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An Experimental Study on Improved Production Performance by Depressurization Combined with CO₂-Enriched Air Injection

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ABSTRACT: Efficiently and safely producing natural gas stored as gas hydrates remains an urgent and, as yet, unsolved challenge. The CO₂ replacement method is attractive for combining methane production and carbon dioxide storage but with low efficiency attributed to a barrier formed at interface between vapor and solid phase. Although there has been previous work in this area, development is restricted by the obscure underlying mechanism of improving recovery efficiency for long-term. In this study, a series of experiments were conducted aiming to obtain a new concept for improved recovery by the combination of depressurization and gas replacement method, in which air and CO₂-enriched air were injected into artificial multilayer hydrate sediment at pressure ranges from 8.5 to 18.7 MPa. The recovery efficiency was investigated using a method that combines three-stage depressurization assisted with CO₂-enriched air injection. Initial production pressure was found have a positive effect on recovery of methane via injection of air, while an opposite influence was observed for injection of CO₂-enriched air. Compared with injecting air, injecting CO₂-enriched air promotes the performance of gas hydrate production up to 74.4% recovery ratio. A novel multilayer hydrate cap mechanism is therefore proposed to describe the improved efficiency during the replacement–depressurization process for the first time. The multilayer hydrate cap and its composition are largely dependent on initial conditions of injected gas, thereby causing limited recovery efficiency. The results obtained from this study are beneficial for future optimization of operation conditions to maximize efficiency and develop planning for natural gas hydrate resources.

1. INTRODUCTION

The total global energy demand is on the rise at its fastest pace in the past decade driven by a robust human development and stronger heating and cooling requisition in many regions. Natural gas demand is particularly pronounced for its green and efficient production and grew at one of its fastest rates for over 30 years, accounting for over 40% of the growth in primary energy.¹ At the same time, global carbon dioxide (CO₂) emission in the atmosphere exceeded 415 ppm in May 2019 as reported by the National Oceanic and Atmospheric Administration (NOAA) from 280 ppm at the start of the industrial revolution.^{2–4} The rise in atmospheric CO₂ is the main contributor to global warming. At no previous time has the need for CO₂ capture technologies been greater. As a result, one of the biggest challenges of today is to fulfill the need to meet rising energy demand while at the same time reducing carbon emissions.

Gas hydrates can hold substantial amounts of methane (CH₄) as the dominant gas species in natural gas.^{5,6} It has been estimated that the volume of gas ranges from 0.82×10^{13} to 2.10×10^{15} m³ thus making it a potentially abundant energy resource.^{7,8} Despite the great abundance of resources around the world, a large portion of these resources are not generally considered producible with existing technology. As a result, gas hydrate production testing has not been actively exploited until recently with aims also converted from an academic curiosity^{9–12} into concerns of energy and environment.^{13–17} To date, a number of exploitation methods have been proposed based on the thermodynamic and physical character-

istics of natural gas hydrates. Among several production methods, depressurization is particularly advantageous and has been studied extensively due to its energy efficiency.^{18–24} Zhao et al.²⁵ analyzed hydrate dissociation behavior via depressurization, finding that all methane hydrate dissociates at the same time at the beginning of depressurization followed by radial spread from outside of hydrates. The rate of methane (CH₄) recovery decreased with higher initial saturation, and production time was reduced under a higher pressure driving force, which was reported by Almenningen et al.²¹ On the basis of successful lab-scale production experiences, the 2002 Research & Development (R&D) program was conducted to quantify and characterize in situ gas hydrate occurrences at the Mallik gas hydrate field, Mackenzie Delta, Canada. This is the first full-scale thermal production but with limited gas flows at a maximum of 101940 m³/day,²⁶ reflecting that the test was a controlled production experiment rather than a long duration test. Advantages of this method are that it is simple, fast, and controllable but the overall observed gas production rate was low throughout. Then in 2007, the BP–U.S. Department of Energy–U.S. Geological Survey (BP–DOE–USGS) collabora-

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Figure 1. Schematic of the experimental setup for hydrate formation and recovery.

