1. INTRODUCTION

Hydrate formation is a type of crystallization process that involves multicomponents and multistages. A research on the microscopic formation of hydrates and the formation mechanism can not only provide valuable physical information for hydrate crystal growth in multiphase transportation pipelines. On this basis, this paper presents a more practical and comprehensive bidirectional growth model of hydrate shells for an actual pipeline system. Thermodynamic phase equilibrium theory and water molecule penetration theory are applied in this model to develop a method for calculating the concentration change of hydrate-forming guest molecules and the permeation rate of water molecules. The temperatures on both sides of the hydrate shell are predicted by the heat transfer equation. The improved hydrate growth model can improve the prediction accuracy of hydrate formation in slurry systems.

Table 1. Theoretical Model of Hydrate Growth

It is known that there are many different factors that affect hydrate formation in different systems, and hydrate formation is a stochastic process, which makes it difficult to develop an integrated theoretical hydrate growth model. Until now, three types of semiempirical models have been established with their different emphases.

Early models were developed based on gas—water experiments, which merely considered the effect of the hydrate formation driving force (e.g., subcooling or the difference in fugacity). Vysniauskas and Bishnoi were the first to propose a semiempirical model for hydrate growth kinetics, presenting that hydrate formation was dependent on the interfacial area.
pressure, temperature, and supercooling degree. Then, based on hydrated crystallization theory and double-film theory, Englezos built a kinetic model using the fugacity difference as the driving force of growth.\(^{15,16}\) Subsequent researchers have suggested several models according to the abovementioned results. However, these models, as shown in Table 2, only considered the driving force of hydrate crystallization. The model presented by Sun\(^{17}\) correlated the hydrate formation rate with the hydrate particle growth and concentration distribution and thus took the effect of the hydrate volume fraction into account, which provided some references for describing hydrate formation in a flow system. The simulated results were consistent with the experimental ones. In the hydrate growth model developed by Kinnari,\(^{18}\) the supercooling degree was regarded as the driving force of hydrate crystallization. This model has limitations for applications because it neglects the influences of mass and heat transfer.

However, the model could be built from only the macro-perspective, if it only considered the kinetic driving force of hydrate crystallization, which cannot characterize the hydrate microgrowth. Lately, researchers have found that the mass transfer and heat transfer also have an effect on the hydrate formation. Here, mass transfer refers to the diffusion of guest or host molecules during hydrate formation, while heat transfer refers to the overall heat exchange, the heat generation during hydrate formation, while heat transfer varies when the experimental system and the conditions change: mass transfer is rate-limiting in most cases, while heat transfer is rate-limiting in some situations, for example, hydrate formation from water dissolved in a gas. Because of the many and complex influencing factors of hydrate formation, researchers have proposed various hydrate growth

models considering either mass transfer\(^{20−22}\) (see Table 3) or heat transfer\(^{23−26}\) (see Table 4) for the convenience of theoretical studies. The models listed in Table 3 regard the mass transfer as the main controlling factor for hydrate continuous growth, neglecting the effects of other controlling factors. Similarly, the models listed in Table 4 chose heat transfer as the main controlling factor.

Moreover, it is known that hydrate nucleation is driven by the intrinsic driving force that depends on either the subcooling degree \(ΔT_{\text{sub}} = T_{\text{eq}} - T_{\text{sys}} > 0\) or and overpressurizing level \(P_{\text{sys}} > P_{\text{eq}}\) of the phase equilibrium state. Thermodynamic models are used to predict the hydrate phase transitions. Recently, Liu et al.\(^{28}\) studied hydrate nucleation in water-waxy oil emulsions and presented that the higher the pressure, the less the mass transfer limitations for hydrate formation. Thus, temperature and pressure not only can be regarded as the thermodynamic criterion for hydrate formation but may also impact mass and heat transfer of the hydrate formation process. In other words, mass transport, heat transport, and thermodynamics of hydrate phase transitions are implicitly linked, which should be considered in the future model development. Nevertheless, there were various degrees of difficulty in describing the hydrate growth process using these mass transfer or heat transfer models, as mentioned above. Any model considering a single controlling factor has limitations in the applicability. Thus, an integrated model considering more main influencing factors could more truly simulate hydrate formation. Related integrated models are listed in Table 5.

In Table 5, Freer\(^{27}\) proposed a hydrate growth rate model combining kinetics and heat transfer. However, the calculated results of the growth rate were smaller than the experimental results. Turner\(^{26}\) combined the mass transfer and kinetic factors together and established the model of hydrate shell inward

### Table 2. Intrinsic Kinetic Model of Hydrate Growth

| researcher | model expression |
|------------|------------------|
| Vysniauskas and Bishnoi\(^{13,14}\) | \(r = A_{t_0} \exp\left(-\frac{\Delta E}{RT}\right) \exp\left(-\frac{a}{\Delta T}\right)\) |
| Englezos et al.\(^{15,16}\) | \(\left(\frac{dn}{dt}\right)_p = \frac{1}{v_0} \frac{A_p}{v_0} (f - f_{eq})\) |
| Sun\(^{17}\) | \(\left(\frac{dn}{dt}\right)_p = k(1 - \eta_{hyd})(f - f_{eq})^2\) |
| Kinnari et al.\(^{18}\) | \(-\eta_{gas} = \eta_k c_T \exp\left(\frac{k_c}{T}\right)\) |

### Table 3. Mass Transfer Model of Hydrate Growth

| researcher | model expression |
|------------|------------------|
| Skovborg and Rasmussen\(^{20}\) | \(\frac{dn}{dt} = k_1 \Delta \nu_{f_0}(x_m - x_g)\) |
| Mori and Mochizuki\(^{21}\) | \(\frac{dn}{dt} = \frac{\delta^2}{\tau^2} \frac{\alpha c \theta}{4k_{p,f} \eta_{p,\text{gas}}} (x_m - x_g)\) |
| Yapa et al.\(^{22}\) | \(\frac{dn}{dt} = -D_{\text{diff}} \eta_{p,\text{gas}} \frac{dC}{dr} \eta_{p,\text{gas}}\) |

### Table 4. Heat Transfer Model of Hydrate Growth

| researcher | model expression |
|------------|------------------|
| Uchida et al.\(^{23}\) | \(\frac{\eta_{\text{gas}}}{\lambda} = \frac{1}{(\rho \eta_{\text{gas}})} \Delta T\) |
| Mori et al.\(^{24}\) | \(\eta_{\text{gas}} = \frac{\sigma A}{4 \rho_0} \frac{1}{\Delta T_{\text{phys}}} \frac{\Delta T}{(\rho_0 \Delta h_0)} (\frac{\rho_0}{\rho_0 \Delta h_{\text{phys}}}^{2/3} + \rho_0 \Delta h_0^{2/3})^{1/2}\) |
| Mochizuki and Morit\(^{15}\) | \(\rho_0 \Delta h_0 \eta_{\text{gas}} = f_{\eta_{\text{gas}}}^{1/2} \left(\frac{\Delta T}{\Delta T_{\text{phys}}} \eta_{\text{gas}} + \rho_0 \Delta h_{\text{phys}}^{2/3} \eta_{\text{gas}}\right)\) |
| Zhong et al.\(^{26}\) | \(\eta_{\text{gas}} = \frac{4 \sigma h_{\text{gas}} Z \rho_0 (T_{\text{eq}} - T_{\text{sys}})}{M_{\text{p}} \Delta H} \left(\frac{\Delta T}{\Delta T_{\text{phys}}} \eta_{\text{gas}} - \rho_0 \Delta h_{\text{phys}}^{2/3} \eta_{\text{gas}}\right)\) |

