

Effect of Deposit Heat Transfer on Natural Gas Hydrate Exploitation by Depressurization

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ABSTRACT

Natural gas hydrate has attracted worldwide attention due to its huge reserves and clean combustion. The depressurization method is the most economical method to extract gas from hydrate. However, the mechanisms of heat transfer affecting hydrate decomposition rate during depressurization are still unclear. In this study, the gas production flux was controlled at 0.032 mol/min during depressurization, and three heat transfer conditions of hydrate deposit were used to decompose hydrate. The results show that the T-P responses of the thermodynamic system will be eventually parallel to the phase equilibrium line of hydrate during depressurization, which is not affected by the deposit heat transfer. After the deposit temperature is controlled by the thermodynamic properties of hydrate, the extra energy will be used to improve the hydrate decomposition rate under a good deposit heat transfer condition. Furthermore, ice formation during depressurization promotes hydrate decomposition, which hinders the decrease of the pressure and temperature of the deposit. Our findings reveal that the temperature of the thermodynamic system cannot be balanced by thermal energy and provide a new insight for the rate control of hydrate decomposition during depressurization from the perspective of deposit heat transfer.

Keywords: Natural gas hydrate, depressurization, deposit heat transfer, ice formation, hydrate decomposition, thermodynamic system

NONMENCLATURE

Symbols

| | |
|---|--------------------------------|
| T | Average temperature of deposit |
| P | Pressure of deposit |

1. INTRODUCTION

Many countries are striving to find efficient and clean energy to alleviate global energy shortages. Natural gas hydrate has huge reserves and is considered a promising energy source in the future. It has been reported that 1 m³ of natural gas hydrate can release 164 m³ of natural gas (mainly methane) under atmospheric temperature and pressure conditions [1, 2]. A series of methods have been proposed to extract methane from hydrate such as depressurization [3], thermal stimulation [4], and CO₂ replacement [5]. The depressurization method is considered to be the most economical and energy-saving method [6].

It is necessary to carry out many experimental studies on hydrate decomposition characteristics by depressurization before commercial exploitation of natural gas hydrate. Chong et al. [7] found that a lower production pressure resulted in a higher gas production and a higher pressure drop rate can improve hydrate decomposition rate. The process of hydrate decomposition is endothermic [8, 9], so it is very important to study the influence mechanism of heat transfer on hydrate decomposition. Oyama et al. [10] investigated the hydrate decomposition characteristics by depressurization method, and the results showed that heat transfer from the surroundings played a key role during the hydrate decomposition process. Li's research group [8, 11] conducted a series of experiments and found that the hydrate decomposition rate increased with the increasing grain size and thermal conductivity of the deposit skeleton. Their findings can provide guidance for exploiting different types of hydrate deposits. However, most researchers mainly focused on the influence of deposit itself on hydrate decomposition. The mechanisms of deposit heat transfer on hydrate decomposition are rarely discussed.

The temperature response of hydrate deposits was controlled by the pressure drop during depressurization

[12]. In order to study the mechanisms of heat transfer on hydrate decomposition, we used the stainless steel reactor to simulate the external deposit, and three heat transfer conditions were simulated by changing the temperature of the outer wall of the reactor. The temperature responses and decomposition rate control mechanism of hydrate deposit under three different heat transfer conditions were analyzed. Furthermore, the ice behavior in the hydrate deposit during depressurization was discussed as well. The results are significant for the control of hydrate decomposition rate during depressurization.

2. EXPERIMENTAL SECTION

2.1 Apparatus and materials

Fig. 1 shows the schematic of experimental system, which mainly consists of a stainless steel reactor, an air bath, an intermediate container, a mass flow controller, a back pressure valve, a gas collector and a data acquisition system. The reactor placed in an air bath is 200 mm in internal diameter, 300 mm in height, and 9.4 L in internal volume. Two production wells (see Fig. 2) are symmetrically located and 65 mm away from the central axis of the reactor. The gas production ports of the production wells are all located at the middle height of the reactor. These two production wells are connected to a 0.5 L intermediate container, and the mass flow controller (Bronkhorst, Netherlands) can control the methane production flux at a set value. The back pressure valve (Fisher, Baumann 51,000, USA) is fully open, and the produced methane is collected by a 40 L gas collector during the whole production process.

