

## One-dimensional approaches for methane hydrate production by CO<sub>2</sub>/N<sub>2</sub> gas mixture in horizontal and vertical column reactor

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**Abstract**—The recovery of methane gas from methane hydrate bearing sediments was investigated by using a continuous stream of a CO<sub>2</sub> and N<sub>2</sub> gas mixture. A long cylindrical high-pressure reactor was designed to demonstrate the recovery of methane from methane hydrate bearing sediments, and the injection rate of the gas mixture was controlled to monitor the amount of recovered methane from methane hydrates. The recovery efficiency of methane gas from methane hydrates is inversely proportional to the flow rate of the CO<sub>2</sub> and N<sub>2</sub> gas mixture. Methane hydrates were synthesized by using two different sediments, having particle size distributions of 75 to 150 μm and 45 to 90 μm with the same porosity, and the recovery efficiency of methane from methane hydrates was also monitored. We confirmed that there is no significant difference in the replacement characteristics by using these two different sediments. Horizontal and vertical flows of the CO<sub>2</sub> and N<sub>2</sub> gas mixture were applied to monitor the effect of flow direction on replacement characteristics. We also confirmed that a similar amount of methane was recovered in horizontal and vertical flows of the CO<sub>2</sub> and N<sub>2</sub> gas mixture at the same flow rate. The present study may help in establishing the process variables for recovering methane gas from methane hydrate bearing sediments in offshore conditions.

Keywords: Methane Hydrate, Sediments, Flow Rate, Flow Direction, Recovery Efficiency, Particle Size

### INTRODUCTION

Clathrate hydrates (gas hydrates) having the physicochemical properties of ice are typical water-based solid crystalline materials in which guest molecules such as methane, nitrogen, and carbon dioxide are captured in host water cavities constructed by the hydrogen-bonded networks of icy materials [1,2]. Gas hydrates are considered one of the most promising unconventional energy resources because a huge amount of natural gas in the form of natural gas hydrates can be stored. In this regard, they could be an important component of future energy strategies [3-6]. As the demand for energy resources increases, the utilization of methane hydrate as a new energy resource has been extensively studied [7-11]. In recent years, depressurization, thermal stimulation, and methane-carbon dioxide replacement techniques have been designed to extract methane gas from methane hydrate deposits [12-14].

Among these techniques, the replacement technique is recognized as a promising option for addressing key issues in energy

and environmental fields, and in particular it can provide the dual functions of natural gas production and carbon dioxide sequestration [14-17]. Ohgaki et al. [14] reported a recovery scenario of CH<sub>4</sub> gas from CH<sub>4</sub> hydrate deposits by using carbon dioxide. They proposed a concept involving the injection of carbon dioxide into CH<sub>4</sub> hydrate layers; the injected CO<sub>2</sub> then disturbs the hydrate-gas equilibrium by changing the gas composition. The carbon dioxide can then be captured in the hydrate cages instead of CH<sub>4</sub>. Due to the dual functions of the replacement technique, microscopic and macroscopic approaches of CH<sub>4</sub>-CO<sub>2</sub> replacement technique have been studied to understand the mechanism and aspects of the replacement technique [17-19]. Later, nitrogen (N<sub>2</sub>) was added as an additional replacement agent to improve the recovery efficiency of CH<sub>4</sub> from CH<sub>4</sub> hydrate deposits [20-25]. Higher recovery efficiency of CH<sub>4</sub> from CH<sub>4</sub> hydrate deposits has been achieved due to the ability of N<sub>2</sub>. Moreover, the addition of N<sub>2</sub> into the injection gas stream can prevent the possible blockage problem of CO<sub>2</sub> in the pipeline, which may occur when CO<sub>2</sub> is used alone in replacement techniques.

Based on these considerations, a replacement technique using a CO<sub>2</sub> and N<sub>2</sub> gas mixture is considered a plausibly viable approach to extract CH<sub>4</sub> from CH<sub>4</sub> hydrate layers and was field-tested on the onshore field of the North Slope of Alaska in the United States [26]. The field-test results revealed that a successful demonstration of the feasibility of the replacement technique by using a CO<sub>2</sub>

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and N<sub>2</sub> gas mixture would be possible with simultaneous recovery of CH<sub>4</sub> and sequestration of CO<sub>2</sub>. The successful test of the replacement technique heralds a promising stage of natural gas production from natural gas hydrate deposits. Nevertheless, a complete understanding of the replacement mechanism and the behavior in a complex CH<sub>4</sub> hydrate-bearing sediment structure is essential for application of the replacement technique in offshore field regions.

This article reports on the recovery of CH<sub>4</sub> from CH<sub>4</sub> hydrate bearing sediments using a continuous stream of a CO<sub>2</sub> and N<sub>2</sub> gas mixture (8:2). A long cylindrical high-pressure reactor was designed to demonstrate the recovery of CH<sub>4</sub> from CH<sub>4</sub> hydrate bearing sediments, and the injection rate of the gas mixture was controlled to monitor the effect of the injection rate on the amount of recovered CH<sub>4</sub> from CH<sub>4</sub> hydrate bearing sediments. We also used two different sediments, having different particle size distributions with the same porosity, to identify the effects of particle size and distributions of sediments on the recovery efficiency of CH<sub>4</sub> from CH<sub>4</sub> hydrates. Finally, horizontal and vertical flows of the CO<sub>2</sub> and N<sub>2</sub> gas mixture were applied to monitor the effect of the flow direction during the replacement process.

