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ENHANCED CH_4 PRODUCTION AND CO_2 SEPARATION BY USING MULTI-DEPRESSURIZATION IN METHANE HYDRATE ACCUMULATIONS

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ABSTRACT

The replacement of CH_4 by injecting CO_2 in methane hydrates is a promising method for simultaneously allowing geologic CO_2 sequestration and CH_4 recovery. However, the carbon dioxide hydrate layer formed on the MH surface acts as a barrier, which causes the slow diffusivity of CO_2. Therefore, in this study, we proposed using an operation of multi-depressurization to increase the diffusivity of CO_2 and enhance the CH_4 recovery in the CH_4/CO_2 replacement processes. The results proved that both the value of the methane replacement rate and the carbon dioxide storage rate increase significantly.

Keywords: hydrate, CH_4 recovery, CH_4/CO_2 replacement, multi-depressurization

1. INTRODUCTION

Natural Gas Hydrates (NGHs), known as one of the most abundant unconventional energy resources on earth, occur worldwide in locations such as the permafrost regions and beneath the sea, also attract attention for the gas production technologies of it [1, 2].

Most of the gas production technologies are based on breaking the thermodynamic equilibrium of natural gas hydrate, which can be summarized by the following four approaches[3, 4]: The first, depressurization, is to decrease the system pressure below that required for hydrate formation at a given temperature[5]; The second, thermal stimulation, increases the system temperature above that required for hydrate formation at a given pressure[6]; The third approach, inhibitor injection, is to inject chemical reagent like methanol to change thermodynamic equilibrium condition; The fourth one is carbon dioxide replacement methods. Inject CO_2 to push out CH_4 from the clathrate hydrate structure while it is stored inside the structure, which means this method impacts not only on future energy systems but also global climate change by allowing geologic CO_2 sequestration [7]. But its application is limited by the low replacement rate and low replacement degree. Bai et al [8]. reported that CH_4/CO_2 replacement initially occurs rather easily on the surface of the MH, but the replacement rate slows significantly as a carbon dioxide hydrate (CH) layer forms on the MH surface. The CH layer acts as a barrier, preventing the penetration of CO_2 molecules into the interior of the MH for further CH_4/CO_2 replacement [9].

In this study, we proposed using multi-depressurization operation to increase the diffusivity of CO_2 and enhance the CH_4 recovery in the CH_4/CO_2 replacement processes. Four experiments were conducted to compare the methane replacement rate and the carbon dioxide storage rate with/without the operation.

2. EXPERIMENTAL SECTION

2.1 Material and apparatus

Two different gases were used in this study, both CH_4 gas and CO_2 gas were supplied by the Dalian Special Gas Co., Ltd., China with purities of 99.99%. Deionized water was obtained from a laboratory water purification system (Aquapro2S, Aquapro International Company LLC, USA). Quartz glass beads (BZ-08, 0.710–0.990 mm, average 0.8 mm, ASONE, Co., Ltd., Japan) were used to simulate the porous medium.

A simplified schematic of the experimental apparatus is shown in Fig 1, which consists of a gas supply system, a cooling bath (F38-EH, JULABO Inc., Germany) ranging from 245 K to 473 K with an estimated precision of ±0.01 K, a high-pressure chamber, a gas chromatograph (GC7900, Techcomp Co., Ltd., China), and a data acquisition system (ADAM4000, Advantech).

The high-pressure chamber made by stainless steel has 100 mm in the inner diameter and 150 mm in the internal height. A pressure transducer (Nagano Co., Ltd., Japan) and four thermocouples (Yamari Industries, Japan), which have precision of ±0.1 MPa and ±0.1 K, are inserted to monitor the pressure and temperature trajectories. Thus, the inside volume of the chamber to hold hydrate sample is 1189 mL.

The gas supplying system includes two gas containers and a high-pressure pump (500D, Teledyne ISCO Inc., USA). The cooling bath contains water and glycol both control the temperature of the pump and the high-pressure chamber. The high-pressure chamber is made by stainless steel.

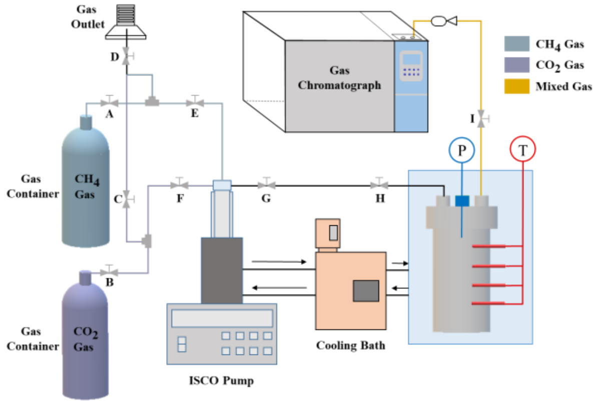

Fig 1 schematic of the experimental apparatus

2.2 *Procedures*

2.2.1 CH_4 hydrate formation

The first step of the experiment is to divide 1170 g clean, dry glass beads and 90 g deionized water into five parts, and mix each part in a clean, airtight plastic bag, then filled them into the high-pressure chamber one by one. Next, put the high-pressure chamber into the cooling bath with a constant temperature of 20°C, then inject the methane gas using the ISCO pump until the pressure increased to about 8.4 MPa after the temperature of the high-pressure chamber has been stable. After that, reduce the temperature of the cooling bath from 20 °C to 2 °C and hold constant during MH formation. The formation of the MH is considered complete after about 50 hours.