https://dx.doi.org/10.1021/acsomega.0c04708
ACS Omega 2020, 5, 33101−33112
growth, which aimed to describe the hydrate growth of water-in-oil emulsion systems. The computing results of this model fit the experimental data fairly well. The gas diffusion parameter was regressed without considering the influence of heat transfer. Jamaluddin\textsuperscript{39} integrated kinetics with the mass transfer and with heat transfer to study hydrate growth. The mass transfer coefficient of gas diffusion in hydrates was determined from the experimental data under various pressures. However, this model simplified the complex flow situation in actual pipelines via the assumption that hydrate was growing on the gas-water interface. Based on these abovementioned studies, Zhao\textsuperscript{30} proposed a model of hydrate shell inward growth by considering the overall intrinsic growth kinetics and heat and mass transfer. However, its growth parameters need to be refined and improved. Furthermore, Shi\textsuperscript{31,32} built an inward and outward hydrate growth shell model based on Zhao’s model,\textsuperscript{30} taking thermodynamics, kinetics, and mass and heat transfer into account. Shi\textsuperscript{31,32} gave out a calculating method for the concentration change of hydrate guest molecules and the permeation rate of water molecules. This model had good prediction precision, but it was related to many parameters that require abundant experimental data of hydrate growth kinetics.

In this work, experiments on hydrate growth in W/O (water-in-oil emulsion) flow systems were conducted to examine the applicability of bidirectional growth of the hydrate shell on a flow system and to determine the direction of improvements.

### 2. RESULTS AND DISCUSSION

#### 2.1. Simulation of the Modified Hydrate Growth Kinetic Model

Based on the results of the growth kinetic experiments (see the Subsection 4.1) and chord length distribution obtained using the FBRM probe, this paper modified the parameters of the bidirectional growth dynamics model of hydrate shells (see the Subsections 4.2 and 4.3). We have simulated the hydrate growth kinetic process for four experimental factors (i.e., pressure, water cut, flow rate, and system temperature set) using the modified model. The simulated results are shown in Figures 1–4.

![Figure 1. Comparison between experimental and simulated data under different pressure conditions (control temperature set $-1 \, ^\circ C$, 30% water cut, 3% AA concentration, and 0.6 m/s flow rate).](image)

The abovementioned comparisons under various experimental conditions indicated that this modified model could well characterize the gas consumption and growth rate change during hydrate formation in a flow system. This model built a good foundation for the subsequent prediction of the hydrate growth kinetics.
2.2. Prediction of the Modified Hydrate Growth Kinetic Model. According to the simulation results of the hydrate growth kinetic experiments, this paper provided relatively abundant and accurate parameters for improving the bidirectional growth kinetic model of hydrate shells. This paper also contributed to the model’s promotion and application in the pipeline system and also laid the theoretical foundation for research on hydrate slurry risk control technology. In detail, can be seen in this table that the simulated results were consistent with the experimental ones, with an average absolute deviation of below 11%. Table 7 shows the values of the model parameters of this modified model in Table 6 under different conditions.

Table 6. Simulated Results of the Modified Hydrate Growth Kinetic Model

| index | environment temperature control (°C) | flow rate (m/s) | pressure (MPa) | water-cut (%) | absolute deviation (%) |
|-------|-------------------------------------|----------------|----------------|---------------|------------------------|
| case 1 | 1                                  | 0.6            | 4              | 30            | 9.65                   |
| case 2 | 1                                  | 0.6            | 5              | 30            | 9.02                   |
| case 3 | 1                                  | 0.6            | 5              | 30            | 6.44                   |
| case 4 | 1                                  | 0.6            | 6              | 30            | 8.67                   |
| case 5 | 1                                  | 0.6            | 6              | 30            | 10.8                   |
| case 6 | 1                                  | 1.0            | 4              | 30            | 4.74                   |
| case 7 | 1                                  | 0.6            | 5              | 30            | 3.95                   |
| case 8 | 1                                  | 1.0            | 4              | 30            | 5.62                   |
| case 9 | 1                                  | 1.0            | 5              | 30            | 3.66                   |
| case 10 | 1                                 | 1.0           | 6              | 30            | 4.78                   |
| case 11 | 1                                | 1.2           | 4              | 30            | 9.36                   |
| case 12 | 1                                | 1.2           | 4              | 30            | 9.09                   |
| case 13 | 1                               | 1.2           | 6              | 30            | 3.85                   |

Table 7. Values of Parameters in the Modified Hydrate Growth Kinetic Model

| index | $D_0^f$ (m$^3$/s) | $\zeta$ | $\epsilon_f$ (m$^3$) | $\zeta$ | $K^f$ |
|-------|-------------------|---------|---------------------|--------|-------|
| case 1 | $4.56 \times 10^{-17}$ | 0.12    | $2.55 \times 10^{-30}$ | 0.68   | $2.22 \times 10^{-7}$ |
| case 2 | $2.06 \times 10^{-16}$ | 0.11    | $2.55 \times 10^{-30}$ | 0.68   | $3.80 \times 10^{-7}$ |
| case 3 | $1.06 \times 10^{-15}$ | 2.05    | $2.55 \times 10^{-30}$ | 0.68   | $3.71 \times 10^{-7}$ |
| case 4 | $5.06 \times 10^{-17}$ | 0.03    | $2.55 \times 10^{-30}$ | 0.68   | $1.02 \times 10^{-6}$ |
| case 5 | $4.36 \times 10^{-14}$ | 0.85    | $2.55 \times 10^{-30}$ | 0.68   | $6.20 \times 10^{-7}$ |
| case 6 | $2.96 \times 10^{-14}$ | 3.35    | $2.55 \times 10^{-30}$ | 0.68   | $1.62 \times 10^{-7}$ |
| case 7 | $1.56 \times 10^{-16}$ | 0.05    | $2.55 \times 10^{-30}$ | 0.68   | $5.62 \times 10^{-7}$ |
| case 8 | $9.96 \times 10^{-17}$ | 0.72    | $2.55 \times 10^{-30}$ | 0.68   | $9.92 \times 10^{-7}$ |
| case 9 | $4.06 \times 10^{-14}$ | 2.12    | $2.55 \times 10^{-30}$ | 0.68   | $1.76 \times 10^{-6}$ |
| case 10 | $2.86 \times 10^{-16}$ | 0.92    | $2.55 \times 10^{-30}$ | 0.68   | $1.46 \times 10^{-6}$ |
| case 11 | $8.56 \times 10^{-17}$ | 8.12    | $2.55 \times 10^{-30}$ | 0.68   | $1.02 \times 10^{-7}$ |
| case 12 | $1.56 \times 10^{-16}$ | 0.32    | $2.55 \times 10^{-30}$ | 0.68   | $1.62 \times 10^{-7}$ |
| case 13 | $4.06 \times 10^{-14}$ | 3.12    | $2.55 \times 10^{-30}$ | 0.68   | $7.62 \times 10^{-7}$ |

Based on the mentioned model parameter values in the simulation, it provided the possibility of predicting the hydrate growth kinetics in a pipeline system, by correlating these values and experimental conditions. Figures 5 and 6 show the predicted results for the other operating conditions, using the model whose parameters came from several chosen experimental conditions. These figures indicate that these model parameters were conducive to a better prediction for the hydrate growth kinetic rules in pipeline systems.