There are 23 temperature measuring points with a precision of ± 0.1 °C in the reactor (see Fig. 2). The pressure sensors used has a precision of ± 0.03 MPa. All the data of pressure and temperature can be monitored by a data acquisition system every 10 s.

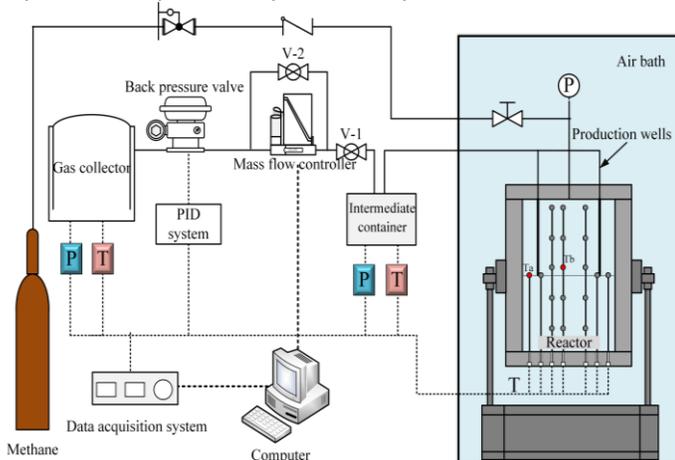


Fig. 1 Schematic of experimental system

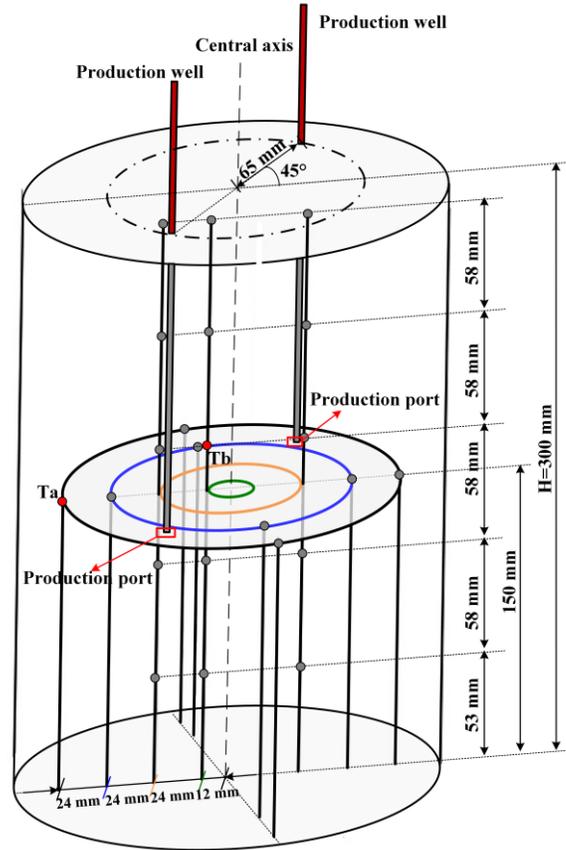


Fig. 2 The distribution of two production wells and temperature measuring points

One kind of glass sand (2.5 g/cm^3 , BZ-01, Japan AS-ONE) was employed to simulate the deposit skeleton. High-purity methane gas (99.99%, Dalian Special Gases Company from China) was used to simulate the natural gas source. All experiments used ultra-pure water produced by a deionizer.

2.2 Procedures

First, 13.1 kg of dry glass sands and 1580 ml of ultra-pure water were mixed thoroughly, and then the wet sands were filled and compacted to a height of 300 mm. After the reactor was purged 3 times using low-pressure methane gas, the reactor was cooled to 2.8 °C. Next, high-pressure methane gas was injected into the reactor several times until the pressure of the reactor finally stabilized at approximately 5.1 MPa. The formation process of the gas hydrate deposit was considered to be finished when the pressure fluctuation of the reactor was less than 0.01 MPa within 6 h.

