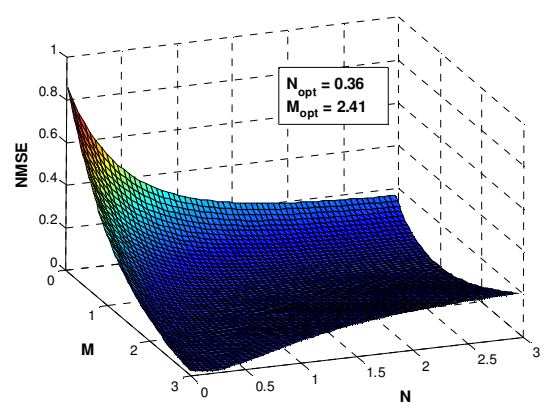


Figure 2 NMSE obtained with hybrid model for various N in predicting permeability of experimental data. (Green: CO_2 hydrate, Red: R-11 Hydrate)

Table 1 lists the NMSE using optimal values for $N = M$ and $N \neq M$ for the proposed hybrid model. As listed in Table 1, only a small reduction in NMSE was achieved for $N \neq M$ over $N = M$ case. Figure 4 shows the permeability and hydraulic conductivity measurements alongside predictions for the hybrid model. From Figure 4, we see that the measured permeabilities were better matched with hybrid model for $N \neq M$ over $N = M$ for both CO_2 and R-11 hydrates. Hence, even a small improvement in NMSE can attribute to better prediction as in the case of hybrid model with $N \neq M$.

Table 1. NMSE performance of hybrid model

Optimization Type	NMSE	
	CO_2 Hydrate	R-11 Hydrate
N = M	0.013	0.051
N ≠ M	0.008	0.048



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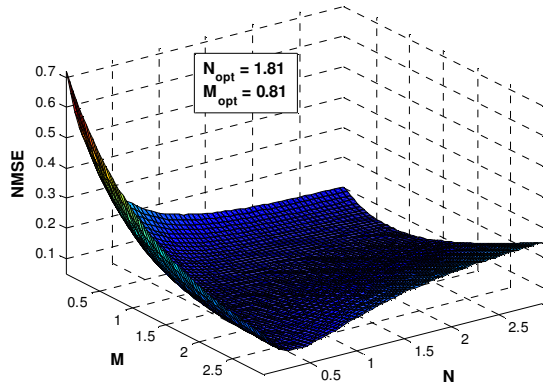
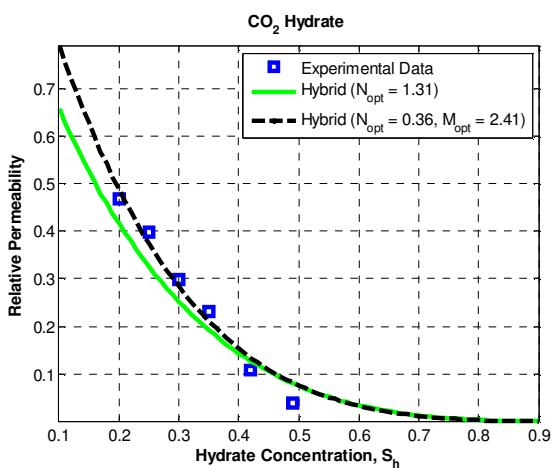
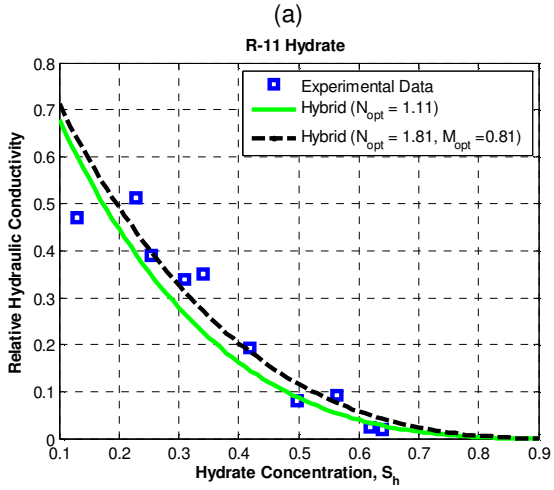


(b)

Figure 3 NMSE obtained with hybrid model for various N and M in predicting permeability of experimental data. (a) CO_2 Hydrate (b) R-11 Hydrate



(a)



(b)

Figure 4. Hybrid model predicted and measured relative permeability/hydraulic conductivity. (a) CO_2 hydrate (b) R-11 hydrate

5.3 Performance Analysis

The NMSE performance of various permeability models in predicting experimental measurements is shown in Figure 5. A better fit model is expected to provide lower NMSE. Similar NMSE was observed for CO_2 hydrate and that of R-11 hydrate indicating good correlation between them. Secondly, both grain coating and pore-filling models showed lower NMSE further corroborating previous research results (Tohidi et al. 2002; Kumar et al. 2010; Ordonez and Grozic 2009). Finally, the proposed hybrid model showed the least NMSE demonstrating the best fit among the permeability models.