3. CONCLUSIONS

The inward and outward hydrate growth shell model was improved and implemented in this work. A more practical comprehensive model describing the bidirectional growth of the hydrate shell for actual flow systems was developed. Various influencing factors, such as the thermodynamics, the intrinsic kinetics of crystallization, the heat transfer and mass transfer, and
so on, were taken into consideration. Moreover, the interphase value problem was solved with the assistance of PVM and FBRM probes. The particle size distribution of the emulsion system before and after hydrate formation was obtained using the probes, which directly quantify two significant parameters for hydrate formation: the nucleation ratio and the initial droplet size. Additionally, five growth kinetic parameters, $K_n$, $D_1$, $\xi$, $c_{H2O}$, and $c_H$, of the hydrate formation in flow systems were optimized through the data obtained from the flow loop experiments conducted in this work. The model had good prediction accuracy, and the absolute deviation between the simulated data of the model and the experimental data was below 11%. The first-hand information for predicting the amount of hydrate formation in flow systems could be obtained using the model, which is of great significance for the flow assurance industry involving the hydrate plugging problem and for hydrate applications.

4. EXPERIMENTAL AND COMPUTATIONAL METHODS

4.1. Experimental Apparatus and Materials

4.1.1. High-Pressure Hydrate Experimental Loop. Experiments were performed in a high-pressure hydrate experimental loop for hydrate formation studies. The schematic diagram of the flow loop is shown in Figure 7. The test section is 30 m long with a diameter of 2.54 cm, which was made of stainless steel and consisted of two rectilinear horizontal lengths. To control the temperature of the experimental fluid, the test section was jacketed with jacket pipes with 5.08 cm diameters, in which the water–glycol mixture circulated with the assistance of water baths. The process temperature control ranges from −20 to 100 °C. Natural gas and liquid phases are, respectively, injected using a plunger compressor and a custom-made magnetic pump into the loop. It should be noted that this pump was designed to have a minimal destructive impact on the hydrates. For more details about the loop, please refer to our previous work.33,34

4.1.2. Hydrate Experimental Loop Instrumentation. A focused beam reflectance measurement (FBRM) probe and a particle video microscopy (PVM) probe are installed at the inlet of the test section, which allowed for the evolution of objects, such as droplets, bubbles, and solid particles, carried out inside the fluid to be monitored. Both the probes’ windows cut the streamlines at 45° angles, beginning at the center of the pipe. The FBRM and PVM probes were used to estimate the initial water droplet ($D_p$) size inside the fluid and to follow the hydrate particle agglomeration with time. The mean square-weighted chord length can give more weight to the larger particles, so it is particularly well adapted to the agglomeration phenomena. More details about the PVM and FBRM probes can be found elsewhere.33

4.1.3. Materials. To better simulate the practical situation, deionized water, civil natural gas (Table 8), and −20# diesel (Table 9) are employed for these tests. An electronic balance is used to weigh the combined antiagglomerant (AA) quality (with a measuring error of ±0.01 g). The quality ratio of the AA/water phase can be adjusted to 1, 2, and 3 wt % through a high-pressure measurement piston pump. The type of the combined AA provided by the Chemical Engineering Department at the China University of Petroleum, Beijing, is a mixture of sorbitan monolaurate (Span 20) and ester polymers.34 Span 20 serves as the emulsifier, and the polymer works as the effective antiagglomerate. The natural gas hydrate formation curve (Figure 8) is obtained using the Chen–Guo35 model (which is able to calculate the phase equilibrium state of the gas mixture containing CO2 and H2S36) with the natural gas composition.

4.1.4. Experimental Procedure. The details of the procedure for the hydrate formation experiments were previously reported.37,38 The specific procedure for one round of hydrate formation and the dissociation experiment was performed as follows:

1. The entire experimental loop was swept with compressed clean air. Then, the loop was evacuated until the vacuum degree reaches 0.09 MPa.

2. The diesel and water (100 vol % liquid loading) were loaded with specific water cut for each test. Water cut is defined here as the volume ratio of water to the total liquid. The diesel volume was fixed at 70 L for all experiments. Natural gas was injected into the separator at room temperature (20 °C) to reach the aimed experimental pressure.

3. The water and oil mixture were circulated at a constant flow rate to form a homogeneous and stable emulsion with the specific AA dosage for each test. The stability of the water/oil emulsion referred to a relatively stable state (dynamic stability) according to the measured data from the FBRM under shearing action. In other words, the emulsion was regarded as stable when the average chord length of droplets fluctuated ±0.2 µm within 2 h.

4. The temperature was decreased gradually to a specific value under the initial pressure and flow velocity. The data acquisition system was started to collect the temperature,
pressure, pressure drop, flow rate, density, and chord length data continuously during the hydrate formation process.

(5) When the pressure, temperature, and flow rate of the loop were stable, the stable situation was maintained for at least 5 more hours.

(6) To dissociate the hydrate slurry, the system was heated at a constant volume using the bath system. The bath temperature was set to 30 °C and all data were collected during the hydrate decomposition process.

(7) A round of the hydrate formation and decomposition experiment was completed when all measured data were stable at the end of the hydrate decomposition process.

(8) When all the experiments were finished, the flow loop was flushed with clean water several times and swept with clean compressed air, and no significant rust was observed. Hence, the influence of rust on hydrate heterogeneous nucleation was not considered in this paper.

4.1.5. Calculation Method of Gas Consumption. As proposed previously, the amount of gas consumption can be calculated based on the equation of states for a real gas, which is shown as eq 1

\[
\dot{n}_g = \frac{P_1 V_{g,1}}{z_1 R T_1} - \frac{P_2 V_{g,2}}{z_2 R T_2}
\]  

where \(\dot{n}_g\) is the moles of gas consumption (mol); \(P_1\) is the system pressure before hydrate formation (Pa); \(P_2\) is the system pressure after hydrate formation (Pa); \(V_{g,1}\) is the gas volume in the separator before hydrate formation (m³); \(V_{g,2}\) is the gas volume in the separator after hydrate formation (m³); \(z_1\) and \(z_2\) are the compressibility factors in the pressures \(P_1\) and \(P_2\).

---

Table 8. Composition of Gas Samples

| composition | mol % | composition | mol % |
|-------------|-------|-------------|-------|
| N₂          | 1.53  | C₁          | 3.06  |
| CO          | 2.05  | iC₄         | 0.33  |
| CO₂         | 0.89  | iC₅         | 0.04  |
| C₁          | 89.02 | nC₆         | 0.01  |
| C₂          | 3.07  |             |       |

Table 9. Composition of -20 # Diesel Oil

| composition | mol % | composition | mol % |
|-------------|-------|-------------|-------|
| C₁₁         | 0.89  | C₁₆         | 6.83  |
| C₁₂         | 3.36  | C₁₇         | 7.99  |
| C₁₃         | 5.38  | C₁₈         | 7.46  |
| C₁₄         | 6.2   | C₁₉         | 6.38  |
| C₁₅         | 6.78  | C₂₀⁺        | 48.73 |

---
respectively and are calculated based on the Peng–Robinson equation of states (PR-EoS). \( R \) is the gas constant \((\text{J/(mol·K)})\); \( T_1 \) is the system temperature before hydrate formation \((\text{K})\); and \( T_2 \) is the system temperature after hydrate formation \((\text{K})\).