tive project at the Mount Elbert was initiated via drawing down pressure within the reservoir below gas hydrate equilibrium conditions, and the gas hydrate was dissociated to produce gas and water.²⁷ In 2008, much larger and longer gas production was accomplished by Canada and Japan with a stepwise draw-down pressure testing to around 4.5 MPa at the Mallik gas hydrate field, achieving sustained gas flow for 6 days with 13000 m³ of gas totally, indicating the first sustainable gas production from hydrate reservoir to surface by the depressurization method. The analysis of net energy spent for running depressurization reported that the total energy produced was about 30 times greater than that consumed.^{28,29} Also, a number of issues concerning the depressurization process are yet to be resolved, not the least of which is geological integrity of the sediment upon production of the vast amounts of gas and coproduced water.³⁰ Thus, a production project of high energy efficiency was expected for future production by depressurization. A more novel method that has been discussed for gas exploitation from gas hydrate reservoirs is a carbon dioxide (CO₂) replacement method via injection of CO₂ or mixtures containing CO₂. This technique has the advantage of both methane production and carbon dioxide storage in the marine sediment as gas hydrates. The idea here is that the chemical potential of methane hydrate is higher than that of CO₂ hydrate meaning that CO₂ hydrates are more stable.^{31–35} As a result, the injection of CO₂ into a hydrate reservoir not only can replace methane with CO₂ but also should reduce the impact of hydrate dissociation on geomechanical stability of the hydrate reservoir. Having the extensive investigations of CH₄–CO₂ exchange methodology on laboratory scale, in 2011–2012, this technology was implemented though a project initiated by DOE and ConocoPhillips at a site on the Alaska North Slope and was maintained for 25 days.³⁶ The program clarified the presence of free water within the gas hydrate reservoir, a finding that gives significant inspiration for researchers to further improve the complex process.³⁷

The world's first marine gas hydrate production test attempt was executed at Nankai Trough, Japan, in March of 2013, with a production rate around 20000 m³/day during the six-day test.³⁸ A second depressurization production attempt followed in 2017 at the nearby location; however, a higher water production rate confined the degree of reduction of pressure. This issue was raised because of the heterogeneous hydrate

reservoir that disturbed the efficiency of gas production. Therefore, the influence of heterogeneity is essential to understand well to achieve longer duration of gas production. Meanwhile, the Chinese government successfully conducted marine gas hydrate production in silty clay sediments in the South China Sea for a continuous 60 day test resulting in about 16000 m³/day of average output. These tests provide significant data and assessment for us to understand the geological controls of the occurrence of gas hydrates. More gas hydrate production testing therefore has been proposed and is being planned for offshore in China, India, and Japan in the future. Also, a new gas hydrate testing project located on the Alaska North Slope was started in 2018 until 2020 to extend production testing operations. While each production test has shown the feasibility of the depressurization or CH₄–CO₂ exchange method at impressive amounts of hydrate resource, each method has drawbacks and only remains effective for a short-term period, which at this point raise questions about the commercial resource potential of gas hydrates. An intense effort in technical advancement would be necessary before full commercial production of methane could be achieved. The next milestone in the field would likely be understanding the mechanism of production tests to access extended-duration production.

CH₄ replacement efficiency was limited by mass transfer due to a newly formed hydrate layer on the surface of the methane hydrate after the initial hours of the rapid replacement stage.³⁹ Thus, attempts have been made focusing on decaying the layer to further elevate recovery efficiency and extend production process. Some depressurizations were experimentally performed in an exceptional manner by investigators, for instance, slow stepwise depressurization,⁴⁰ multistage depressurization^{41,42} and depressurization in combination with thermal stimulation,^{43–45} water injection,^{46–48} or gas injection.^{49–52} Although hydrate production behavior in sandstone is relatively well-known, hydrate production in multilayer sediments has scarcely been investigated by researchers. The majority of natural gas hydrates are spatially distributed in subsurface marine reservoirs. The characteristics of these reservoirs are highly variable. Experiments done to date are limited to simulation of hydrate production in single media.^{53–55} In reality, the reservoirs may occur in sandstone deposits, gravel, sand, clay, or silt sediments.^{56–59} Davidson⁶⁰ found that the properties of the deposits are significant to their

production performance. Several decades later, laboratory workers investigated hydrate production behavior in simulated sediments. In recent years, effort has been expended researching deep-water gas hydrate exploration and production by gas and oil companies to determine the potential of natural gas hydrates as a source of hydrocarbons. Research on the production of methane from multilayer hydrate reservoirs is, however, scarce in the literature. In addition, studies on the synergistic effect of the combination of injection of CO₂-enriched air and depressurization in hydrate reservoirs are seldom reported.