To extract methane gas from hydrate, the temperature of the air bath was adjusted to the set value T_1 . The mass flow controller was set at 0.032 mol/min, and the back pressure valve was set to fully open. The V-1 was opened and V-2 was closed. When the pressure difference between the reactor and the gas collector was lower than 0.2 MPa in the later stage of depressurization, the mass flow controller was closed and V-2 was opened.

The production process of the gas hydrate deposit was finished when the pressure of the gas collector was stable. Initial conditions and production parameters are shown in Table 1.

Table 1 Initial conditions and production parameters

| Case | T_0 (°C) | P_0 (MPa) | S_h (%) | q (mol/min) | T_1 (°C) |
|------|------------|-------------|-----------|---------------|------------|
| 1 | 2.8 | 5.0 | 38 | 0.032 | 2.8 |
| 2 | 2.8 | 5.1 | 38 | 0.032 | 4.8 |
| 3 | 2.8 | 5.1 | 37 | 0.032 | 6.6 |

^a The symbols are defined as follows: T_0 and P_0 are the average temperature and pressure of deposit before production, respectively. S_h is the initial hydrate saturation; q is the rated gas production flux; T_1 is the temperature of air bath during the exploitation process.

The detailed data processing process can refer to our previous study [12]. In brief, the total methane production refers to the change of methane moles in the gas collector. The methane production from hydrate, also called decomposed hydrates, is the difference between the mole increment of methane in the gas collector and the mole decrement of methane in the reactor and intermediate reactor before and after production.

3. RESULTS AND DISCUSSION

In this section, the evolutions of pressure, temperature, hydrate decomposition characteristics and ice behaviors during the typical slow depressurization process were discussed. The control mechanisms of three heat transfer conditions of hydrate deposit on hydrate decomposition rate were analyzed.

3.1 Typical hydrate decomposition during the slow depressurization process

Fig. 3 shows the methane production, pressure and average temperature profiles in Case 1. Time zero represents the beginning of gas production. Lines a and b indicate the start of hydrate decomposition and the turning point of hydrate decomposition rate, respectively. When the total methane was produced at a rated gas flux of 0.032 mol/min, the pressure and average temperature of the hydrate deposit decreased almost linearly, and only the free methane in pores was produced. Gas hydrate began to decompose with approximately 0.022 mol/min at 68 min. Due to the endothermic effect of hydrate decomposition and Joule-Thomson effect [13], the temperature drop rate of hydrate deposit was higher than that of the previous stage. In addition, the pressure drop rate of this stage was lower than that of the previous stage, which can be

attributed to the methane accumulation caused by the hydrate decomposition [14].

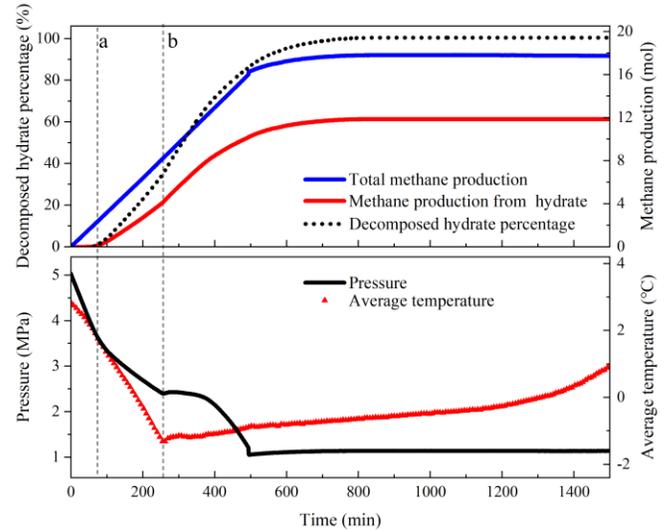


Fig. 3 Methane production, pressure and average temperature profiles in Case 1

After that, the hydrate decomposition rate increased significantly at 256 min, and the corresponding pressure and average temperature increased slightly. It was speculated that the heat released by ice formation promoted the hydrate decomposition, and the hydrate decomposition rate was slightly higher than the set gas flux, resulting in a slight increase of pressure. With the decrease of hydrate decomposition rate, the deposit pressure began to decrease gradually at approximately 380 min. At approximately 495 min, the pressure difference between the reactor and the gas collector was lower than 0.2 MPa, which affected the normal operation of the mass flow controller. However, the hydrate only decomposed by approximately 86.5%. Therefore, the mass flow controller was closed and V-2 was opened to decompose the remaining hydrate.