## EXPERIMENTAL SECTION

### 1. Materials

CH<sub>4</sub> gas with a minimum purity of 99.99 mol% and a N<sub>2</sub> and CO<sub>2</sub> gas mixture with a desired concentration of 80 mol% of N<sub>2</sub> and 20 mol% of CO<sub>2</sub> were purchased from Special Gas (Korea). Glass beads with particle size distributions of 75 to 150 μm and 45 to 90 μm were supplied by Well Trading Inc. Detailed chemical compositions and physical properties of the glass beads are provided in Table 1(a) and (b). Ultra-high purity water was obtained from a Millipore purification unit.

### 2. Experimental System Configurations

A schematic diagram of the experimental system configuration is shown in Fig. 1. The long cylindrical high-pressure reactor was constructed using SS304 with dimensions of 6.5 cm for the inner diameter and 100 cm for the total length. The system temperature of the high-pressure reactor was controlled by a circulating air-bath (Jeio Tech, Korea). The system temperature, pressure, and injected gas amount were recorded by LabView program. Four K-type thermocouple probes were placed along the cell sidewalls. A

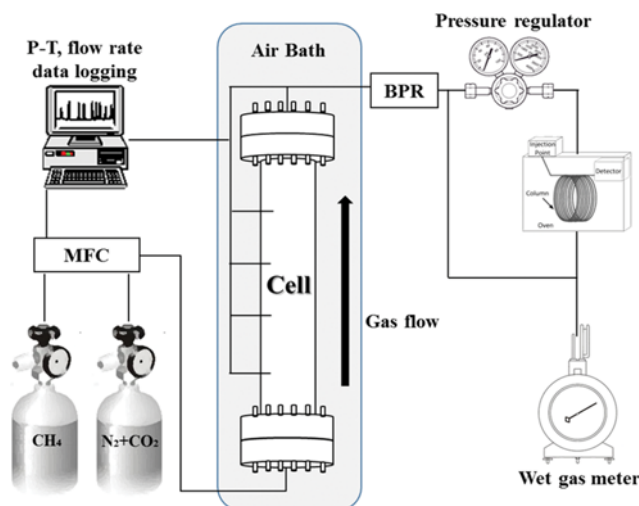


Fig. 1. Schematic diagram of experimental set-up for producing methane from methane hydrate bearing sediments in column reactor.

mass flow controller (BROOKS, model 5850E) was used to control and monitor the injection rate of the N<sub>2</sub> and CO<sub>2</sub> gas mixture. A back-pressure regulator (BPR) at the production port was used for maintaining the pressure of the system and a line pressure regulator was used for controlling the pressure and volume of gas samples for gas chromatography (YL-6100, YoungLin). A wet gas meter (W-NK-1, Shinagawa) was used to monitor and measure the amount of the produced gas volume.

### 3. Methane Hydrate Formation

Glass beads (particle size distributions of 75 to 150 μm and 45 to 90 μm) were used to describe CH<sub>4</sub> hydrate bearing sediments. The high-pressure reactor was filled with the glass beads and ultra-purified water. The initial porosity of the experimental system was controlled between 36–37%. After loading the glass beads and ultra-purified water, excess water in the high-pressure reactor was drained. After removing the excess water, the remaining water is adsorbed onto the glass beads, indicating an irreducible water phase, some of which could be turned into CH<sub>4</sub> hydrate, and water saturation was calculated by the ratio of the adsorbed water volume in the pore space to the volume of the total pore space in our experimental system. Water saturation was approximately 39%, and detailed information on the porosity and water saturation of each experimental run is listed in Table 2. The high-pressure cell was then placed into an air-bath set at 288 K. CH<sub>4</sub> gas was injected into the high-pressure cell and the amount of injected gas was recorded by the program LabView. After pressuring the reactor up to 95 bar, the system temperature was lowered to 274 K to form the hydrate. CH<sub>4</sub> gas was refilled after hydrate formation in an amount corresponding with the amount of consumed gas, and the extra amount of injected gas was recorded by LabView. The CH<sub>4</sub> hydrate saturation rate of our experimental system was approximately 50% and the hydrate saturation (hydrate conversion) rate was calculated by using the following equation.

$$Y_{\text{formation}} = \frac{n_{\text{CH}_4} * 6.133}{n_{\text{water}}} \quad (1)$$

Table 1. (a) Chemical compositions and (b) physical properties of glass beads

(a)						
Elements	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	CaO	K <sub>2</sub> O
Composition	71-74	0.2-1.5	12-15	1.5-3.8	8-10	0-0.2
(b)						
Specific gravity				2.5 g/cm <sup>3</sup>		
Hardness				MOHS 5.5		
Softening point				1003 K		
Annealing point				823 K		
Refraction index				1.51-1.52		