4.2. Establishment of the Hydrate Growth Kinetic Model. Hydrate growth is a complex, exothermic, and system-dependent process with multiple stages. Hydrate growth is influenced by many factors, such as thermodynamics, kinetics, mass and heat transfer, and so on. There was thus a practical significance for establishing a model that comprehensively considers the influencing factors for the hydrate crystal growth in the mixture transportation pipelines.

Free water and oil phases tend to form water-in-oil emulsions in the multiphase transportation pipelines. Therefore, the hydrate shell that formed at the interface of water and oil would become the obstacle of the hydrate’s continuous growth. A continuous hydrate growth process, as shown in Figure 9, on one hand required enough hydrate guest molecules that could diffuse from the oil phase through the hydrate shell to the internal surface contacting with water (H/W) and on the other hand required water molecules to permeate through the shell to the hydrate outside the surface with the oil phase (H/O) via the capillary force. Meanwhile, hydrate formation is an exothermic process, with its released heat exchanged with the surroundings of the hydrate shell. Therefore, once the pressure and temperature met the requirements of hydrate formation, the hydrate continuous growth demanded a sufficient driving force for the crystallization kinetics, successive gas and water mass transfer, and sufficiently fast heat removal.

The fundamental modeling procedures of the hydrate inward and outward growth shell model are presented. The model applied thermodynamic phase equilibrium theory and water molecule penetration theory to give a calculating method for the concentration change of hydrate guest molecules and the permeation rate of water molecules. Through investigating the thermodynamics of hydrate formation of \( \text{CH}_4–\text{CO}_2–\text{N}_2 \) systems, Kvamme et al. presented that the dynamics of gas solubility into liquid water and dynamics of hydrate formation on gas/water interfaces are controlled by interface concentrations and adsorption of different gas components onto liquid water varies. Thus, it should be noted that the phase equilibrium curve of the components in the thin oil–water interface where hydrate nucleation occurs is not the same as Figure 8 because the interfacial adsorption composition is different from the composition of the bulk gas (dissolved natural gas) in Table 8. Considering that the mole fraction of \( \text{CO}_2, \text{N}_2, \) and \( \text{H}_2\text{S} \) in natural gas used in this work is relatively low and for simplification, it is assumed that the concentrations of each component in the oil and those at the H/O interface are equal at the beginning of the simulation. The temperatures on both sides of the hydrate shell were predicted by the heat transfer model. The differential concentration of guest molecules between this thermodynamic condition and the equilibrium condition was regarded as the kinetic crystal driving force of the hydrate formation and growth. At the same time, it used a decreasing mass transfer coefficient with continuous hydrate growth to describe the problem of the mass transfer efficiency decreasing with the thickened hydrate shell.

According to the abovementioned modeling procedures, the hydrate inward and outward growth shell model mainly included a hydrate inward growth shell model, a hydrate outward growth shell model, a decreasing mass transfer coefficient model, and a hydrate shell temperature prediction model. The following are the descriptions of the developments of these four models.

4.2.1. Hydrate Inward Growth Shell Model. The calculation of the hydrate shell’s inward growth was based on (1) the diffusion rate that hydrate guest molecules diffused to the H/W interphase and (2) the consuming rates of the guest and water molecules during hydrate crystallization. Moreover, these three rates satisfied the mass balance at the H/W interphase during the hydrate growth process.

(1) Diffusion rate of hydrate guest molecules to the H/W interphase

The boundary conditions were the concentrations of the hydrate guest component \( i \) at the H/W and H/O interphases (i.e., \( \pi_{H/W,i} \) and \( \pi_{H/O,i} \) respectively). According to Fick’s second diffusion law, the concentration distribution of the component \( i \) was

\[
\pi_i = \left( \frac{1}{1/r_{in} - 1/r_{out}} \right) C_{\pi_{H/O,i}} - \frac{C_{\pi_{H/W,i}}}{r} + \frac{C_{\pi_{H/O,i}}}{r_{in}} - \frac{r_{out}}{r_{out}} \right) \tag{2}
\]

where the subscript ‘in’ indicates the H/W interphase and the subscript ‘out’ represents the H/O interphase. Then, the gas diffusion rate \( W_{i}^{\text{diff}} \) (mol/s) of the component \( i \) at the H/W interphase was calculated according to the concentration distribution

\[
W_{i}^{\text{diff}} = -4\pi(r_{in}^{\Delta r - 1})^2 D_i \left. \frac{d\pi_i}{dr} \right|_{r=r_{in}^{\Delta r - 1}} = -4\pi D_i \left( \frac{C_{\pi_{H/O,i}} - C_{\pi_{H/W,i}}}{1/r_{in}^{\Delta r - 1} - 1/r_{out}^{\Delta r - 1}} \right) \tag{3}
\]

where \( r_{in}^{\Delta r - 1} \) and \( r_{out}^{\Delta r - 1} \) (m) are the inner and outer radii of the hydrate shell at the \( \Delta t - 1 \) time step, respectively; and \( D_i \) (m²/s) and \( C_i \) (mol/m³) are the diffusion rate and concentration of the component \( i \) at radius \( r \), respectively.

The overall diffusion rate \( W^{\text{diff}} \) was the sum of all diffusion rates of the guest components, which can be written as follows

\[
W^{\text{diff}} = \sum_{i=1}^{N} -4\pi D_i \left( \frac{C_{\pi_{H/O,i}} - C_{\pi_{H/W,i}}}{1/r_{in}^{\Delta r - 1} - 1/r_{out}^{\Delta r - 1}} \right) \tag{4}
\]

(2) Consuming rates of the guest and water molecules at the H/W interphase

The consumption rate of the guest molecules at the H/W interphase \( W^{\text{con}}_{i} \) (mol/m³) could be gained from the modified hydrate crystallization kinetic model by Englezos (15,16)
where \( C_{eq}, \) and \( \Omega_{eq,i} \) are the concentration (mol/m³) and the concentration parameter (mol·MPa·m⁻³) of the component \( i \) under the balanced conditions, respectively, and \( \Omega_{H/W,i} \) and \( \Omega_{H/O,i} \) are the concentration and the concentration parameter of the component \( i \) at the H/W interface under thermodynamic phase equilibrium, respectively, and \( K_i^s \) is the kinetic constant of the component \( i \) during hydrate growth, mol·MPa·m⁻³.s⁻¹.

The relation between the consumption rate \( W_{w,H/W} (\text{mol/s}) \) of water molecules at the H/W interface and the varying rate of the droplet radius (inner radius of the hydrate shell) is

\[
W_{w,H/W} = \frac{d}{dt} \left( 4\pi r_{in}^3 \rho_w \right)_{r_{in}=r_{in}-\Delta r} = 4\pi r_{in}^2 \rho_w \frac{dr_{in}}{M_w} dt
\]

(6)

where \( t \) is time, s; \( M_w \) is the molar mass of water molecules, g/mol; and \( \rho_w \) is the water density, kg/m³.