For these reasons, improved technology should be developed to increase hydrate recovery ratio for long-term production. Understanding the underlying mechanism is a priority toward this purpose. Since field tests are generally costly and time-consuming, laboratory work plays an important role in the development of gas production technologies. It is to such a novel technology that this paper is presented. In this study, we examined the factors that influence hydrate production from multilayer sediments by injection of air and CO₂-enriched air. Recovery of CH₄ with simultaneous CO₂ storage was investigated. A combined production method was introduced where gas injection and depressurization were used. Based on our experimental results, a novel hydrate mixture cap attenuation mechanism was proposed for gas production via depressurization with CO₂-enriched air for the first time. The results are of interest for development of a comprehensive description of gas hydrate production technology.

2. EXPERIMENTAL METHODOLOGY

2.1. Experimental Apparatus. Figure 1 presents a schematic diagram of the apparatus for gas hydrate formation and recovery. The whole experimental apparatus consists of the main reactor and two buffer cells. The main reactor with adjustable volume was designed to synthesize methane hydrate on the simulated multilayer seafloor and to perform multistep depressurization with CO₂-enriched air. The apparatus has an internal volume of 520 mL, with an inner diameter of 5 cm and length of 35 cm, and maximum working pressure of 25 MPa. A movable piston inside the reactor divides the cell into two separate sections. One is connected to a high precision syringe pump (Teledyne ISCO). The other section is used to perform hydrate formation and swapping. Internal pressure is adjusted for injection or expulsion of liquid water through appropriate operations with the syringe pump, removing the need to decrease the amount of gas. A circulating bath regulates the experimental temperature by circulating coolant through the jacket surrounding the reactor. To eliminate the influence of heat upon injection of air, gases were precooled for 6 h before being transferred to the main reactor from the two buffer cells whose volumes are 315 and 365 mL, respectively. Gas injection rates were controlled by a mass flow controller (Bronkhorst EL-FLOW). During the experiments, the data acquisition unit recorded the following parameters as a function of time: temperature, pressure, volume changes of the syringe pump, gas injection rates, and amount of gas fed in and out of the reactor. The pressure transducers and thermocouples were calibrated using a pressure test gauge with an error of 0.05% and a digital thermometer with a tolerance of 0.01 °C, respectively.

2.2. Materials. For all the experiments, methane, carbon dioxide, and synthetic air (O₂ 20 mol % and N₂ 80 mol %) were supplied by Air Liquid with a certified purity of 99.995%. Quartz sand with 50–70 mesh particle size was purchased from Sigma-Aldrich. Sandstone was obtained from Obernkirchener Sandstein. Appropriate sizes of sandstone samples were cut and polished before cleaning. The distilled water used in the study was made in the lab. The properties of sandstone and quartz sand are listed in Table 1.

Table 1. Physical Properties of Multilayer Samples

properties	sandstone A	sandstone B	quartz sand
weight (g)	69.17	63.63	35.92
diameter (mm)	37.21	36.92	
length (mm)	35.20	34.87	
pore volume (mL)	4.72	4.61	9.8

2.3. Experimental Procedure. **2.3.1. Sample Preparation.** An unconsolidated three-layer sample with rubber surround was loaded in the main reactor. The sandstone was cleaned with methanol and toluene for the removal of organic and inorganic material. The clean sandstone and sand were subsequently dried at 373 K for over 24 h. A simulated reservoir with three layers representing hydrate-bearing marine sediment is shown in Figure 2. The layers consist of sandstone A, quartz sand, and sandstone B (from left to right).

Figure 2. Multilayer hydrate sediment.

The assembled multilayer sediment was immersed in distilled water overnight before being placed in an ultrasonic bath for 4 h to achieve even distribution of water. X-ray computer tomography scans were conducted to confirm the distribution, which is shown in Figure 3 for

Figure 3. A typical CT value curve for dry and water saturated sediment.

both wet and dry sediments. CT values for sediment cross-section at each position were obtained. The CT value at each layer, equivalent to sample density, is nearly equal for both dry and water-saturated sediment, indicating water evenly distributed in each layer of the sediment.