To verify the speculation that ice formation occurred in the hydrate deposit at 256 min, Fig. 4 shows the spatial temperature changes of the hydrate deposit in Case 1. The blue background represents the period in which the gas production flux was controlled at a rated gas flux of 0.032 mol/min. As shown in Fig. 4, the obvious thermal buffering of T_a (located in the outer ring of the deposit) and T_b (located in the inner ring of the deposit) was observed at 256 min and 364 min, respectively. The results show that there was ice formation in the hydrate deposit [7], and the ice formation in the inner ring of the deposit was later than that in the outer ring. However, the temperature of the outer ring was higher than that of the inner ring. Therefore, the icing sequence is mainly controlled by water content rather than heat transfer.

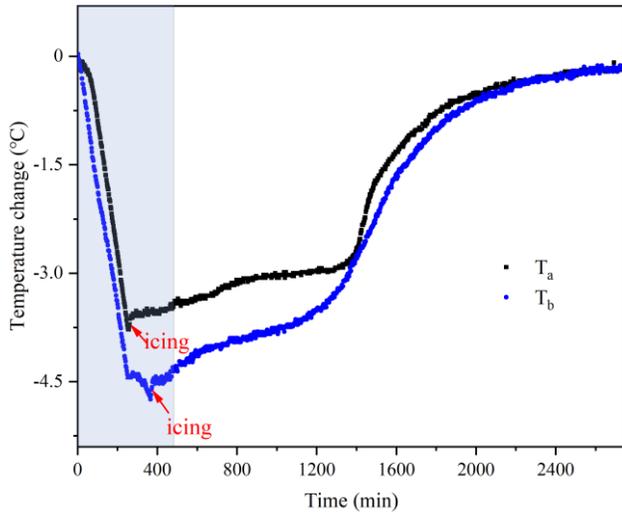


Fig. 4 Spatial temperature changes (T_a and T_b shown in Fig. 2) of the hydrate deposit in Case 1

3.2 Hydrate decomposition under different heat transfer conditions of hydrate deposit

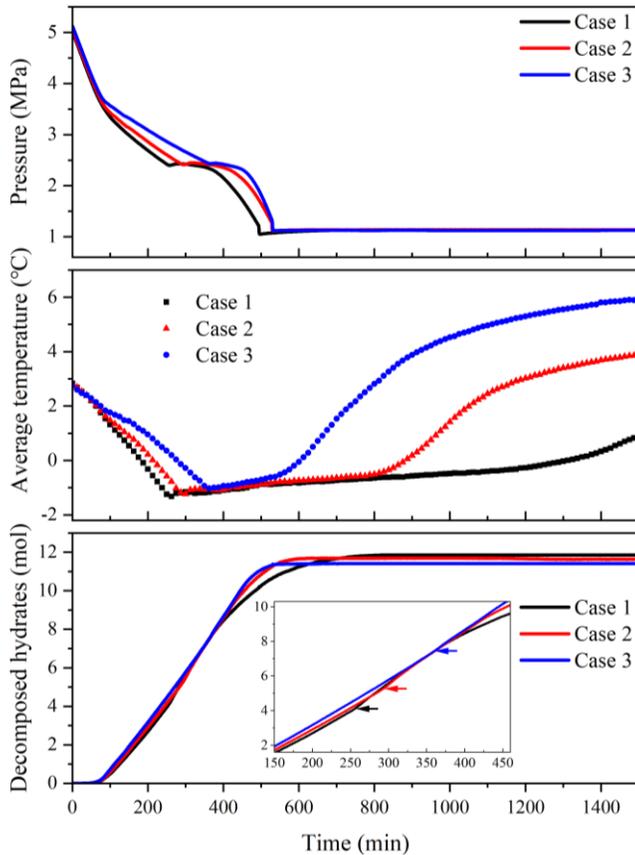


Fig. 5 Comparison of pressure, average temperature and decomposed hydrates profiles in Cases 1-3

