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Depressurization induced gas production from hydrate deposits with low gas saturation in a pilot-scale hydrate simulator

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HIGHLIGHTS

- Hydrate samples with low gas saturations are synthesized in a 3-D simulator.
- Hydrate is dissociated using depressurization method in a single vertical well.
- Production behaviors predicted by the kinetic and equilibrium models are compared.
- The equilibrium model is found to be more preferred than the kinetic model.

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ABSTRACT

The kinetic behaviors of methane hydrate dissociation under depressurization in porous media are investigated through experimental and numerical simulations. Hydrate samples with low gas saturations ($S_G \leqslant 0.10$) are synthesized in the pilot-scale hydrate simulator (PHS), a novel three-dimensional pressure vessel with effective inner volume of 117.8 L. Three experimental runs with different production pressure at the central vertical well have been carried out. The intrinsic dissociation rate constant k_0 is fitted to be approximately 4578 kg/(m^2 Pa s) using the experimental data of run 1, and it is used for the kinetic simulation in all the three runs. The whole production process can be divided into two stages: the free gas and mixed gas production (stage I) and the gas production from hydrate dissociation (stage II). Both the experimental and numerical simulation results show that the gas production rate increases with the decrease of the production pressure, while the water extraction rate will rise much higher if the wellbore pressure is dropped extremely low. The free gas saturation is found to be a key factor that affects the overall production behaviors of marine hydrate deposits. In addition, the comparisons of the kinetic and equilibrium models indicate that the kinetic limitations are very small in the PHS. The hydrate dissociation under depressurization in the PHS is mainly controlled by the mass and heat transfer processes.

1. Introduction

Natural gas hydrates are crystalline solid compounds in which water and gas molecules are bounded in the ice-like crystal lattices called hosts under suitable pressure and temperature conditions. The hydrate-forming gases are usually small and light molecules, such as CH_4, C_2H_6 and CO_2, and they can exist with water in the form of structure I, II and H hydrate, depending on the gas species and the formation conditions [1]. The reaction of methane hydrate formation and dissociation is generally described by the following equation:

$$CH_4 + N_H H_2O \iff CH_4 \cdot N_H H_2O + \Delta H \quad (1)$$

where N_H is the hydration number, and ΔH is the enthalpy of hydrate formation or dissociation. $N_H = 6.0$ is the average hydration number, while $N_H = 5.75$ corresponds to complete hydration [1]. Natural gas hydrates have attracted global attentions as a kind of new and potential energy resource in recent years, and they are proved to exist widely in the permafrost and in deep ocean sediments [2]. The crystallization process in Eq. (1) has also been widely investigated as a potential strategy for methane separation from gas mixtures in recent years [3–6].

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Nomenclature

A_S	reaction surface area, m^2
f_{eq}	equilibrium fugacity, Pa
f_g	gas fugacity, Pa
F_a	area adjustment factor
k	kinetic rate constant, kg/(m^2 Pa s)
k_0	intrinsic rate constant, kg/(m^2 Pa s)
K	intrinsic permeability, m^2
m_H	hydrate mass, g
m_W	mass of produced water, g
$m_{W,inj}$	total water for hydrate formation, g
M_H	molar mass of hydrate, g/mol
M_W	molar mass of water, g/mol
n_m	remaining methane amount, mol
n_{m0}	total gas for hydrate formation, mol
N_H	hydration number, 5.75
N_V	number of voids
P	pressure, MPa
P_W	wellbore pressure, MPa
Q_H	average hydrate dissociation rate, g/min
Q_P	average gas production rate, L/min
Q_W	average water production rate, g/min
r, z	cylindrical coordinates, m
r_p	radius of sand grain, m
R	gas constant, 8.314 J/(mol K)
S	phase saturation
t	time, s
T	temperature, K
v_m	molar volume of gas, mL/mol
$V_{G,inj}$	total gas for hydrate formation, L
V_P	total volume of produced gas, L
V_{pore}	total pore volume, mL
x	percentage of hydrate dissociation
ΔE_a	activation energy, J/mol
Δt	production time, min
ρ_H	hydrate density, g/mL
ρ_W	water density, g/mL
β	reduction exponent
ϕ	porosity
λ	van Genuchten exponent – Table 4