Experiments were carried out in two stages. In the first stage methane gas hydrate is formed, and the same procedure was followed for all runs. The second stage consisted of air or CO₂-enriched air injection and was associated with three stages of depressurization.

2.3.2. Hydrate Formation Process. The first step of the experimental procedure is the hydrate formation in the multilayer sediment. The rubber sleeve, containing the water-saturated multilayer sediment, was placed inside the cell at room temperature. The volume of the hydrate formation cell was set at 100 mL by controlling the high precision syringe pump. The cell was purged with methane several times to ensure the absence of air. Subsequently, methane was

injected at a controlled rate into the cell until the desired pressure was achieved, sufficiently higher than the equilibrium pressure at the working temperature. The amount of gas injected was recorded from the highly precise syringe pump. The inlet of the cylinder was then closed for 2 h where the pressure stabilized and gases dissolved in the water. Subsequently, the temperature was decreased to its working value, and temperature and pressure data were logged. To obtain a high conversion of methane hydrate and homogeneously distributed hydrates, a temperature ramping method was used. When the pressure of the cell was constant for more than 24 h, the hydrate formation period was considered complete. The amount of hydrate formed is determined from the difference between the initial and final pressure in the cell. The conversion to hydrates is then estimated by an equation-of-state assuming a hydration number of 5.67.⁵

After the hydrate formation was complete, the methane in the gas phase was removed by injecting air or CO₂-enriched air in the high-pressure cylinder. The production phase of the experiment could then proceed. The amount of gas consumed was calculated based on the pressure difference between the beginning and end of the experiments; thus the amount of hydrate can be obtained as the decrease of methane in the vapor phase.

$$\Delta n_H = n_{g,0} - n_{g,t} = \left(\frac{PV}{ZRT} \right)_0 - \left(\frac{PV}{ZRT} \right)_t \quad (1)$$

where $n_{g,0}$ and $n_{g,t}$ are the amount of gas at time 0 and t , P represents pressure in the system, T is the experimental temperature, V is the volume of the gas phase, and Z is the compressibility factor obtained from the Peng–Robinson equation of state.⁶¹ R is the universal gas constant.

The initial hydrate saturation can be calculated by the following equation:

$$S_H = S_w \times \frac{\Delta n_H \times 5.67}{n_{H_2O}} \times 1.25 \times 100\% \quad (2)$$

where S_w is the initial water saturation in the sediment before hydrate formation and n_{H_2O} refers to the total number of moles of water in the system.

2.3.3. Methane Production Process. After CH₄ hydrate formation, air or CO₂-enriched air was injected into the pressure cell to sweep the residual CH₄ gas at a controlled rate, ensuring the absence of CH₄ in the gas phase. During the sweep, the pressure inside the cell was kept unchanged with the aid of a back-pressure controller. The gas from the outlet valve was analyzed by gas chromatography (Agilent 7890A). The sweep stage was terminated once no free CH₄ remained in the gas phase.

During hydrate soaking in the air or CO₂-enriched air for replacement, CH₄ produced from the hydrates was detected by GC at some time intervals. In the later part of this work, a three-stage depressurization method was introduced in the subsequent replacement process. During the reaction, the composition of gas collected from the cell is measured by GC. Approximately 100 μ L of the gas phase was removed during each sampling process, too little to affect the process equilibrium as a result of a decrease in the amount of gas. At the end of each complete experiment, the temperature was increased to 25 °C to dissociate all the remaining hydrate. This confirmed the total amount of methane in the hydrate. The recovery ratio was calculated as follows

$$\text{CH}_4 \text{ recovery ratio} = \frac{(n_{\text{CH}_4,v})_t}{\Delta n_H} \times 100\% \quad (3)$$

in which $(n_{\text{CH}_4,v})_t$ is methane in the gas phase at any time t during the recovery period, which was calculated by eq 4.

$$(n_{\text{CH}_4,v})_t = y_{\text{CH}_4} n_{M,g} \quad (4)$$

y_{CH_4} and $n_{M,g}$ are the mole fraction of methane and mole amount of gas mixture in the vapor phase of the reactor, respectively. The performance of CO₂ capture was investigated by calculation of the

storage ratio of CO₂ during the replacement process, which is based on the composition of CO₂ in the vapor phase.

$$\text{CO}_2 \text{ storage ratio} = \frac{(n_{\text{CO}_2,v})_0 - (n_{\text{CO}_2,v})_t}{(n_{\text{CO}_2,v})_0} \times 100\% \quad (5)$$

where $(n_{\text{CO}_2,v})_0$ and $(n_{\text{CO}_2,v})_t$ are the number of moles of CO₂ at the beginning of replacement and sampling time t during the replacement process.

