Experimental Study on the Influence of Micron SiO₂ on the Kinetics of Hydrate Formation

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Abstract. In order to explore the kinetic mechanism of hydrate formation in a system containing micron-sized SiO₂ particles, this paper uses a high-pressure reactor device with stirring function to record changes in pressure, temperature and torque during the growth of hydrates through a data acquisition system, based on the conservation of mass in the system The principle and gas equation of state calculate the kinetic parameters of hydrate formation such as gas consumption in the reactor, hydrate formation rate and induction time, and analyze the influence of particle size and particle concentration on the kinetic characteristics of hydrate formation based on the experimental results. The experimental results show that the particle content has no obvious effect on the average growth rate of hydrate in the range of 1%-7%, but increasing the particle content can effectively reduce the hydration induction time; when the particle size is in the range of 2.5-85 μm, the larger the particle size, the shorter the hydrate induction time and the greater the hydrate growth rate.

1. Introduction

With declining land oil production, increasing attention to environmental issues, and gradual adjustments in the energy structure, natural gas is regarded as an efficient and clean energy source that can replace coal and oil. Since natural gas hydrate has the characteristics of decomposition or formation under changes in temperature and pressure, which affects the drilling and production process of hydrate reservoirs, efficient and safe development of hydrates is the main direction for studying hydrates, among which hydrate formation kinetics Characteristic research has attracted much attention.

In the process of hydrate mining, with the increase of external temperature, there are complicated multiphase flow of mud, hydrate, methane gas, and seawater in the pipeline. There are few reports on the hydrate dynamics in the system containing micron-sized particles in the flowing state. Therefore, the study of hydrate growth kinetic parameters is the basis and key to ensure the safe and efficient drilling and production.

Compared with porous media, adding solid particles to the flow system may not change the thermodynamic properties of hydrates, but the studies by Park[1], Kim[2], Song[3] and others have shown that in the liquid phase, the addition of nanoparticles will affect hydrates, and the properties of different particles will have different effects. In order to explore the kinetic mechanism of hydrate in a
system containing micron-sized particles in a flowing state, this paper carried out a study on the growth characteristics of hydrate in a system containing micron SiO$_2$ under agitation. The pressure, temperature, and torque changes with time were measured using a high-pressure reactor. Based on the principle of conservation of mass and the gas equation of state, the induction time, hydrate growth rate and other kinetic parameters are calculated, and the hydrate growth law in the system is analyzed from the aspect of mass transfer, which provides basic experimental data for drilling, production and transportation of hydrates containing sandy systems in pipelines.

2. Materials and Methods

2.1. Experimental apparatus and procedure

The hydrate formation reactor is shown in Figure 1. the visualized high-pressure reactor has a volume of 600 mL, and a four-blade rotor is installed in the reactor, and the upper blade is fixed at the air-water interface, which causes disturbance at the air-water interface to increase the gas-water contact area and facilitate the dissolution of methane gas in the water; the lower blade agitates the liquid in the reactor to prevent the sedimentation of silicon powder.

![Figure 1 Schematic diagram of experimental device](image)

The experiment uses deionized distilled water, obtained by HITECH SCIENCE TOOL ultra-pure water machine; the experimental gas is 99% methane gas, purchased from Tongzhou Hongren; the solid phase particles are microsilica produced by Aladdin Biochemical Technology Co., Ltd., and the particle sizes are respectively 2.5 μm, 10 μm, 25 μm, 85 μm, the molar mass is 60.08 g·mol$^{-1}$.

The weighed microsilica is mixed with distilled water and then added to the reactor, and stirred at a rate of 400 r·min$^{-1}$ to make the suspension system evenly distributed in the reactor; set the temperature of the constant temperature bath to cool down the reactor, use a booster pump to pressurize the gas to a preset pressure, inject the pressurized CH$_4$ gas into the buffer bottle and cool it to the same temperature. After the temperature in the kettle drops to the preset temperature, open the valve and inject CH$_4$ gas into the reactor to the preset temperature (8 MPa); Keep the temperature of the constant temperature bath unchanged, record the pressure and temperature changes with time, and react until the pressure in the kettle remains stable for 6 hours, that is, the hydrate formation is considered complete and the reaction is terminated. The experimental parameter settings are shown in Table 1, during the whole experiment, the initial pressure is 8 MPa, the initial temperature is 2 ℃, and the rotor speed is 400 rpm.

| Parameter            | Parameter value     |
|----------------------|---------------------|
| Solid content (%)    | 1, 3, 5, 7          |
| Particle size (μm)   | 2.5, 10, 25, 85     |

2.2. Data processing

The rate of methane consumption and the induction time required for hydrate formation are important.
parameters for the study of hydrate formation reaction. The amount of methane in the gas phase at different times is calculated as follows:

\[ n_g = \frac{PV}{ZRT} \]  

(1)

The method for calculating CH4 gas consumption is as follows:

\[ \Delta n = \left( \frac{PV_1}{Z_1} - \frac{PV_2}{Z_2} \right) \times \frac{1}{RT} \]  

(2)

where \( \Delta n \) methane consumption; \( P \) is methane gas pressure; \( T \) is methane temperature; \( R \) is gas constant, 8.314 J·mol⁻¹·K⁻¹.