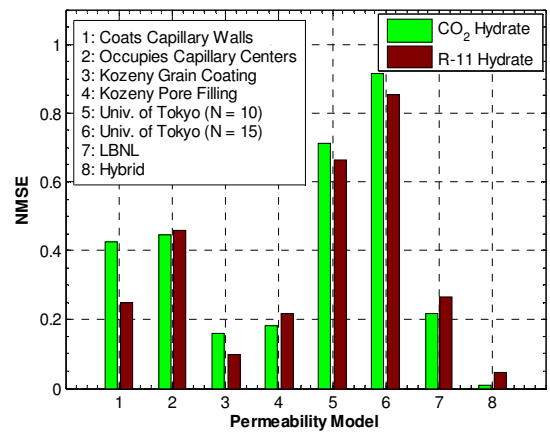
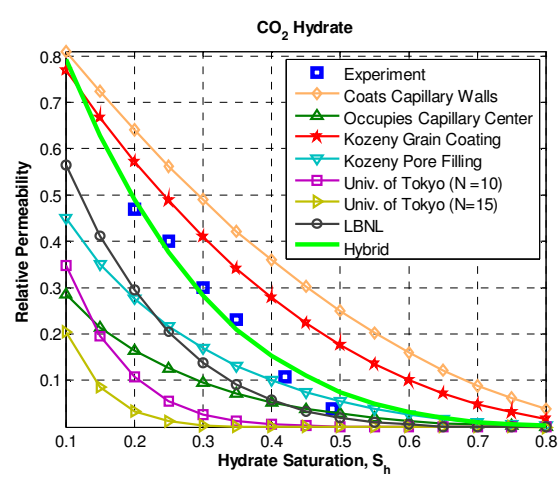
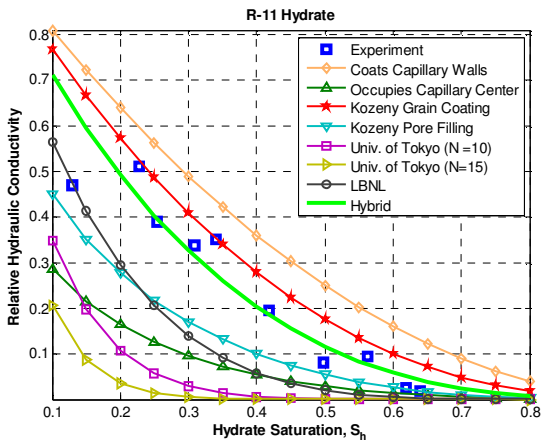


Figure 5 Performance of permeability models in predicting CO_2 hydrate and R-11 synthetic hydrate. (Lower NMSE yields better prediction)

Figure 6 shows the predicted and measured relative permeability for CO_2 hydrate and the relative hydraulic conductivity for R-11 hydrate. The hybrid model used the optimal values of N and M that were reported in Section 5.2. The experimental permeability and hydraulic conductivity measurements were in close agreement with the predicted values of hybrid model. This does not come as surprise as the hybrid model showed the least NMSE among the various permeability models.



(a)



(b)

Figure 6 Predicted and measured relative permeabilities\hydraulic conductivities for various permeability models

6 CONCLUSIONS

Experimental permeability and hydraulic conductivity measurements using CO_2 hydrate and R-11 synthetic hydrate were used to validate the prediction performance of several theoretical models. The NMSE was used to quantify the prediction performance of the permeability models. Lower NMSE values were obtained for pore-filling and grain coating models corroborating previous research. A novel hybrid model based on the weighted combination of pore-filling and grain coating model was proposed. The weighting parameters of the hybrid model were selected to yield least NMSE to ensure better fit experimental permeability measurements. The optimized values were similar among CO_2 and R-11 hydrate corroborating the use of R-11 hydrate as a realistic proxy for CO_2 hydrate. The hybrid model showed considerably better performance than existing models in predicting permeability/hydraulic conductivity measurements for both CO_2 and R-11 hydrates.

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