(3) Mass balance of the hydrate growth at the H/W interface

The hydrate growth at the H/W interface satisfied the following mass balance relation

\[
W_{g,H/W} = - \beta W_{w,H/W}
\]

(7)

where \( \beta \) is the hydration number, indicating the occupied percentage in the hydrate holes.

According to the mass balance in eq 7, the concentration of \( i \) at the H/W interface, \( C_{H/W,i} (\text{mol/m³}) \), could be deduced as

\[
C_{H/W,i} = \frac{C_{H/O,i} + \Omega_{eq,i} - \Omega_{eq,i} (r_{in}^3/r_{in}^3 - 1)/D_{i,i}}{1 + \Omega_{eq,i} (r_{in}^3/r_{in}^3 - 1)/D_{i,i}}
\]

(8)

where \( r_{in}^3 \) is the radius of the hydrate shell within the calculation time step \( \Delta t \), which only considered the hydrate inward growth.

Combining eqs 4–8, the changing rate of the inner radius of the hydrate shell with time is

\[
\frac{dr_{in}}{dt} = \frac{\beta M_w}{\rho_w} \sum_{i=1}^{N} \left( \frac{\Omega_{eq,H/O,i} - \Omega_{eq,i} C_{eq,i}}{1/K_i^s + \Omega_r (r_{in}^3/r_{in}^3 - 1)/D_{i,i}} \right)
\]

(9)

Equation 9 is a nonlinear function of the hydrate shell inner radius, which can be iteratively solved using the fourth-order Runge–Kutta numerical algorithm.

4.2.2. Hydrate Outward Growth at the H/O Interphase.

The hydrate formation and growth at the H/O interphase mainly depended on the total volume flow rate of water molecules penetrating from the hydrate shell from the inside to the outside. Thus, this paper applied and modified the water molecule permeation model proposed by Mori.\(^\text{21}\) The total volume flow rate through the hydrate shell was estimated using a Hagen–Poiseuille flow driven by the capillary pressure, which is given by

\[
q_w = n_{cap} \frac{r_{cap}^3 \cos \theta_{cap}}{\chi} \frac{\pi \sigma}{4 \mu_w (r_{out}^{-1} - r_{in}^{-1})}
\]

(10)

where \( n_{cap} \) is the number density of capillaries; \( r_{cap} \) is the radius of the capillaries, m; \( \chi \) denotes the tortuosity of the capillaries, m; \( \theta_{cap} \) is the water-side contact angle on the capillary wall, rad; \( \sigma \) is the water/condensate oil interfacial tension, N/m; and \( \mu_w \) is the viscosity of water, Pa·s.

Research showed that none of these capillary parameters could be measured easily.\(^\text{21}\) For simplification, a porous parameter, \( \epsilon_H \), was defined to describe the property of the hydrate shell.

\[
\epsilon_H = \frac{n_{cap} r_{cap}^3 \cos \theta_{cap}}{\chi}
\]

(11)

Therefore, the total volume of water permeating in the calculated time step \( \Delta t \), \( V_{w,H/O} \), is given by

\[
V_{w,H/O} = \frac{\pi \epsilon_H \rho_w \Delta t}{4 \mu_w (r_{out}^{-1} - r_{in}^{-1})}
\]

(12)

4.2.3. Decrease in the Mass Transfer Coefficient. Considering the influence of the hydrate shell on the mass transfer, the hydrate shell model described the attenuation of the hydrate growth mass transfer parameters in the logarithmic function of the hydrate forming the volume fraction \( \psi \), which refers to the logarithmic functions used to describe the \( C_{14} \) attenuation rule of an organic body

\[
D_{i,i} = D_{0,i}^H \ln (\psi), \quad \psi > 0
\]

(13)

\[
\epsilon_{H,i} = -\epsilon_{H,i}^0 \ln (\psi), \quad \psi > 0
\]

(14)

where \( D_{0,i} \) and \( \epsilon_{H,i}^0 \) are the initial diffusivity of the gas and the initial porous parameter of the hydrate shell with \( \psi = 0 \), respectively, and \( \xi \) and \( \zeta \) are the mass transfer efficiency parameters adjusted by the experimental data.

4.2.4. Temperatures of Both Sides of the Hydrate Shell. The heat generation of the hydrate formation was given by Sloan and Koh.\(^\text{1}\) The total heat released during the hydrate formation of a single water droplet in the calculated time step \( \Delta t \), \( Q_{heat} \), could be defined as

\[
Q_{heat} = \frac{\Delta H}{M_w} (V_{w,H/W} + V_{w,H/O})
\]

(15)

where \( \Delta H \) is the heat of the hydrate formation, J, which can be calculated by the residual thermodynamics model developed by Kvamme et al.\(^\text{44–46}\) \( \rho_w \) is the density of water, kg/m³, and \( M_w \) is the molar weight of water, g/mol.

Then, Fourier’s law was applied to model the heat transfer through the hydrate shell. The boundary conditions at both sides of the hydrate shell are given as follows

\[
\frac{\lambda_w}{\lambda_w + \lambda_l} \frac{Q_{heat}}{4\pi \Delta t (r_{in}^{-1} - r_{out}^{-1})} = -\frac{\lambda_l}{\lambda_w + \lambda_l} \frac{dT}{dr}_{r_{in}} \bigg|_{t=r_{in}}
\]

(16)

\[
\frac{\lambda_l}{\lambda_w + \lambda_l} \frac{Q_{heat}}{4\pi \Delta t (r_{in}^{-1} - r_{out}^{-1})} = -\frac{\lambda_l}{\lambda_w + \lambda_l} \frac{dT}{dr}_{r_{out}} \bigg|_{t=r_{out}}
\]

(17)

where \( \lambda_w \) and \( \lambda_l \) are the thermal conductivity of the water and condensate oil, respectively, W/K·m, \( r_{in}^{-1} \) and \( r_{out}^{-1} \) are the hydrate shell inner diameter and outer diameter, respectively, m. As a result, the temperature change, which was on both sides of the hydrate shell, could be estimated by combining eqs 15–17.

There were six key parameters for the calculation of the hydrate inward and outward growth shell model: the kinetic constant \( K_i^s \), initial diffusivity of gas molecules \( (D_{0,i}^H) \), mass transfer efficiency of gas molecules \( (\xi) \), initial porosity...
parameter of the hydrate shell ($\epsilon_0^H$), mass transfer efficiency of water ($\zeta$), and initial droplet diameter ($d$). Shi et al.\textsuperscript{31,32} used the experimental data to obtain the range of these parameters.\textsuperscript{31} In this paper, the hydrate inward and outward growth shell model was used to predict the hydrate growth process of a flow system in the flow loop. The results are shown in Figure 10. The predicted data were calculated with the hydrate growth model using the parameters that were regressed from another flow loop. It can be seen from Figure 10 that the model parameters gained from autoclaves were inadequate to characterize the growth process in a flow system, especially at the hydrate growth controlling stage (mass or heat transfer stage). Therefore, it was necessary to improve the hydrate inward and outward growth shell model by removing some idealized assumptions and providing more practical growth parameters to enhance the prediction precision for a flowing system.