3. RESULTS AND DISCUSSION

3.1. Methane Hydrate Production Behavior by Injection of Air. Air is abundant and easily obtained, which makes it a convenient and economic alternative to flue gases, which require transportation. In this work, two series of experiments were conducted by injection of air and CO₂-enriched air. Each series was carried out at an identical temperature in order to investigate the changes of reservoir pressure, gas production rates, and gas recovery ratios during methane hydrate production. Air injection experiments were conducted in multilayer sediments at injection pressures of 8.5 MPa, 10.2 MPa, and 18.7 MPa and a production temperature of 274.7 K.

Figure 4 shows the recovery ratio of methane over time under these different pressures when synthetic air was injected

Figure 4. Recovery ratio of CH₄ with injection of air under different initial pressures as a function of time.

into a simulated hydrate reservoir. The evolution of methane recovery ratio reveals how methane is released. A fast methane release stage associated with rapid methane hydrate decomposition is followed by a longer lasting slow methane release stage as the system approaches a new equilibrium. It can be seen that the recovery of methane increased rapidly during the first 25 h as the chemical potential difference of between methane in the gas phase and methane in the solid hydrate phase dominates the driving force for methane production. The graph also shows that the production behavior can be divided into two stages: at the beginning of production, methane gas is rapidly liberated from the solid hydrate reservoir, and afterward a nearly stable recovery is shown with respect to time, which is the second stage. During this stage, hydrate decomposition was constrained due to the gradually decreasing difference of methane chemical potential between the two phases and additionally a decreased contact area between air and hydrate. The equilibrium boundary also

gradually moves toward the CH₄-rich hydrate region due to the continuous liberation of CH₄ until a new thermodynamic equilibrium is achieved. The importance of the influence of initial pressure on methane recovery was explored in the pressure range 8.5 to 18.7 MPa. Figure 4 compares the recovery of methane at three different pressures in the same sediment. Recovery ratios rapidly increase in the initial period of the production followed by a stage where the ratio increases more slowly. The same behavior was observed at all experimental pressures. This shows that the recovery ratio of methane from simulated hydrate increases as the initial production pressure increases.

Figure 5 shows a typical profile of the recovery ratio of methane over time by the introduction of three stages of

Figure 5. Typical experiment for CH₄ recovery ratio with time during three stages of depressurization at 274.7 K and 18.7–5.1 MPa.

depressurization. Once the pressure of the system was reduced, an apparent sudden rise of recovery ratio is obtained. The gas production behavior of each pressure reduction period exhibits a similar pattern, showing two stages of gas release.

The pressure and temperature profile during the depressurization operation is shown in Figure 6. The conditions of each experiment and results are summarized in Table 2.

Figure 7 presents the recovery changes with elapsed time throughout the procedure, indicating that the introduction of depressurization can improve the performance of methane recovery efficiency and the final recovery ratio positively based on the initial recovery pressures. If only the effect of gas injection is considered, 23.2% methane recovery was achieved at 18.7 MPa. This increases to 51.7% when pressure in the system is reduced. The H-L_w-V phase equilibrium pressure for air is 18.3 MPa at 274.7 K,⁶² which excludes the possibility of recovery ratio increment due to inclusion of air hydrate.

3.2. Production Behavior with Injection of CO₂-Enriched Air. Replacement experiments were conducted at the identical temperature of 275.3 K under three different initial pressures ranging from 8.5 to 14.5 MPa. Methane recovery and CO₂ storage ratio were measured to explore methane production behavior and CO₂ storage performance with production time. Kang et al.⁶³ concluded that the use of high-CO₂ in air leads to replacement-dominant hydrate recovery during production. In this study, CO₂-enriched air (20 mol % CO₂ + 80 mol % air) was introduced into a simulated hydrate reservoir using the procedure described in section 2.3.3.