The compressive factor can be calculated as follows[4]:

\[ Z = 1 + \left( A_1 + \frac{A_2}{T_{pr}} + \frac{A_3}{T_{pr}^3} \right) + \left( A_4 + \frac{A_5}{T_{pr}} \right) \rho_r^3 + \left( \frac{A_6}{T_{pr}} \right) \rho_r^5 - \frac{A_7}{T_{pr}^3} \rho_r^2 \left( 1 + A_8 \rho_r^2 \right) e^{-A_9 \rho_r^2} \]  

(3)

where \( A_i \) is given parameters( \( A_1 = 0.31506237 \), \( A_2 = -1.0467099 \), \( A_3 = -0.57832729 \), \( A_4 = 0.53530771 \), \( A_5 = -0.61232032 \), \( A_6 = -0.10488813 \), \( A_7 = 0.68157001 \), \( A_8 = 0.68446549 \); \( T_{pr} \) is comparative temperature; \( P_{pr} \) is comparative pressure; \( \rho_r \) is methane comparative density. \( T_{pr} \), \( P_{pr} \) and \( \rho_r \) can be calculated by the following formula:

\[ P_{pr} = \frac{P}{P_C} \quad T_{pr} = \frac{T}{T_C} \quad \rho_r = 0.27 \left( \frac{P_{pr}}{ZT_{pr}} \right) \]  

(4)

where \( P_C \) is critical pressure of methane gas; \( T_C \) is methane temperature. The calculation method of the water phase volume and hydrate phase volume is as follows:

\[ V_{wi,j} = V_{wi,j-1} - 6(\Delta n_g,j)M_w / \rho_w \]  

\[ V_h = V_{hi,j-1} - 7(\Delta n_g,j)M_h / \rho_h \]  

(5)

(6)

where \( M_h \) is molar mass of hydrate; \( \rho_h \) is density of hydrate. The consumption of methane gas in the reactor is calculated by the following formula:

\[ r = (\Delta n / \Delta t) / (V_w + V_h) \]  

(7)

where \( r \) is methane consumption rate; \( \Delta t \) is time interval, and can be set in the data acquisition system. The average gas consumption rate is calculated as follows:

\[ R = \frac{r_1 + r_2 + \cdots + r_m}{m} \]  

(8)

The calculation method of induction time in this paper is as follows:

\[ t_{ind} = t_{eq} - t_{eq} \]  

(9)

where \( t_{ind} \) is induction time; \( t_{eq} \) is the time required for the system to appear turbid; \( t_{eq} \) is the time required for the system to reach equilibrium. Calculate the induction time according to this formula, and take the average of the three experiments.
3. Results and discussion

3.1. The effect of particle content on the growth of methane hydrate

![Figure 2 Changes of pressure, torque and temperature in the growth process of CH4 hydrate in suspension systems with different microsilica content](image)

The gas pressure change curve of methane in the reactor is shown in Figure 2, the process can be divided into the following four parts: (1) The pressure drops rapidly during the dissolution of methane gas; (2) The pressure in the hydrate induction stage tends to be stable. Because the initial pressure is much greater than the phase equilibrium pressure at the experimental temperature, the hydrate crystallizes faster and the induction time is shorter; (3) The hydrate grows rapidly after the formation of critical-size hydrate crystal nuclei, which consumes methane gas in the reactor; (4) The pressure of the system continues to drop, and the driving force for the formation of hydrates weakens. With the massive formation of hydrates, the concentration of salt in the system increases, the growth resistance of hydrates increases, the pressure gradually stabilizes, and the complete formation reaction stops.

![Figure 3 The average gas consumption rate and induction time of methane hydrate formation under different silicon powder content](image)
As shown in Figure 3, the hydrate induction time of the system with microsilica is significantly shorter than that of the system without microsilica, indicating that the presence of microsilica in the system can effectively shorten the hydrate induction time, which is the same as the results of Lee[5] et al. The reason is: in the experimental system, the surface of microsilica can provide a solid-liquid interface for hydrate nucleation. The existence of this interface makes the critical energy barrier for hydrate nucleation lower, thereby reducing the energy required for nucleation, resulting in easier nucleation of hydrates in the system. In addition, within the scope of the experiment, as the content of fine silicon powder in the system increases, the hydrate induction time shows a downward trend. When the content of microsilica is 3%, the induction time is shorter than other systems.

3.2. The effect of particle size on the growth of methane hydrate

Figure 4 shows that when the hydrate is completely formed, the gas phase pressure in the system is basically stable at about 4 MPa, indicating that the particle size of the microsilica basically does not affect the final hydrate formation.
Figure 5 Influence of microsilica size on methane hydrate induction time and average growth rate in suspension system

As shown in Figure 5, when the particle size of the microsilica is in the range of 2.5-85 μm, the induction time decreases with the increase of the particle size, indicating that the hydrate nucleation rate is faster in the large particle size suspension system. The reason is: with the same particle mass fraction, the smaller the particle size, the larger the specific surface area, which leads to more gas adsorbed on the surface of the particles, which is conducive to the nucleation of hydrates. The capillary force also has a certain influence on the nucleation of hydrates. However, in the stirring system, there is no capillary force between the particles, the surface of the microsilica may be smoother and the pore structure may not be much, and the adsorbed gas is limited.

4. Conclusions
The high-pressure reactor test device with stirring function was used to study the hydrate formation characteristics in the microsilica suspension system in the flowing state, and the average growth rate and induction time of the hydrate were calculated under different experimental conditions. The research results showed that: (1) in the range of 0-7% of the mass concentration of microsilica, as the content of microsilica increases, the hydrate induction time in the system generally decreases, and the hydrate growth rate increases. The hydrate growth rate after adding microsilica to the system is significantly higher than that of the system without microsilica, but the content of silicon micro-powder has no obvious influence on the average growth rate of hydrate; (2) when the particle size of microsilica is in the range of 2.5-85, the induction time decreases with the increase of particle size, and the average growth rate of hydrate increases with the increase of particle size

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