4.3. Modified Parameters of the Hydrate Growth Kinetic Model. It can be determined from the abovementioned analysis that the hydrate inward and outward growth shell model could be well applied to pipeline systems when it has more appropriate model parameters, which is a difficult and important point of this paper and is also the key to expanding the application range of the hydrate inward and outward growth shell model. This model cannot predict well the growth process for a flow system because of the lack of kinetic growth parameters in such a system. To solve these problems, the original model parameters must inevitably be adapted to the growth rules in the pipeline systems.

Here, the abovementioned six key parameters, $K^I$, $D^I_{lo}$, $\xi$, $\epsilon^I_0$, $\zeta$, and $d$, are mainly studied. The former five are model parameters of the hydrate inward and outward growth shell model, while the last $d$ is the interfacial parameter of the hydrate initial formation. The value of $d$ is directly related to the following model’s precision on the simulation and prediction. As a result, it was significant to analyze and demonstrate the key parameters during the growth process in a flow system to make sure the reasonable values and to improve the prediction precision and the application range of the modified model.

4.3.1. Initial Droplet Diameter ($d$) for Flow Systems. Surfactants usually exist in multiphase flow systems, resulting in the formation of oil–water emulsions. On one hand, surfactants themselves may influence hydrate formation.\textsuperscript{17} On the other hand, in the hydrate growth process of a flow system, the interphase area of dispersed and continuous phases influenced by surfactants directly affects the reaction area of following hydrate growth. Researchers\textsuperscript{15,16,20−26,28−33} took this interphase area as the most significant parameter in all their growth kinetic models (including intrinsic kinetic models, heat transfer kinetic models, mass transfer kinetic models, and those integrating these three aspects). Meanwhile, the determination of the interphase parameter was also the focus in the pipeline slurry system. Researchers\textsuperscript{15,16,20,28} have given various approximate calculation methods. The problem of the droplet size was inevitable in all these approximation methods for flow systems and was usually settled in simplified ways,\textsuperscript{28,30,31} for example, taking the initial droplet size to be a certain value or using the empirical correlation without considering their distribution characteristics. However, the droplet size deviated from its actual value in all of these simplified approaches, affecting the simulation and prediction of subsequent hydrate shell models.

Therefore, to solve the abovementioned problem, this paper proposed a new method to determine the initial droplet size in a slurry system, according to the abundant hydrate growth experimental data and the microscope measuring technology (FBRM probe and PVM probe). This new method can obtain a better initial droplet size and then provide a basis for the following model simulations. In detail, first, the chord length distribution (CLD) of the initial droplets was measured by FBRM for the flow system, as shown in Figure 11; second, the average chord length of the droplets in the system could be gained from the CLD of the initial droplets; third, the average droplet size ($d$) was determined from the transforming relationship between the average chord length data (provided by FBRM) and the average size data (provided by PVM) under these certain conditions; and finally, the interphase area for the initial droplet reaction of the hydrate growth under these conditions was obtained.

After the abovementioned modification, the initial droplet size and interphase area parameters would be more consistent with the actual situation, and then, the simulation and prediction would be more precise with the subsequent hydrate inward and outward growth shell model.

With the assistance of our PVM probe, it was determined that there was only a certain portion of water droplets that could participate in hydrate nucleation and form the shell, rather than the ideal situation where all the droplets dispersed in the continuous oil phase would.\textsuperscript{36} This fact differed from the assumption of several researchers’ current models.\textsuperscript{28,30−33} It can then be determined that the predicted results would deviate.

![Figure 10. Comparison between experimental data and predicting data from the hydrate growth kinetic model (5 MPa and 30% water cut).](https://dx.doi.org/10.1021/acsomega.0c04708)

![Figure 11. Chord length distribution (CLD) of droplets in the system.](https://dx.doi.org/10.1021/acsomega.0c04708)
from the actual ones, if the model hypothesis that all droplets nucleated and formed shells was still applied in a flow system. This assumption led to the improper value of the parameter in the hydrate inward and outward growth shell model, which was also a general problem for some models. Therefore, for the abovementioned problem, this paper for the first time used the hydrate nucleation ratio parameter to characterize the number of microdroplets (the interphase parameter) participating in the actual initial hydrate formation in a pipeline system. This modification could adjust the growth parameter to better reflect actual situations. Here is the determination method for the hydrate nucleation ratio. According to research by Turner, the sizes of the droplets/particles were basically unchanged in the beginning of hydrate growth for a slurry system, that is, the hydrate particles were directly transformed from the dispersed droplets. However, Figure 12 shows that the total droplet/particle numbers collected by FBRM decreased because of the different optical properties of the water droplets and hydrate particles. Based on this discrepancy, this paper regarded the decreased portion of the total amount of droplets/particles as the numbers of droplets/particles participating in the actual hydrate growth and defined the ratio of the deduced droplet number to its total number as the nucleation ratio for the initial hydrate growth.

It can be seen in Figure 12 that the total number of microdroplets was basically kept stable before the hydrate formation, while it decreased remarkably after the hydrate nucleation. Therefore, the reduced number of overall droplets in this stage could characterize the hydrate nucleation number of water droplets in the initial hydrate formation. It should be noted that the decreased number was not the result of particle agglomeration but instead from the different optical properties between the particles and droplets. After this process, it could further modify and improve the contact area between the dispersed and continuous phases according to the particle data monitored in the experiments. Further research studies should be conducted to study the direct effect of the Span series (Span 20 in this work) and other surfactants on hydrate formation using MD simulations to improve the model.

4.3.2. Kinetic Parameters of the Hydrate Inward and Outward Growth Shell Model. The kinetic model studies of hydrate growth are mainly in an autoclave at present, compared to the few studies in the flowing pipeline system. Most of the parameters in hydrate shell models thus come from experimental data in an autoclave. Because of the discrepancy in the flow rules and heat/mass transfer between autoclaves and actual pipelines, the parameters in the hydrate shell models changed correspondingly with various experimental devices and systems. As a result, the model parameter value gained from an autoclave still could not be applied to a pipeline system.

Therefore, this paper directly studied pipeline systems to collect adequate experimental data for hydrate growth kinetics. The parameters of the kinetic model were then regressed for this system according to the experimental data and the modified droplet size and the nucleation ratio. Finally, the relation between the growth parameters and experimental conditions was built through the influence of the experimental conditions on the growth kinetic parameters. This relation also provides data for the following prediction of the hydrate inward and outward growth shell model.