**Table 2. Details of the experimental settings and results for the replacement process**

Run	Injection flow rate (sccm)	Size of glass beads ( $\mu\text{m}$ )	Flow direction	Porosity (%)	Water saturation (%)	Hydrate conversion (%)	Run time (min)	Replacement efficiency (%)
Run1	100	75-150	Vertical			49.2	2500	39.3
Run2	200	75-150	Vertical	36.7	39.1	50.6	1500	34.3
Run3	400	75-150	Vertical			49.9	1000	27.8
Run4	200	45-90	Vertical	37.3	38.7	51.7	1500	35.6
Run5	200	75-150	Horizontal	36.2	39.8	48.8	1500	34.3

where the cage occupancy of  $\text{CH}_4$  hydrate is assumed to be 1.0 in large cages of structure I hydrate and 0.75 in small cages of structure I hydrate,  $Y_{\text{formation}}$  is the hydrate conversion rate,  $n_{\text{water}}$  indicates the amount of residual water (the amount of irreducible water phase) in the porous media, and  $n_{\text{CH}_4}$  is the moles of consumed  $\text{CH}_4$  during hydrate formation. The moles of consumed  $\text{CH}_4$  during hydrate formation is calculated by the pressure drop due to hydrate formation, and the compressibility factor obtained by the generalized compressibility factor diagram for  $\text{CH}_4$  gas was considered for this calculation. After refilling the extra gas ( $\text{CH}_4$  gas), the experimental set-up was maintained to confirm that no additional  $\text{CH}_4$  hydrate conversion took place in the system.

#### 4. Replacement Process using $\text{N}_2$ and $\text{CO}_2$ Gas Mixture

Initially,  $\text{CH}_4$  hydrate was formed by using glass beads having particle size distributions of 75 to 150  $\mu\text{m}$ . An  $\text{N}_2$  (80 mol%) and

$\text{CO}_2$  (20 mol%) gas mixture was injected after the hydrate formation. Injection rates of 100, 200, and 400 sccm (standard cubic centimeters per minute) of the  $\text{N}_2$  (80 mol%) and  $\text{CO}_2$  (20 mol%) gas mixture were used in this study, and the amount of injected gas was recorded by LabView. Representative pressure and temperature trace data during hydrate formation as well as the replacement process are plotted in Fig. 2. With the injection of the gas mixture, the system pressure of the high-pressure cell was controlled by a back-pressure regulator. The composition of escaped gas from the top of the high-pressure reactor was continuously checked (every 3 min) by gas chromatography. The total amount of escaped gas was measured by a wet-gas meter. After the experiments, a composition analysis of escaped gas was performed to identify the replacement efficiency of the experiments. The recovery efficiency of  $\text{CH}_4$  gas from  $\text{CH}_4$  hydrate was calculated by the ratio of the  $\text{CH}_4$  gas produced during the replacement process to the  $\text{CH}_4$  gas consumed during hydrate formation. From gas chromatography analysis data and wet gas meter data, the following equation was used for calculating the recovery efficiency of  $\text{CH}_4$  gas from  $\text{CH}_4$  hydrate.

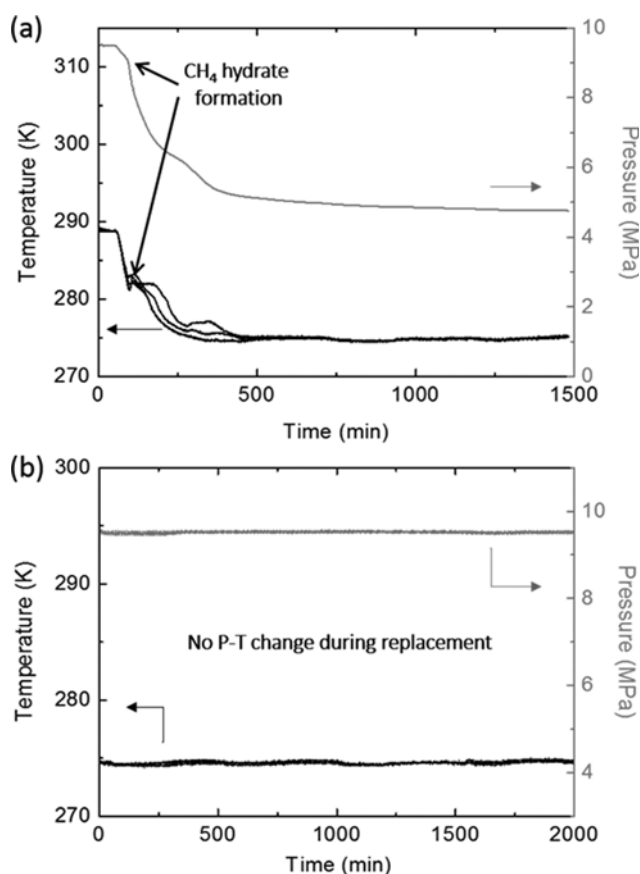
$$Y_{\text{production}} = \frac{V_{\text{produced}}}{V_{\text{formation}}} \quad (2)$$

$$V_{\text{produced}} = V_{\text{total}} \cdot x_{\text{CH}_4} - V_{\text{pore}} \quad (3)$$

$$V_{\text{formation}} = V_{\text{consumed}} \quad (4)$$

where  $Y_{\text{production}}$  is the recovery efficiency of  $\text{CH}_4$  gas from  $\text{CH}_4$  hydrate,  $V_{\text{produced}}$  is the volume of  $\text{CH}_4$  produced from  $\text{CH}_4$  hydrate during the replacement process,  $V_{\text{total}}$  is the total volume of produced gas (mixture of  $\text{CH}_4$ ,  $\text{N}_2$  and  $\text{CO}_2$ ) during the replacement process,  $x_{\text{CH}_4}$  is the mole fraction of  $\text{CH}_4$  in the total volume of produced gas ( $V_{\text{total}}$ ) that can be calculated from a compositional analysis via gas chromatography,  $V_{\text{pore}}$  indicates the volume of  $\text{CH}_4$  gas in pore space,  $V_{\text{formation}}$  is the volume of  $\text{CH}_4$  in the hydrate phase, and  $V_{\text{consumed}}$  is the volume of consumed  $\text{CH}_4$  during hydrate formation, which is proportional to the volume of  $\text{CH}_4$  in the refill process after hydrate formation.