Figure 6. Temperature and pressure profile during gas production via air injection.

The recovery ratio of methane reveals the absolute recovery ability, which is in the light of the composition of increment of methane in the vapor phase. CO₂ in the vapor phase was captured simultaneously. Figure 8a shows that, at the beginning of the replacement stage, the CH₄ recovery ratio increased dramatically within 20 h. Gradually, a slower release of methane was detected with time from 15 to 30 h followed by a stable period. Compared with the recovery ratio obtained by injection of air, the addition of CO₂ into air significantly increased the yield, in this case up to 41.5% at 8.5 MPa. Additionally, initial production pressure has a negative influence on methane recovery, but a positive effect on CO₂ storage ratio, illustrated in Figure 8b. Researches on gas hydrate production are mostly focused on the methane recovery,^{32,33} while little attention has been paid to the potential for CO₂ storage. Figure 8b presents the profile of CO₂ storage percentage as production proceeds. At the early methane rapid release stage, CO₂ in the vapor phase also shows a sudden decrease corresponding to the fast capture of CO₂. This indicates a fast conversion of CO₂ gas into hydrate. Yang et al.⁶⁴ showed a similar fashion of methane hydrate decomposition and CO₂ storage process for flue gas induced methane hydrate dissociation on a single layer of sediment. Based on the results shown in Figure 8, it is concluded that at the start of injection, methane was rapidly liberated from the solid hydrate phase due to the chemical potential difference of methane between vapor and solid phase, resulting in a rapid change in gas composition. Simultaneously, a mixed hydrate layer from injected gas covers the methane hydrate, which blocks the subsequent transfer of methane into the vapor phase. The effects of pressure on methane recovery exhibit very different behavior between injecting air and injecting CO₂-enriched air. The two opposite patterns of methane recovery and CO₂ storage evolution demonstrate that there is a new hydrate formed by injected gas on the surface of the methane hydrate. A higher production pressure corresponds to

Table 2. Gas Hydrate Production Conditions and Recovery Ratios

	1st stage of production			2nd stage of production			3rd stage of production		
initial water saturation (%)	16.4	20.2	31.6						
initial hydrate saturation (%)	57.5	53.3	42.7						
initial pressure (MPa)	18.7	10.2	8.5	9.5	7.1	6.8	5.6	4.8	5.1
production temperature (K)	274.7	274.7	274.7	274.7	274.7	274.7	274.7	274.7	274.7
CH ₄ recovery ratio (%)	23.2	12.1	10.8	40.1	27.3	25.8	51.7	36.6	34.6

Figure 7. CH₄ recovery ratio with time during three stages of depressurization at 274.7 K.

a larger driving force (the difference between the actual pressure and the pressure at the equilibrium boundary). This driving force increases with pressure; thus a strengthened hydrate formed from injected gas, which slows methane hydrate decomposition. A proposed explanation for this process is shown in the next section. A larger driving force is imposed for forming hydrate from injected gas with high injection pressure, resulting in an elevated storage ratio. Over the course of the production, both methane recovery and CO₂ storage gradually reach a constant value. This indicates that decreasing production pressure can significantly increase the recovery ratio of methane from the hydrate reservoir.

After the system reached a steady composition in the vapor phase, a staged decreasing pressure experiment was done in order to investigate the production behavior. The operation was conducted again after the second stage of stability was reached. Figure 9 shows the CH₄ recovery ratio changes during the decreasing pressure experiments. As shown in the figure, after recovery of CH₄ is stable in each stage, the ratio has

Figure 9. Variation of the recovery of methane with time during the replacement process at different initial pressures and at 275.3 K.

always increased to a higher value stage in a short time, and then gradually reaches a new steady level, lasting for a longer time. The enhanced recovery is clear, especially under lower pressure (8.5 MPa).