Subscripts and superscripts

0	denotes initial state of hydrate formation
00	denotes initial state of hydrate dissociation
A	aqueous phase
B	boundary
cap	capillary
end	represents end point
G	gas phase
H	solid hydrate phase
irA	irreducible aqueous phase
irG	irreducible gas
n	permeability reduction exponent – Table 4
n_G	gas permeability reduction exponent – Table 4

In order to extract the methane gas from gas hydrates, the following methods have been proposed for hydrate dissociation: (1) depressurization [7,8], in which the pressure of the deposit is dropped below the dissociation pressure; (2) thermal stimulation [9–11], in which heat is provided manually to the deposit to raise the temperature above the equilibrium temperature; (3) thermodynamic inhibitor injection [12,13], in which chemicals, such as salts and alcohols, are used to shift the equilibrium pressure–temperature conditions. Among them, the depressurization is generally thought to be the most promising and technically feasible method for field hydrate dissociation because of its economic effectiveness [7,14,15].

In order to investigate the hydrate dissociation and gas production behaviors in porous media, people have built up some three-dimensional (3D) experimental apparatus specifically for the simulation of hydrate formation and decomposition process. Yang et al. [8] developed a middle-sized cylindrical reactor (100 mm in height and 300 mm in diameter), and carried out the hydrate formation experiment using frozen sand instead of wet sand with pore water. Then the formed hydrate sample was dissociated by depressurization method. Pang et al. [16] investigated the kinetic behaviors of methane hydrate dissociation using thermal method in a stainless steel reactor of 10 L, and they observed a dramatically reduced dissociation rate phenomenon – “buffered dissociation” due to the ice melting. Recently, we have also developed two 3D hydrate simulators for the investigation of hydrate formation and dissociation: a cubic hydrate simulator (CHS, 5.8 L) and a pilot-scale hydrate simulator (PHS, 117.8 L). Both the depressurization [7,15] and the thermal stimulation [10,17–20] methods have been applied for methane hydrate dissociation in porous media in the two apparatus.

Another effective way to describe the dynamic properties of hydrate dissociation is to construct the numerical simulation code based on the experimental data. Generally, there are two approaches for the mathematic description of hydrate dissociation in porous media: the equilibrium model and the kinetic model. For the equilibrium model, hydrate dissociates spontaneously and immediately when the pressure or temperature decreases below the equilibrium level. Recently, Li et al. [7,17,21] have validated the effectiveness of the equilibrium model of the TOUGH + HYDRATE (T + H) code [22] using the experimental data from the CHS and the PHS mentioned above. Under the kinetic model, the hydrate dissociation is a rate-dependent process that is affected by the kinetic reaction rate constant and other relevant parameters. It is usually described by the Kim–Bishnoi model [23], which is generally formulated as follows:

$$\frac{\partial m_H}{\partial t} = -kA_S(f_{eq} - f_g) \qquad (2)$$

where m_H is the mass of the hydrate (kg); k is the reaction rate constant (kg/(m^2 Pa s)); A_S is the reaction surface area (m^2); f_g and f_{eq} are the local fugacity and the equilibrium fugacity of methane gas under the local temperature, respectively (Pa). The kinetic constant k is generally expressed as $k = k_0\exp(-\Delta E_a/RT)$, in which k_0 is the intrinsic reaction rate constant (kg/(m^2 Pa s)), ΔE_a stands for the activation energy (J/mol), R is the gas constant (J/(mol K)), and T is the local temperature (K). The local temperature means the temperature of the hydrate deposit, and it is measured as the average temperature of the thermocouples in the experiment. So far, only a few reports about the kinetic option for hydrate dissociation simulation can be found in the literature. Moridis et al. [24] analyzed the methane hydrate dissociation data from a sequence of tests under thermal stimulation, and further estimated the kinetic dissociation parameters by means of inverse modeling. After that, Kowalsky and Moridis [25] compared the use of kinetic and equilibrium reaction models for predicting the methane hydrate dissociation behaviors in porous media. It was found that the simulated results of both reaction models were remarkably similar in large-scale hydrate