After finishing the replacement process under the different injection rates applied as experimental conditions, the glass beads and the ultra-purified water were removed from the reactor and different glass beads, having particle size distributions of 45 to 90  $\mu\text{m}$ , were charged with ultra-purified water. The porosity of the experimental system remained similar for the experimental system regardless of the different glass beads. The hydrate formation and the replacement process were then conducted again under a 200 sccm injection rate to monitor the effects of particle size and distribu-



**Fig. 2. Temperature and pressure data during overall experimental procedure. (a) Hydrate formation, (b) replacement reaction.**

tion. Finally, the glass beads and water were removed again, and the reactor was charged with glass beads having particle size distributions of 75 to 150  $\mu\text{m}$ . The reactor vessel was then placed in the horizontal direction to monitor the effect of the direction of the injection gas stream. In Table 2, experimental results for the recovery efficiency of CH<sub>4</sub> gas from CH<sub>4</sub> hydrate are summarized.

## RESULTS AND DISCUSSION

CH<sub>4</sub> hydrate deposits exist in complex sediment layers. Several studies have focused on the formation mechanism and phase behavior of CH<sub>4</sub> hydrate in the sediment layers [2-9]. The differences in thermodynamic conditions as well as the geometrical complexity of CH<sub>4</sub> hydrates bearing sediments could induce peculiar characteristics of methane recovery during the replacement reaction, and thus microscopic observations of methane recovery during the replacement reaction have been investigated to understand the mechanism and effects of porous media in hydrate deposits [22-24].

We focused on the effects of process variables for recovering methane gas from methane hydrate bearing sediments in offshore conditions. CH<sub>4</sub> hydrates were synthesized in glass beads (particle size distributions of 75 to 150  $\mu\text{m}$  and 45 to 90  $\mu\text{m}$ ). The porosity of the experimental system was controlled at around 0.36, as shown in Table 2. Excess water phase in the high-pressure reactor was drained and the remaining water phase was controlled at around 0.39, and thus 14% (e.g.,  $0.36 \times 0.39 \times 100\% = 14.04\%$ ) of the pore space in the high-pressure reactor was filled with irreducible water. CH<sub>4</sub> gas was injected up to 95 bar after charging the pore space of the reactor with the glass beads and water phase, and the formation of CH<sub>4</sub> hydrate could be observed from the sudden pressure drop as well as the temperature fluctuation during hydrate formation. As shown in Fig. 2(a), the pressure of the reactor drastically decreased as CH<sub>4</sub> hydrate was formed. At the same time, the system temperature of the reactor also fluctuated by the exothermic reaction of CH<sub>4</sub> hydrate formation [2].

After the pressure of the system stabilized, additional CH<sub>4</sub> gas was charged to the desired pressure of 95 bar. The temperature and pressure of the system were continuously monitored after refilling CH<sub>4</sub> gas, and further hydrate formation did not occur. The gaseous mixture of N<sub>2</sub> (80 mol%) and CO<sub>2</sub> (20 mol%) was injected at a constant flow rate (100, 200, and 400 sccm). The conversion rate of CH<sub>4</sub> hydrate in our experimental system was approximately 50%, and as such N<sub>2</sub> and CO<sub>2</sub> hydrate could form in the remaining water phase instead of the replacement reaction. However, the pressure and temperature of the system were not significantly changed during the replacement reaction, as shown in Fig. 2(b), and thus we could rule out the possibility of N<sub>2</sub> and CO<sub>2</sub> hydrate formation in the remaining water phase. Even though the pressure and temperature conditions of the experimental system were not significantly changed, the components of the system in the vessel were continuously changed. Initially, the high-pressure reactor was filled with the glass beads, the irreducible water phase, CH<sub>4</sub> hydrate, and CH<sub>4</sub> gas. As the gaseous mixture of N<sub>2</sub> (80 mol%) and CO<sub>2</sub> (20 mol%) was injected into the reactor, the stream of gaseous mixture could start to displace CH<sub>4</sub> gas, indicating that the

vapor composition of the high-pressure reactor might be changed with time. The difference in the vapor and hydrate phase compositions can provide the driving force of the replacement reaction, implying a favorable reaction of CH<sub>4</sub> production and CO<sub>2</sub>/N<sub>2</sub> storage in the hydrate cages.