Meanwhile, the storage percentage of CO₂ over the same course is presented as Figure 10. The pressure of the system is decreased at 168 and 266 h where a change in the ratio is seen. It should be noted that the operating conditions at 14.5 MPa and 275.3 K are well above the hydrate equilibrium boundary for the injected gas,⁶³ indicating a methane lean mixed hydrate is formed as a barrier for further recovery. This boundary is shifted toward the CH₄-rich region as the replacement process proceeds. These results show that the first pressure reduction in the system led to a slight decrease in CO₂ storage ratio and increase in CH₄ storage percentage, implying that this pressure reduction can decompose the methane lean mixed hydrate layer at the surface formed during the previous stage whereby storage of CO₂ decreases from 42.9% to 39.5%. Thus, the gas

Figure 8. (a) CH₄ recovery ratio and (b) CO₂ storage ratio at different pressures at 275.3 K as the function of time.

Figure 10. CO₂ storage ratio evolution during the replacement process under different initial pressures at 275.3 K.

hydrate layer is exposed to a higher contact area with the injected gas. As the layer decomposes, this stage proceeds with the phase boundary moving toward the CO₂-rich region and contributes to a CO₂-rich hydrate barrier simultaneously. An increase of both CH₄ recovery and CO₂ storage ratio is observed at 266 h, where the second depressurization is performed, indicating that methane in the unexploited hydrate much more easily penetrates through the mixed hydrate barrier attributed to the attenuated hydrate layers due to depressurization. Similarly, the attenuated hydrate layer by further depressurization could leave some water molecules, which are more easily incorporated with CO₂ molecules under this condition, leading to an increased tendency in CO₂ storage ratio.

A great enhancement of CH₄ recovery ratio is observed after each depressurization is conducted at pressure of 8.5 MPa, though there is a slight decrease in CO₂ storage ratio. This condition is not enough to induce a barrier from injected gas at the initial stage of injection compared with that at 14.5 MPa. A sharp rise in CH₄ recovery ratio is obtained after depressurization is applied to attenuate the weak mixed hydrate cap, which has increased the opportunity for methane gas to escape the unexploited hydrate reservoir.

CH₄ recovery and CO₂ storage ratio at the end of each stage is summarized Table 3. It is shown that initial injection pressure has an influence on overall ratio even inconsistent with that at every stage. The figure shows that an initial exploitation condition well above the phase equilibrium boundary of the injected gas facilitates CO₂ storage while decreasing performance for CH₄ recovery in comparison of pressures carried out in this study. The introduction of depressurization is more efficient for CH₄ recovery under lower initial production pressure. It was indicated by Yang et al. that the permeability of porous media was important for the

mass transfer process, which is the main constraint for methane recovery before the introduction of depressurization.

3.3. Novel Proposed Mechanism of Production Behavior. On the basis of the results obtained above, we proposed a multilayer hydrate cap attenuation mechanism for explaining the production behavior via injected gas combined with depressurization. When injecting air in this study, the initial condition of injected gas cannot form a hydrate on the interface between vapor and hydrate solid, and methane gas is released mainly driven by the difference between methane vapor and hydrate phase, which was predicted as in Figure 11a.

Figure 11. Proposed mechanism for production by nonreplacement combined with depressurization.

While the system is in equilibrium, methane hydrate decomposition equals its reverse, resulting a stable recovery ratio of methane. The first depressurization is employed as illustrated in Figure 11b. The decrease in pressure affects the fugacity of methane in the vapor phase, and decomposition can thus continue, which happens in similar manner as the second depressurization is conducted in Figure 11c.

Combined with the above mechanism for the nonreplacement process, a cap attenuation mechanism was thus speculated. Figure 12 shows a proposed mechanism for explaining methane hydrate production behavior by CO₂–air injection combined with depressurization, which consists of five steps. Step 1 is an interfacial decomposition process similar to step 1 in Figure 11. After CO₂-enriched air was injected into the hydrate reservoir, injection gas spread out and filled the space above the solid methane hydrate as shown in Figure 12a. Once injection gas occupies the vapor space, the cages of CH₄ hydrate probably become unstable, and some methane molecules leave the hydrate cages driven by the chemical potential difference between the gaseous and solid phase described in step 1. This assumption is consistent with Ota et al.⁶⁵ and Xu et al.⁶⁶ Results from the first stage of Figure 4 also macroscopically support this process, a fast increase in recovery ratio of methane followed by a small tendency that is in agreement with the work of Seo et al.⁶⁷ In contrast, the molecules of injected gas that have transferred to decom-