2.2.2 CH_4/CO_2 replacement

After MH formation has completed, the temperature of the cooling bath is reduced from 2 °C to -5 °C, where MH hydrates have self-preservation phenomenon when releasing pressure to 0.1 MPa[10]. Then inject the carbon dioxide gas, still using the ISCO pump until the pressure increased to about 3 MPa after the temperature of the high-pressure chamber has been stable. After that, raise the temperature of the cooling bath from -5 °C to 2 °C and hold constant during carbon dioxide hydrates formation.

The whole process of the formation of carbon dioxide hydrates also need about 50 hours. During which, an operation of decrease and increase pressure is performed repeatedly, which we called multi-depressurization operation, to increase the diffusivity of CO_2 in the CH_4/CO_2 replacement. In order to show the effect of this operation, we conducted two experiments in advance without any operation during the formation of carbon dioxide hydrates. The temperature and pressure conditions of the whole process with/without the operation are shown in figure 2.

After carbon dioxide hydrates formation has completed, the temperature of the cooling bath is reduced from 2 °C to -5 °C, too. Then release the pressure of the high-pressure chamber to 0 MPa quickly after the temperature has been stable. After that, raise the temperature of the cooling bath from -5 °C to 20 °C and hold constant until the hydrates has decomposed totally, collect the gas sample at this time. Finally, inject the gas sample into the gas chromatograph to analyze the proportion of gas components in the sample.

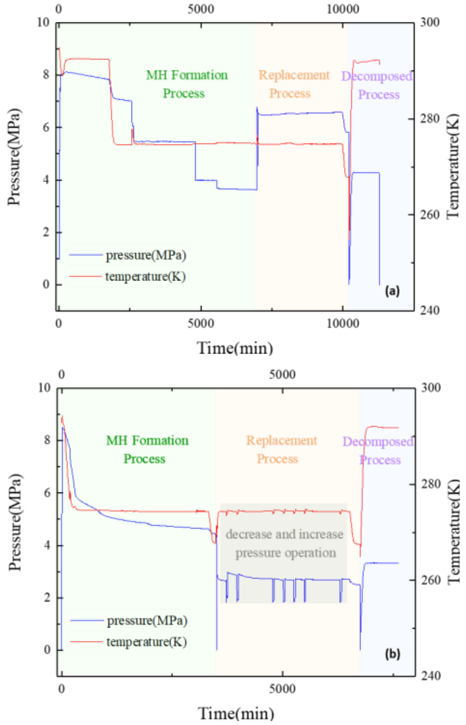

Fig 2 temperature and pressure conditions of the whole process

2.3 Calculations

In order to obtain the methane replacement rate η_{CH_4} and the carbon dioxide storage rate η_{CO_2}, we calculate the basic parameters of the high-pressure chamber at first (Eqs(1)- (4)), and then the amount of substance of the gas in the high-pressure chamber at different times(Eqs(5)- (14)).

The equations used are as follows:

$$V_{BZ} = m_{BZ} / (G_{BZ} \times \rho_w) \tag{1}$$

$$V_{pore} = V_{cell} - V_{BZ} \tag{2}$$

$$\varphi = V_{pore} / V_{cell} \tag{3}$$

$$S_w = (m_w / \rho_w) / V_{pore} \tag{4}$$

Here, V_{cell}=1189 mL, G_{BZ}=1.25, and ρ_w=1 g/mL.

Because of the high pressure and low temperature state of the high-pressure chamber, we use equation of state for actual gases to calculate the amount of substance of the gas. The compressibility factors used are calculated by R-K equation of state.

$$V_{CH_4}^{ini} = V_{pore} - (m_w / \rho_w) \tag{5}$$

$$n_{CH_4}^{ini} = (P_{CH_4}^{ini} \times V_{CH_4}^{ini}) / (Z_{CH_4}^{ini} \times R \times T_{CH_4}^{ini}) \tag{6}$$

$$V_{CH_4}^{fin} = V_{pore} - 1.25(m_w / \rho_w) \tag{7}$$

$$n_{CH_4}^{fin} = (P_{CH_4}^{fin} \times V_{CH_4}^{fin}) / (Z_{CH_4}^{fin} \times R \times T_{CH_4}^{fin}) \tag{8}$$