## AUTHOR INFORMATION

### Corresponding Authors

**Xiaofang Lv** — Jiangsu Key Laboratory of Oil and Gas Storage & Transportation Technology, Changzhou University, Changzhou, Jiangsu 213016, People’s Republic of China; orcid.org/0000-0003-2316-4537; Phone: +86 0519-8329-0280; Email: lvxiaofang5@cczu.edu.cn, lvxiaofang5@126.com

**Yang Liu** — Jiangsu Key Laboratory of Oil and Gas Storage & Transportation Technology, Changzhou University, Changzhou, Jiangsu 213016, People’s Republic of China; Phone: +86 0519-8329-0280; Email: chrisblack@foxmail.com

### Authors

**Bohui Shi** — National Engineering Laboratory for Pipeline Safety/MOE Key Laboratory of Petroleum Engineering/Beijing Key Laboratory of Urban Oil and Gas Distribution Technology, China University of Petroleum-Beijing, Beijing 102249, People’s Republic of China

**Shidong Zhou** — Jiangsu Key Laboratory of Oil and Gas Storage & Transportation Technology, Changzhou University, Changzhou, Jiangsu 213016, People’s Republic of China; orcid.org/0000-0001-8468-1226

**Yun Lei** — Jiangsu Key Laboratory of Oil and Gas Storage & Transportation Technology, Changzhou University, Changzhou, Jiangsu 213016, People’s Republic of China

**Pengfei Yu** — Jiangsu Key Laboratory of Oil and Gas Storage & Transportation Technology, Changzhou University, Changzhou, Jiangsu 213016, People’s Republic of China

**Jimiao Duan** — Department of Fuel, Army Logistics University of PLA, Changjing 401311, People’s Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04708

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (grant no. 5184046 & 52004039 & 51904330 & 51974037), PetroChina Innovation Foundation (grant no. 2018D-5007-0602), and Natural Science Research Project of Jiangsu Colleges and Universities (grant no. 18KJB440001).
NOMENCLATURE

\( r \) consumption rate of methane, m³/min
\( A \) constant
\( a, b, c \) constants
\( P \) pressure, Pa
\( t \) time, s
\( k_a \) constant of reaction rate, mol/(m²·MPa·s)
\( k_d \) constant of mass transfer, mol/(m²·Pa·s)
\( A_p \) surface area of hydrate particles, m²
\( f \) fugacity of the gas phase, MPa
\( f_{eq} \) fugacity of the gas phase at the equilibrium state, MPa
\( k \) constant of reaction rate, mol/min
\( v_{H2O} \) hydrate volume fraction in the liquid phase
\( r_{gas} \) gas constant, J/(mol·K)
\( T \) temperature, K
\( \Delta T \) subcooling degree, K
\( \sigma \) interfacial tension of water and the guest
\( \lambda \) heat conductivity coefficient of environment around the hydrate shell, J/(s·mm·K)
\( \rho_{H2O}, \rho_{gas}, \rho_{g} \) density of water, gas, kg/m³
\( \Delta h_i \) latent heat of hydrate formation, J/kg
\( c_{p,H2O}, c_{p,gas} \) heat capacity of water and gas, J/(kg·K)
\( k_w, k_g \) thermal diffusivity of water and gas, m²/s
\( \lambda_{H2O}, \lambda_{gas} \) thermal diffusivity of the hydrate and water
\( T_{eq} \) equilibrium temperature, K
\( T_{bulk} \) temperature of bulk water, K
\( W_{i,H/W} \) gas diffusivity rate of the component \( i \) at the H/W interphase, mol/s
\( D_{i} \) diffusion rate of the component \( i \) at radius \( r \), m²/s
\( C_{i} \) concentration of the component \( i \) at radius \( r \), mol/m³
\( W_{H/W} \) consuming rate of guest molecules at the H/W interphase, mol/m³
\( C_{eq}, \Omega_{eq} \) concentration and concentration parameter of the component \( i \) under the balanced conditions, mol/m³ and mol·MPa/m³
\( K_r \) kinetic constant of the component \( i \) during hydrate formation and growth, mol·MPa²·s⁻²
\( M_w \) molar mass of water molecules, g/mol
\( g_{H/W} \) gas consumption rate of water molecules at the H/W interphase, mol/s
\( x_{eq} \) fugacity of the gas phase at the thermodinamic phase equilibrium, mol/m³
\( \omega_{H/W} \) consuming rate of water molecules at the H/W interphase, mol/s
\( K_w \) constant of temperature, K
\( D_{H/W} \) diffusion rate of gas molecules
\( \psi \) mass transfer efficiency
\( \delta \) porosity of the hydrate layer
\( \theta \) contact angle of water and guest molecules, rad
\( \mu_{H2O}, \mu_{gas} \) dynamic viscosity of water saturated by guest molecules, Pa·s
\( \sigma \) interfacial tension of water and the guest fluid, N/m
\( \tau \) capillary curvature
\( f_{diff} \) effective coefficient of diffusion, m²/s
\( C \) moles of gas in a unit hydrate shell, mol/m³
\( r \) radial distance of gas bubbles, m
\( r_b \) radius of the hydrate shell, m
\( \psi_i \) irregular dimension coefficient of nonspherical gas bubbles
\( v_i \) hydrate growth rate, mm/s
\( \rho_{H2O} \) density of hydrate, water and gas, kg/m³

REFERENCES

(1) Koh, C. A.; Sloan, E. D. Clathrate Hydrates of Natural Gases, 3rd ed.; CRC Press: New York, 2008.
(2) Duc, N. H.; Chaussy, F.; Herri, J.-M. CO₂ capture by hydrate crystallization - A potential solution for gas emission of steelmaking industry. Energy Convers. Manage. 2007, 48, 1313–1322.
(3) Kenarsari, S. D.; Yang, D.; Jiang, G.; Zhang, S.; Wang, J.; Russell, A. G.; Wei, Q.; Fan, M. Review of recent advances in carbon dioxide crystallization - A potential solution for gas emission of steelmaking. Energy Convers. Manage. 2013, 69, 2379–2387.
(4) Zheng, J.; Bhatnagar, K.; Khurana, M.; Zhang, P.; Zhang, B.-Y.; Linga, P. Semiclathrate based CO₂ capture from fuel gas mixture at ambient temperature: Effect of concentrations of tetra-n-butylammonium fluoride (TBAF) and kinetic additives. Appl. Energy 2018, 217, 377–389.
(5) Lv, Y.-N.; Wang, S.-S.; Sun, C.-Y.; Gong, J.; Chen, G.-J. Desalination by forming hydrate from brine in cyclodisperation system. Desalination 2017, 413, 217–222.
(6) Fakharian, H.; Ganji, H.; Naderifar, A. Desalination of high salinity produced water using natural gas hydrate. J. Taiwan Inst. Chem. Eng. 2017, 72, 157–162.
(7) Liu, Y.; Chen, B.; Chen, Y.; Zhang, S.; Guo, W.; Cai, Y.; Tan, B.; Wang, W. Methane storage in a hydrated form as promoted by leucines for energy storage application. Appl. Energy 2018, 227, 33101–33112.
(12) Vysniauskas, A.; Bishnoi, P. R. A kinetic study of methane hydrate formation. Chem. Eng. Sci. 1983, 38, 1061–1072.

(13) Vysniauskas, A.; Bishnoi, P. R. Kinetics of ethane hydrate formation. Chem. Eng. Sci. 1985, 40, 299–303.

(14) Englezos, P.; Kalogerakis, N.; Dholabhai, P. D.; Bishnoi, P. R. Kinetics of formation of methane and ethane gas hydrates. Chem. Eng. Sci. 1987, 42, 2647–2658.

(15) Englezos, P.; Kalogerakis, N.; Dholabhai, P. D.; Bishnoi, P. R. Kinetics of gas formation from mixtures of methane and ethane. Chem. Eng. Sci. 1987, 42, 2659–2666.

(17) Sun, C. Y. The Kinetics of Hydrate Formation/Dissociation and Related Topics Doctor Dissertation. PhD Thesis, China University of Petroleum (Beijing), Beijing, China, 2001.

(18) Kinnari, K.; Labes-Carrier, C.; Lunde, K.; Hemmingsen, P.; Davies, S. R.; Boxall, J. A.; Koh, C. A.; Solan, E. D. Hydrate plug formation prediction tool—a new tool for flow assurance in the oil industry. Proceedings of the 6th International Conference on Gas Hydrates (ICGH6-2008): Vancouver, Canada, July 6–10, 2008.