Table 3. Depressurization Conditions and Recovery Ratio

	1st stage of production			2nd stage of production			3rd stage of production		
initial water saturation (%)	19.2	25.1	28.5						
initial hydrate saturation (%)	55.9	49.4	46.2						
initial pressure (MPa)	14.5	10.6	8.5	10.2	8.1	5.3	6.4	6.7	3.3
CH ₄ recovery ratio (%)	13.9	35.9	41.5	16.1	46.7	58.6	17.1	50.3	74.4
CO ₂ storage ratio (%)	40.1	35.1	8.4	39.9	31.7	7.8	41.7	38.6	7.4

Figure 12. Proposed mechanism for production by replacement combined with depressurization.

position sites can penetrate, leading to a new hydrate from the injected gas at intervals of vapor phase and solid methane hydrate. The formation of the new hydrate acting as a cap rapidly forms a mass transport barrier that slows down any further transfer of methane shown as Figure 12b, which has previously been shown using a theoretical approach, concluding that methane gases transport through this hydrate, in order to sustain further growth, is extremely slow, and even to grow 1 mm may take several hours.⁶⁸ The main diffusion of gas in this step occurs on the interface between newly formed hydrate cap and solid hydrate, the second stage in Figure 4. The thickness of cap hydrate is mainly controlled by initial injection pressure of the system, which subsequently influences following recovery performance. The composition of the vapor phase changes as methane gas is released. The phase equilibrium boundary gradually moves toward the CH₄-rich region. Compared with results from the nonreplacement process, CH₄ recovery ratio relatively increases slowly due to existence of the barrier. As mentioned from the above results, there is a transition period between the fast and slow stage, leading to continuous occurrence of CH₄ recovery and CO₂ storage. This could be attributed to existence of another barrier hindering the replacement process going further. We speculated that the refreshing molecules in vapor keep being encaged with residue water molecules; thus, another hypothetical hydrate layer is proposed formed based on the vapor composition in the presence of CH₄ mixed hydrate as shown in Figure 12c. Figure 12d illustrates depressurization applied to the system once equilibrium is reached. The introduction of depressurization moves the equilibrium state of the system; thus the hydrate cap formed by CO₂ enriched injected gas becomes unstable resulting in a new unstable hydrate cap. As a result, more methane hydrate in the unexploited hydrate reservoir decomposes, and more methane penetrates the two

possible hydrate caps into the vapor phase. This explains the faster recovery shown in Figure 9 where pressure was reduced. Step 5 shows the second pressure decrement period where that the cap is further attenuated in a manner similar to step 4, the injected gas hydrate layer in the absence of CH₄ also being influenced by the depressurization. This attenuated second layer contributes to increased methane recovery. It can be concluded that the introduction of depressurization attenuates the hydrate caps on the hydrate reservoir, improving the production efficiency of methane from the hydrate. This mechanism is important for development of a complete description of the technology of gas hydrate production.

4. CONCLUSION

This work presents an experimental study of the gas recovery and CO₂ storage behavior from multilayer methane hydrate sediment by using an air or a CO₂-enriched air replacement method combined with depressurization. Results from experiments show that injecting air into a methane hydrate reservoir is a feasible and potentially an economical method for methane production but with low recovery. Injecting CO₂-enriched air demonstrated significantly increased production efficiency of methane while also storing CO₂ in relation to initial production pressures. The introduction of depressurization can increase methane recovery in both scenarios. Recovery ratios are shown to increase when a three-stage depressurization method was introduced in the process at three different initial injection pressures at the same gas hydrate reservoir temperature.

Pressure reduction with gas injection significantly increased methane production efficiency, while its improvement on CO₂ storage performance is not as remarkable as that for CH₄ recovery. Based on the hydrate production behavior, a novel multilayer hydrate cap attenuation mechanism was proposed

for gas production behavior via depressurization with CO₂-enriched air for the first time, which well explained the behavior during the production process; the multilayer hydrate cap and its composition are largely dependent on initial conditions of injected gas, thereby causing limited recovery efficiency. The introduction of 3 stages of depressurization can prolong this production process and most importantly enhance recovery ratio via attenuating such multilayer caps. The results obtained from this study provide important insights for optimizing operation conditions to maximize efficiency and prolong production period for field hydrate production. The novelty and originality of the work are a proposed new multilayer hydrate cap mechanism and an improved recovery method for gas from hydrate layers.

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Notes

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