To demonstrate the recovery efficiency of CH<sub>4</sub> from CH<sub>4</sub> hydrate bearing sediments and identify the effect of flow rate in injection gas, the compositional information of CH<sub>4</sub>, N<sub>2</sub>, and CO<sub>2</sub> gas with time at 100, 200, and 400 sccm injection is shown in Fig. 3. As the gaseous mixture of N<sub>2</sub> and CO<sub>2</sub> was initially injected into the reactor, CH<sub>4</sub> gas was discharged from the top of the reactor

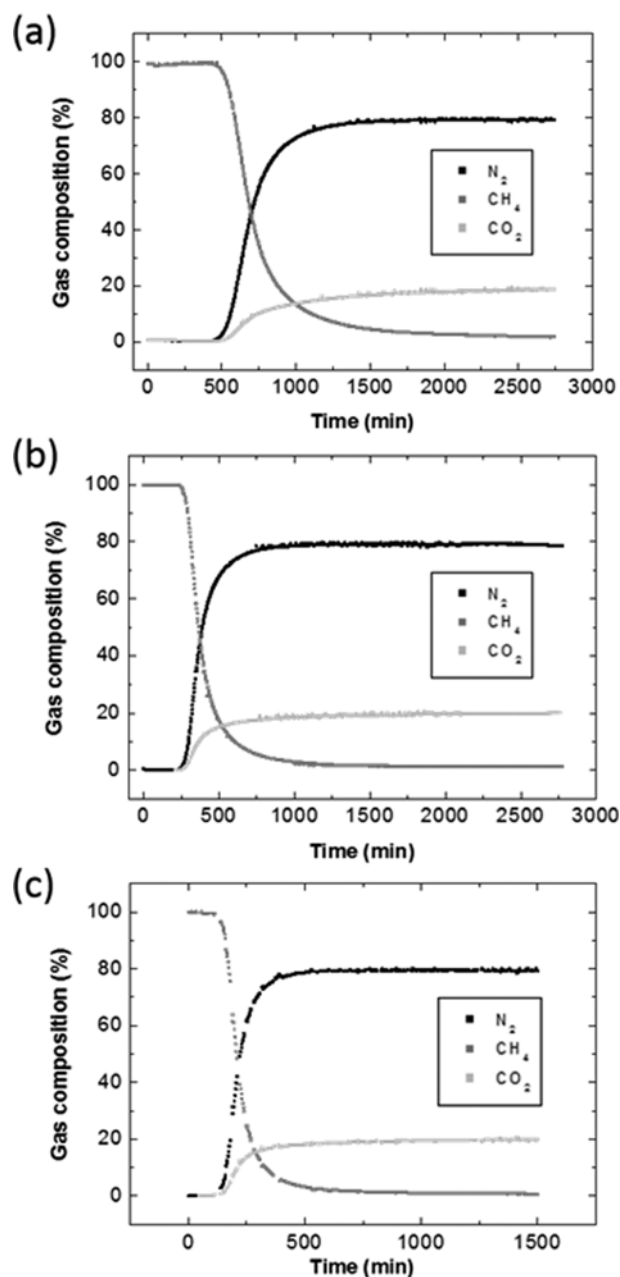


Fig. 3. Composition change in produced gas with (a) 100 sccm, (b) 200 sccm, and (c) 400 sccm injection rates for vertical direction (size of glass beads: 75-150  $\mu\text{m}$ ).

and the injected  $N_2$  and  $CO_2$  could interact with  $CH_4$  hydrate from the bottom of the reactor. Therefore, the escaped  $CH_4$  from the top of the reactor was composed of pore-filling (void space) and recovered  $CH_4$  gas at the early stage of the replacement reaction, and  $N_2$  and  $CO_2$  gas could not reach the top section of the reactor. Later, the gaseous mixture of  $N_2$  and  $CO_2$  could reach the middle and top sections of the reactor, and thus the replacement reaction could occur at the interface of the hydrate and the gas phase at the middle and top sections of the reactor. The composition change of  $CH_4$ ,  $N_2$ , and  $CO_2$  in the produced gas was integrated to identify the total composition of produced gas from the top of the reactor as well as the recovery efficiency of  $CH_4$  gas from  $CH_4$  hydrate bearing sediments. The composition of  $CH_4$  gas in the produced gas continuously decreased with the lapse of time, and the replacement reaction was finished (Run time in Table 2) when the composition of  $CH_4$  gas was less than 2 mol%. The total amount of produced gas at the top section was measured with a wet gas meter and recorded as 412 L for the experiment with a 100 sccm injection rate. At the same time, the composition ratio of produced  $CH_4$ ,  $N_2$ , and  $CO_2$  gas was 0.313, 0.566, and 0.121, respectively. Therefore, the amount of produced  $CH_4$  gas (pore filling  $CH_4$  gas+recovered  $CH_4$  gas) was estimated as 129 L ( $412 \times 0.313 = 129$  L). The amount of pore filling  $CH_4$  gas was 104 L, which was monitored during the pressurization process of  $CH_4$  gas for the hydrate formation process. Therefore, 25 L of  $CH_4$  gas could be evaluated as the recovered  $CH_4$  gas from  $CH_4$  hydrate bearing sediments in the experiment with a 100 sccm injection rate. The amount of  $CH_4$  gas in the hydrate phase could be calculated by the amount of refilling  $CH_4$  gas. In the experiment with a 100 sccm injection rate, the amount of refilling  $CH_4$  gas was recorded as 63.6 L. Therefore, the recovery efficiency of  $CH_4$  gas from  $CH_4$  hydrate bearing sediments in the experiment with a 100 sccm injection rate could be considered as 39.3% ( $25 \text{ L} / 63.6 \text{ L} \times 100\% = 39.3\%$ ). The recovery efficiency of other experiments was also calculated in the same manner, and the results are tabulated in Table 2.