(19) Li, Y.; Li, X.; Zhou, W.; Li, H.; Xin, F.; Li, Y. Kinetics of ethylene hydrate formation in water-in-oil emulsion. J. Taiwan Inst. Chem. Eng. 2017, 70, 79–87.

(20) Skovborg, P.; Rasmussen, P. A mass transport limited model for the growth of methane and ethane gas hydrates. Chem. Eng. Sci. 1994, 49, 1131–1143.

(21) Mori, Y. H.; Mochizuki, T. Mass transport across clathrate hydrate films - a capillary permeation model. Chem. Eng. Sci. 1997, 52, 3613–3616.

(22) Yapa, P. D.; Zheng, L.; Chen, F. A model for deepwater oil/gas blowouts. Mar. Pollut. Bull. 2001, 43, 234–241.

(23) Uchida, T.; Ikeda, I. Y.; Takeyai, S.; Ebinuma, T.; Nagao, J.; Narita, H. CO2 hydrate film formation at the boundary between CO2 and water: effects of temperature, pressure and additives on the formation rate. J. Cryst. Growth 2002, 237–239, 383–387.

(24) Mori, Y. H. Estimating the thickness of hydrate films from their lateral growth rates: application of a simplified heat transfer model. J. Cryst. Growth 2001, 223, 206–212.

(25) Mochizuki, T.; Mori, Y. H. Clathrate-hydrate film growth along water/hydrate-former phase boundaries-numerical heat-transfer study. J. Cryst. Growth 2006, 290, 642–652.

(26) Zhong, D. L.; Liu, D. P.; Wu, Z. M. Modeling of natural gas hydrate formation on a suspended water droplet. Proceedings of the 4th International Conference on Gas Hydrates (ICGH 2002): Yokohama, Japan, May 19–23, 2002.

(27) Freer, E. M.; Sami Selim, M.; Dendy Sloan, E. Methane hydrate film growth kinetics. Fluid Phase Equil. 2001, 185, 65–75.

(28) Turner, D. J.; Miller, K. T.; Dendy Sloan, E. Methane hydrate formation and an inward growing shell model in water-in-oil dispersions. Chem. Eng. Sci. 2009, 64, 3996–4004.

(29) Jamaluddin, A. K. M.; Kalogerakis, N.; Bishnoi, P. R. Hydrate plugging problems in undersea natural gas pipelines under shutdown conditions. J. Petrol. Sci. Eng. 1991, 5, 323–335.

(30) Zhao, J. K. Study on Flow Properties of Hydrate Slurry in Multiphase Pipeline Doctor Dissertation. PhD Thesis, China University of Petroleum (Beijing), Beijing, China, 2009.

(31) Shi, B.-H.; Gong, J.; Sun, C.-Y.; Zhao, J.-K.; Ding, Y.; Chen, G.-J. An inward and outward natural gas hydrates growth shell model considering intrinsic kinetics, mass and heat transfer. Chem. Eng. J. 2011, 171, 1308–1316.

(32) Shi, B. H. Study on the Characteristics of Hydrate Growth and Flow in Gas-Condensate Multiphase Pipeline. PhD Thesis, China University of Petroleum (Beijing), Beijing, China, 2012.

(33) Shi, B.-H.; Song, S.-F.; Lv, X.-F.; Li, W.-Q.; Wang, Y.; Ding, L.; Liu, Y.; Yang, J.-H.; Wu, H.-H.; Wang, W.; et al. Investigation on natural gas hydrate dissociation from a slurry to a water-in-oil emulsion in a high-pressure flow loop. Fuel 2018, 233, 743–758.

(34) Chen, J.; Liu, J.; Chen, G.-J.; Sun, C.-Y.; Jia, M.-L.; Liu, B.; Si, S.; Ren, N. Insights into methane hydrate formation, agglomeration, and dissociation in water-diesel oil dispersed system. Energy Convers. Manage. 2016, 114, 886–891.

(35) Chen, G.-J.; Guo, T.-M. A new approach to gas hydrate modelling. Chem. Eng. J. 1998, 71, 145–151.

(36) Aromada, S. Â.; Kvarme, B. Impacts of CO2 and H2S on the risk of hydrate formation during pipeline transport of natural gas. Front. Chem. Sci. Eng. 2019, 13, 616–627.

(37) Lv, X.; Shi, B.; Wang, Y.; Gong, J. Study on Gas Hydrate Formation and Hydrate Slurry Flow in a Multiphase Transportation System. Energy Fuel 2013, 27, 7294–7302.

(38) Lv, X.; Gong, J.; Li, W.; Shi, B.; Yu, D.; Wu, H. Experimental study on natural gas hydrate slurry flow. SPE J. 2013, 19, 206–214.

(39) Kvarmed, B.; Kuznetsova, T.; Kivelæ, P.-H. Adsorption of water and carbon dioxide on Hematite and consequences for possible hydrate formation. Phys. Chem. Chem. Phys. 2012, 14, 4410–4424.

(40) Ding, L.; Shi, B.; Wang, J.; Liu, Y.; Lv, X.; Wu, H.; Wang, W.; Lou, X.; Gong, J. Hydrate deposition on cold pipe walls in water-in-oil (w/o) emulsion systems. Energy Fuel 2017, 31, 8865–8876.

(41) Li, Y.; Shi, B.; Ding, L.; Yong, Y.; Zhang, Y.; Ma, Q.; Lv, X.; Song, S.; Yang, J.; Wang, W.; et al. Investigation of Hydrate Agglomeration and Plugging Mechanism in Low-Wax-Content Water-In-Oil Emulsion Systems. Energy Fuel 2018, 32, 8986–9000.

(42) Peng, D.-Y.; Robinson, D. B. A new two-constant equation of state. Ind. Eng. Chem. Fundam. 1976, 15, 59–64.

(43) Kvarme, B. Thermodynamic limitations of the CO2/N2 mixture injected into CH4 hydrate in the Ignik Sikumi field trial. J. Chem. Eng. Data 2016, 61, 1280–1295.

(44) Kvarme, B.; Aromada, S. A.; Gjerstad, P. B. Consistent Enthalpies of the Hydrate Formation and Dissociation Using Residual Thermodynamics. J. Chem. Eng. Data 2019, 64, 3493–3504.

(45) Kvarme, B. Consistent thermodynamic calculations for hydrate properties and hydrate phase transitions. J. Chem. Eng. Data 2020, 65, 2872–2893.

(46) Kvarme, B. Enthalpies of hydrate formation from hydrate formers dissolved in water. Energies 2019, 12, 1039.

(47) Kvarme, B.; SelvÅg, J.; Saeidi, N.; Kuznetsova, T. Methanol as a hydrate inhibitor and hydrate activator. Phys. Chem. Chem. Phys. 2018, 20, 21968–21978.

(48) Liu, Y.; Shi, B.; Ding, L.; Ma, Q.; Chen, Y.; Song, S.; Zhang, Y.; Yong, Y.; Lv, X.; Wu, H.; et al. Study of hydrate formation in water-in-waxy oil emulsions considering heat transfer and mass transfer. Fuel 2019, 244, 282–295.