Fig. 5 shows the comparison of pressure, average temperature and decomposed hydrates profiles in Cases 1-3. Before hydrate decomposition, the evolutions of pressure and average temperature of the hydrate deposits in Cases 1-3 were close, which indicated that the three heat transfer conditions in this study had little influence on the free methane release stage. After

hydrate decomposition, the drop rates of the pressure and temperature of Case 3 were slower than those of Cases 1 and 2, and the corresponding hydrate decomposition rate was faster than that of Cases 1 and 2. The results show that a good heat transfer condition of hydrate deposit can promote hydrate decomposition. As shown in Fig. 5, the deposit pressures of Cases 2 and 3 stopped decreasing, and the corresponding hydrate decomposition rates accelerated significantly at approximately 295 and 360 min, respectively. These experimental phenomena of Cases 2 and 3 were similar to those of Case 1, and the reason was that icing promoted hydrate decomposition.

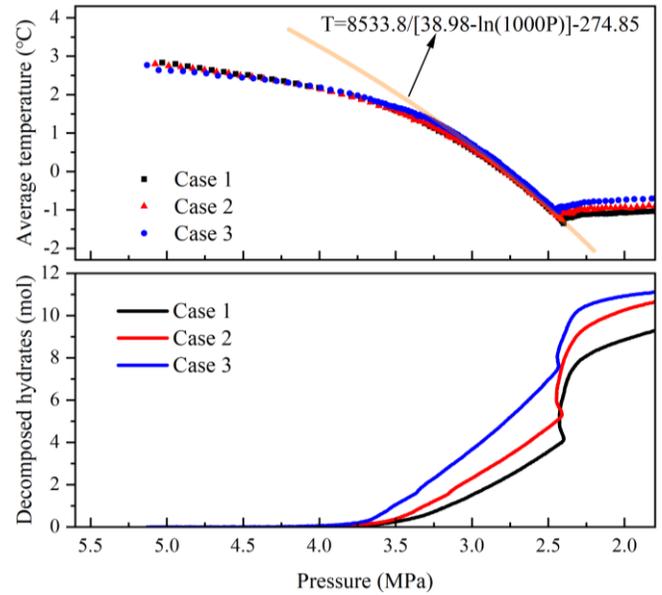


Fig. 6 Responses of average temperature and decomposed hydrate with deposit pressure in Cases 1-3

To investigate the influence mechanism of deposit heat transfer on hydrate decomposition, Fig. 6 shows the responses of average temperature and decomposed hydrate with deposit pressure in Cases 1-3. Hydrate began to decompose when the deposit pressure decreased to approximately 3.75 MPa. When the pressure was further reduced to the same pressure, the decomposition rate of hydrate deposit with good heat transfer was higher than that of hydrate deposit with poor heat transfer. As shown in Fig. 5 and Fig. 6, the evolutions of pressure and average temperature over time after hydrate decomposition in Cases 1-3 were different significantly. However, the T-P responses almost coincided and gradually conformed to $T [^{\circ}\text{C}] = 8533.8 / [38.98 - \ln(1000P [\text{MPa}])] - 274.85$, which paralleled the phase equilibrium line of methane hydrate described by Kamath [15]. The above results show that when the deposit temperature is controlled by the thermodynamic properties of hydrate, if the available energy of the deposit increases (corresponding to a good

heat transfer condition of the hydrate deposit), it can be used to improve the hydrate decomposition rate.

4. CONCLUSIONS

In this study, the mechanism of heat transfer on hydrate decomposition rate during slow depressurization was studied by using three heat transfer conditions of natural gas hydrate sandy deposits. During the slow depressurization process, controlled by the thermodynamic properties of the hydrate, the T-P responses of the three hydrate deposits with different heat transfer conditions are gradually parallel to the phase equilibrium line of methane hydrate, satisfying $T [^{\circ}\text{C}] = 8533.8 / [38.98 - \ln(1000P [\text{MPa}])] - 274.85$. Therefore, a good deposit heat transfer can improve the hydrate decomposition rate under the same pressure. The ice formation significantly improves the hydrate decomposition rate and changes the temperature and pressure of the hydrate deposit. The results can be of help to understand the rate control of hydrate decomposition during depressurization from the angle of deposit heat transfer.

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