Figs. 3(b) and 3(c) present the composition change of produced  $CH_4$ ,  $N_2$ , and  $CO_2$  gas with 200 and 400 sccm injection rates. In Table 2, the recovery efficiency of  $CH_4$  gas and the run time for the replacement reaction are also tabulated. With the injection rate of 100 sccm (run1 in Table 2), 39.3% of methane was recovered from the hydrate deposits in a period of 2,500 min (run time). The increase of the injection rate in the  $N_2$  and  $CO_2$  gas mixture (200 sccm and 400 sccm) could induce a decrease of the replacement reaction period (1,500 min for 200 sccm and 1,000 min for 400 sccm), but the recovery efficiency of  $CH_4$  gas from the hydrate deposits decreased to 34.3% for 200 sccm (run 2 in Table 2) and 27.8% for 400 sccm (run 3 in Table 2). The replacement reaction can occur at the interface of the gas and hydrate phases, and thus a faster injection rate could provide a faster replacement environment to the system (faster production of pore-filling  $CH_4$  gas with faster injection of the  $N_2$  and  $CO_2$  gas mixture), whereas a faster injection rate may fail to provide sufficient time for reaction of the  $CH_4$  hydrate with the  $N_2$  and  $CO_2$  gas mixture. These results indicate that the recovery efficiency of  $CH_4$  gas from  $CH_4$  hydrate bearing sediments is inversely proportional to the injection rate of the  $CO_2$  and  $N_2$  gas mixture, whereas the replace-

ment reaction was shortened.

The role of  $N_2$  as a replacement agent has been investigated in previous studies, and Park et al. [20] reported that the injection of  $N_2$  could improve the replacement ratio due to the ability of  $N_2$  to induce easy exclusion of  $CH_4$  from small cages of structure I hydrate. Furthermore, an enhancement of the replacement efficiency (85% recovery of methane from hydrate layers) could be observed when  $N_2$  was introduced in the replacement agent (80 mol% of nitrogen). However, the replacement efficiency in porous media with a continuous flow of a  $N_2$  and  $CO_2$  gas mixture was lower compared to that of our system ( $\sim 39.3\%$  at 100 sccm injection rate). Therefore, we can predict that the ability of  $N_2$  in our experimental conditions to improve the replacement efficiency may not be significant, but the addition of  $N_2$  can provide kinetic promotion effects in the replacement reaction. At the early stage of the replacement reaction,  $N_2$  and  $CO_2$  gas cannot reach the top of the reactor, and consequently the signals of  $N_2$  and  $CO_2$  gas in gas chromatography are not observed. After  $N_2$  and  $CO_2$  gas reach the top of the reactor, the signals from the produced  $N_2$  and  $CO_2$  gas can be observed and the ratio of  $N_2/CO_2$  gas for 100, 200, and 400 sccm injection rates is presented in Fig. 4. During the early stage of the replacement reaction, the ratio of  $N_2/CO_2$  gas slowly increased from  $\sim 3$  and eventually reached the maximum value. Finally, it slowly decreased to  $\sim 4$ . These results imply that  $N_2$  is more mobile than  $CO_2$ , and thus the introduced  $N_2$  will displace  $CH_4$ , and the gas phase composition will be also changed.  $CH_4$  hydrate may start to dissociate due to the composition change by  $N_2$ , which can replace  $CH_4$  in small cages. Later,  $CO_2$  could start to replace  $CH_4$  in large cages. Dornan et al. [25] reported that the substitution of  $N_2$  in small cages of structure I hydrate has a positive free energy, and thus the preferential occupation of  $CO_2$  with a negative free energy eventually may dominate the replacement reaction, implying that there is a maximum value of the  $N_2/CO_2$  ratio. These kinetic promotion effects of  $N_2$  in the replacement reaction could be suggested from the variation of the  $N_2/CO_2$  ratio during the replacement reaction shown in Fig. 4, but further study is required for a more concrete conclusion.

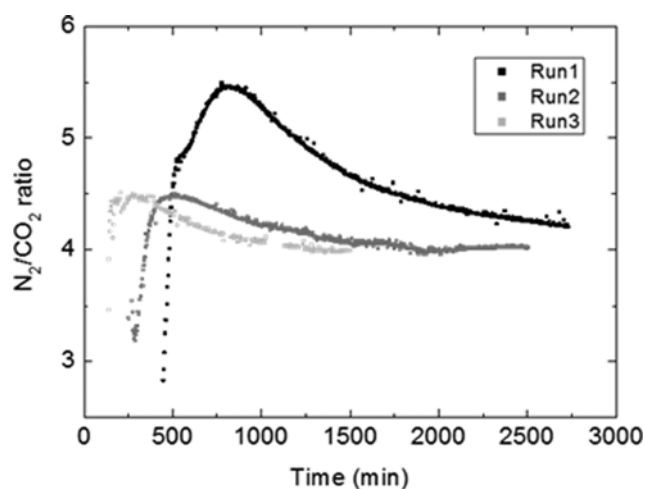


Fig. 4. Ratio change of produced  $N_2$  and  $CO_2$  gas mixture from the top of the reactor.