$$n_{MH} = n_{CH_4}^{fin} - n_{CH_4}^{ini} \tag{9}$$

$$\begin{aligned} V_{CO_2}^{ini} = V_{pore} &- (m_w - 6n_{MH} \times M_w) / \rho_w \\ &- n_{MH} \times M_{MH} / \rho_{MH} \end{aligned} \tag{10}$$

$$n_{CO_2}^{ini} = (P_{CO_2}^{ini} \times V_{CO_2}^{ini}) / (Z_{CO_2}^{ini} \times R \times T_{CO_2}^{ini}) \tag{11}$$

$$n_{mix} = (P_h^{fin} \times V_h^{fin}) / (Z_h^{fin} \times R \times T_h^{fin}) \tag{12}$$

$$n_{mix,CH_4} = n_{mix} \times x_{CH_4} \tag{13}$$

$$n_{mix,CO_2} = n_{mix} \times x_{CO_2} \tag{14}$$

Then the methane replacement rate η_{CH_4} and the carbon dioxide storage rate η_{CO_2} can be calculated as follows:

$$\eta_{CO_2} = n_{mix,CO_2} / n_{CO_2}^{ini} \tag{15}$$

$$\eta_{CH_4} = (n_{MH} - n_{mix,CH_4}) / n_{MH} \tag{16}$$

2.4 Analysis and results

The experimental conditions and parameters of the experiments are shown in Table 1. A 50 h test of CH_4/CO_2 replacement have been conducted in two CH_4 hydrate samples (Case 1 and 2); moreover, another two tests (Case 3 and 4) concerned about the combination of CH_4/CO_2 replacement and multi-depressurization to enhance CH_4 recovery and CO_2 sequestration.

Table 1
Experimental conditions and parameters.

Case	1	2	3	4
φ	0.404	0.405	0.409	0.409
Sw	0.187	0.188	0.185	0.185
$T_{CH_4}^{ini}(K)$	292.5	289.1	295.3	294.2
$P_{CH_4}^{ini}(MPa)$	8.860	8.020	8.520	8.520
$T_{CH_4}^{fin}(K)$	274.7	274.8	267.7	267.7
$P_{CH_4}^{fin}(MPa)$	4.381	3.620	4.230	4.450
$T_{CO_2}^{ini}(K)$	276.7	276.5	270.3	270.3
$P_{CO_2}^{ini}(MPa)$	2.453	3.170	3.040	3.050
$T_h^{fin}(K)$	292.0	292.3	292.1	291.8
$P_h^{fin}(MPa)$	4.610	4.270	4.070	3.330
$\Delta P(MPa)$	0.000	0.000	0.700	0.800
$\Delta t(h)$	0.000	0.000	3.5or12	3.5or13
η_{CH_4}	0.154	0.229	0.363	0.503
η_{CO_2}	0.185	0.124	0.423	0.367

In previous study[11], it has been found that the replacement reaction could be divided into two stages: (i) a fast surface reaction for the relatively short hours and (ii) a gradual, slow process as a result of the resistance to diffusion through the formed mixed hydrate layers for the rest hours. Thus, multi-depressurization operation is used in this study to increase the diffusivity of CO_2 in the second stage, and to enhance CH_4 replacement and CO_2 storage ultimately.

Figure 3 compares the methane replacement rate η_{CH_4} and the carbon dioxide storage rate η_{CO_2} with/without the multi-depressurization operation using the data of the mean value of case 1 and 2， 3 and 4 respectively. From this figure, we could see that the mean value of η_{CH_4} increase from 0.191 to 0.433, and η_{CO_2} increase from 0.155 to 0.395 respectively, which suggests that the multi-depressurization operation would be a promising gas production method for geologic CO_2 sequestration and CH_4 recovery.

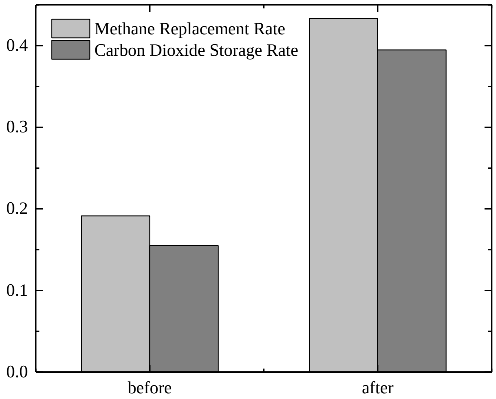

Fig 3 methane replacement rate and the carbon dioxide storage rate with/without multi-depressurization operation

3. CONCLUSIONS

In this study, we proposed the multi-depressurization operation to enhance geologic CO_2 sequestration and CH_4 recovery. The methane replacement rate and the carbon dioxide storage rate were discussed, and the conclusion could be drawn as:

The multi-depressurization operation is an effective method to increase the diffusivity of CO_2 in the CH_4/CO_2 replacement process, it simultaneously increased the value of the methane replacement rate and the carbon dioxide storage rate by nearly twice.

In addition, further studies need to be done in order to investigate the microscopic mechanism of multi-depressurization methods for hydrate exploitation.

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