In deep sea sediments, CH<sub>4</sub> hydrates might be formed in several kinds of porous media. Here, we used two different sediments, having different particle size and distributions but the same porosity, to identify the effects of particle size and distributions of

sediments on the recovery efficiency of CH<sub>4</sub> from CH<sub>4</sub> hydrates. CH<sub>4</sub> hydrates were also formed by using glass beads having a particle size distribution of 45 to 90  $\mu\text{m}$ . To minimize the effects of porosity, water saturation, and hydrate saturation, the experimental conditions for these factors were controlled at similar values, as shown in Table 2. Figs. 5 and 6 show the composition change of produced CH<sub>4</sub>, N<sub>2</sub>, and CO<sub>2</sub> gas and the change of the N<sub>2</sub>/CO<sub>2</sub> ratio with the glass beads having a particle size distribution of 45 to 90  $\mu\text{m}$  at a 200 sccm injection rate (run 4 in Table 2), respectively. In Fig. 5(b), the composition change of produced CH<sub>4</sub> gas with the glass beads having a particle size distribution of 45 to 90  $\mu\text{m}$  (run 4 in Table 2) and 75 to 150  $\mu\text{m}$  (run 2 in Table 2) at the 200 sccm injection rate is presented. We could not observe significant differences in the composition change. In addition, the recovery efficiency of CH<sub>4</sub> gas from CH<sub>4</sub> hydrate layers for run 4 was calculated and it was recorded as 35.6%. This replacement efficiency is slightly larger than the value (34.3%) of the recovery efficiency for run 2, but it is not significantly different. The smaller particle size and distributions may provide larger surface area for replacement reactions in porous media systems, but we cannot observe a significant effect of particle size distributions on the replacement characteristics in our experimental conditions. This

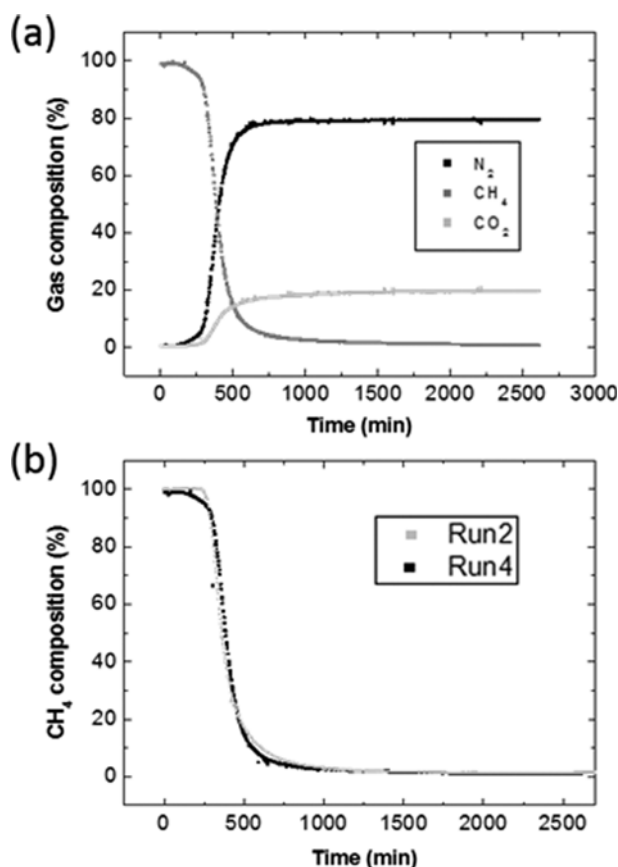


Fig. 5. (a) Composition change in produced gas with 200 sccm injection rate for glass beads (45–90  $\mu\text{m}$ ), (b) comparison of methane composition by using two different glass beads.

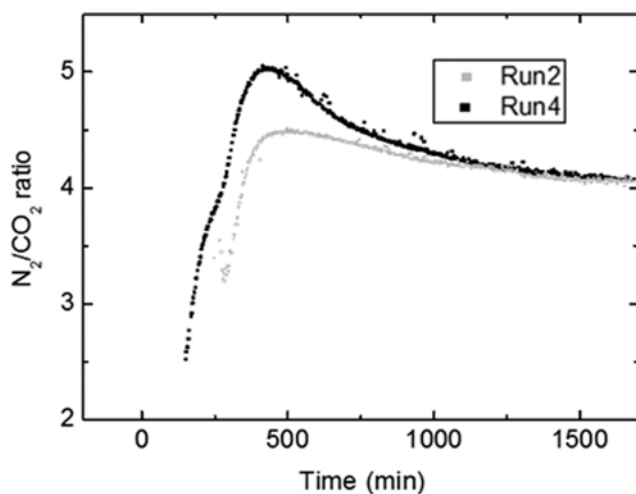


Fig. 6. Ratio change of produced N<sub>2</sub> and CO<sub>2</sub> gas mixture from the top of the reactor after changing the size of glass beads (run 4 for 45–90  $\mu\text{m}$ ).

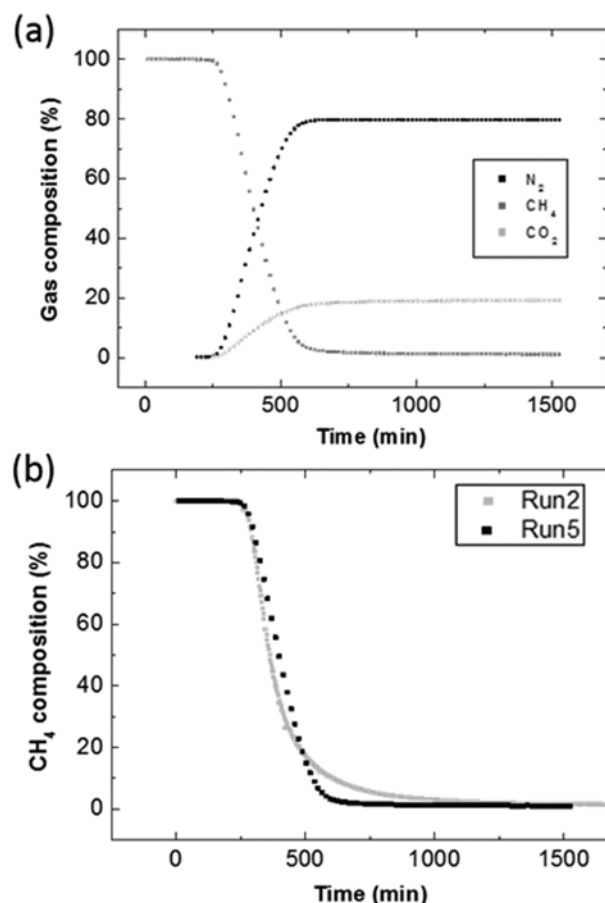


Fig. 7. (a) Composition change in produced gas with direction change of flow (horizontal direction with an injection rate of 200 sccm), (b) comparison of methane composition by using different flow directions.

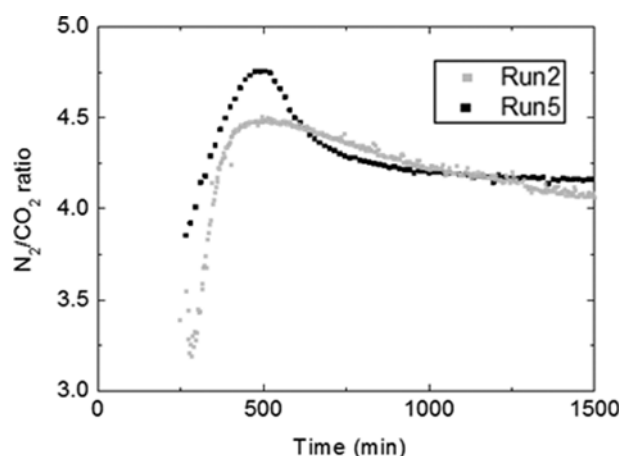


Fig. 8. Ratio change of produced  $N_2$  and  $CO_2$  gas mixture from the top of the reactor after changing the direction of flow (run 5 for horizontal).

may be due to small amounts of irreducible water phase and hydrate phase in the pore space of the high-pressure reactor.

Finally, we also identified the effects of horizontal and vertical flow of the  $CO_2$  and  $N_2$  gas mixture on the replacement process.  $CH_4$  hydrates were formed again by using glass beads having a particle size distribution of 75 to 150  $\mu m$ , but the high-pressure reactor was placed in the horizontal direction to provide a horizontal flow of the  $CO_2$  and  $N_2$  gas mixture. Figs. 7 and 8 show the composition change of  $CH_4$ ,  $N_2$ , and  $CO_2$  gas with glass beads having a particle size distribution of 75 to 150  $\mu m$  at a 200 sccm injection rate by using vertical (run 2 in Table 2) and horizontal (run 5 in Table 2) flows of the gas mixture, and the ratio of  $N_2/CO_2$  gas during the replacement reaction. The recovery efficiency of  $CH_4$  gas from  $CH_4$  hydrate layers for run 5 was also calculated and recorded as 34.3%. From the results of run 2 and run 5, similar amounts of methane recovery were achieved in the horizontal and vertical flows of the  $CO_2$  and  $N_2$  gas mixture at the same flow rate. The direction of the gas flow stream (horizontal and vertical flow of  $CO_2$  and  $N_2$  gas mixture) may not induce significant changes in the replacement reaction behaviors.

In conclusion, the key findings of our study are as follows: 1) the recovery efficiency of methane at 100, 200, and 400 sccm flow rates is inversely proportional to the flow rate of the  $CO_2$  and  $N_2$  gas mixture, whereas the replacement reaction was shortened. These results imply that the optimized injection rate of the gas mixture should be determined for the replacement technique in offshore conditions; 2) the differences in the particle size and distributions of sediments do not exert significant effects on the replacement characteristics in our experimental conditions (small amounts of irreducible water phase and hydrate phase). Our experimental conditions may represent finely disseminated hydrate phases, which are the large majority of hydrates in the ocean; and 3) the effects of the direction of gas flow stream (horizontal and vertical flow of  $CO_2$  and  $N_2$  gas mixture) on the recovery efficiency of methane from hydrate deposits are negligible with a continuous stream of gas mixtures. Based on an understanding of the methane hydrate replacement characteristics, this work could be helpful in

establishing the process variables for recovering methane gas from methane hydrate bearing sediments in offshore conditions.

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## NOMENCLATURE

- $n_{CH_4}$  : the moles of consumed  $CH_4$  during hydrate formation
- $n_{water}$  : the amount of residual water (the amount of irreducible water phase) in the porous media
- $V_{consumed}$  : the volume of consumed  $CH_4$  during hydrate formation
- $V_{formation}$  : the volume of  $CH_4$  in hydrate phase
- $V_{pore}$  : the volume of  $CH_4$  gas in pore space
- $V_{produced}$  : volume of produced  $CH_4$  from  $CH_4$  hydrate during replacement process
- $V_{total}$  : the total volume of produced gas (mixture of  $CH_4$ ,  $N_2$  and  $CO_2$ ) during replacement process
- $x_{CH_4}$  : mole fraction of  $CH_4$  in the total volume of produced gas ( $V_{total}$ )
- $Y_{formation}$  : the hydrate conversion rate
- $Y_{production}$  : the recovery efficiency of  $CH_4$  gas from  $CH_4$  hydrate

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