

Article

Experimental Study on the Distribution Characteristics of CO₂ in Methane Hydrate-Bearing Sediment during CH₄/CO₂ Replacement

Jianye Sun ^{1,2} , Xiluo Hao ^{1,2} , Chengfeng Li ^{1,2,3}, Nengyou Wu ^{1,2,*} , Qiang Chen ^{1,2,*} , Changling Liu ^{1,2}, Yanlong Li ^{1,2} , Qingguo Meng ^{1,2}, Li Huang ^{1,2}  and Qingtao Bu ^{1,2} 

- ¹ Key Laboratory of Gas Hydrate, Ministry of Natural Resources, Qingdao Institute of Marine Geology, Qingdao 266237, China; sjianye@mail.cgs.gov.cn (J.S.); haoxiluo@mail.cgs.gov.cn (X.H.); lchengfeng@mail.cgs.gov.cn (C.L.); qdliuchangling@163.com (C.L.); ylli@qnlm.ac (Y.L.); mengqing@126.com (Q.M.); lihuangocean@163.com (L.H.); buqingtao@mail.cgs.gov.cn (Q.B.)
- ² Laboratory for Marine Mineral Resources, Pilot National Laboratory for Marine Science and Technology, Qingdao 266237, China
- ³ College of Physics and Opto-Electronic Engineering, Ocean University of China, Qingdao 266100, China
- * Correspondence: wuny@ms.giec.ac.cn (N.W.); chenqiang_hds@126.com (Q.C.)

Abstract: CH₄/CO₂ replacement is of great significance for the exploitation of natural gas hydrate resources and CO₂ storage. The feasibility of this method relies on our understanding of the CH₄/CO₂ replacement efficiency and mechanism. In this study, CH₄/CO₂ replacement experiments were carried out to study the distribution characteristics of CH₄ and CO₂ in hydrate-bearing sediments during and after replacement. Similar to previously reported data, our experiments also implied that the CH₄/CO₂ replacement process could be divided into two stages: fast reaction and slow reaction, representing CH₄/CO₂ replacement in the hydrate-gas interface and bidirectional CH₄/CO₂ diffusion caused replacement, respectively. After replacement, the CO₂ content gradually decreased, and the methane content gradually increased with the increase of sediment depth. Higher replacement percentage can be achieved with higher replacement temperature and lower initial saturation of methane hydrate. Based on the calculation of CO₂ consumption amounts, it was found that the replacement mainly took place in the fast reaction stage while the formation of CO₂ hydrate by gaseous CO₂ and water almost runs through the whole experimental process. Thus, the pore scale CH₄/CO₂ replacement process in sediments can be summarized in the following steps: CO₂ injection, CO₂ diffusing into sedimentary layer, occurrence of CH₄/CO₂ replacement and CO₂ hydrate formation, wrapping of methane hydrate by mixed CH₄-CO₂ hydrate, continuous CO₂ hydrate formation, and almost stagnant CH₄/CO₂ replacement.

Keywords: CH₄/CO₂ replacement; gas hydrate; distribution characteristics



Citation: Sun, J.; Hao, X.; Li, C.; Wu, N.; Chen, Q.; Liu, C.; Li, Y.; Meng, Q.; Huang, L.; Bu, Q. Experimental Study on the Distribution Characteristics of CO₂ in Methane Hydrate-Bearing Sediment during CH₄/CO₂ Replacement. *Energies* **2022**, *15*, 5634. <https://doi.org/10.3390/en15155634>

Academic Editors: Ingo Pecher, Zachary M. Aman, Ray Boswell and Ross Anderson

Received: 28 June 2022

Accepted: 2 August 2022

Published: 3 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Natural gas hydrate (mainly methane hydrate) widely occurs in the seabed on the continental margin and permafrost area [1]. The huge reserves of natural gas hydrate make it an alternative energy source. Thus, hydrate production method research and field pilot production tests are attracting worldwide attention [2]. At present, the main hydrate exploitation methods include depressurization, heat stimulation, chemical additive injection, and CO₂ replacement [3–7]. Among the above methods, depressurization has long been considered as the most feasible method in field exploitation, even though there are still risks of sand production, formation instability, and production stagnation for long-term mining. In recent years, a CH₄/CO₂ replacement method has attracted worldwide interests as a win-win method for simultaneous CH₄ recovery and CO₂ storage, captured by absorption, adsorption, and membrane separation [8–11]. The feasibility of gas production

from hydrate by CH₄/CO₂ replacement was first confirmed by Ohgaki et al. [12]. The replacement of CH₄ from methane hydrate by CO₂ is thermodynamically and kinetically feasible by obtaining -3.49 kJ/mol for the Gibbs free energy [13–16]. As CO₂ hydrate is more stable than CH₄ hydrate at the same temperature and pressure, the CH₄/CO₂ replacement method for hydrate production can maintain the mechanical stability of the sediments [17,18]. In 2012, a CH₄/CO₂ replacement method was adopted in a test production of natural gas hydrate conducted in Alaska [19,20]. The production results proved the theoretical feasibility of this method. Unfortunately, the low replacement efficiency restricted the practical application.

Owing to the advantages in stabilizing the hydrate reservoir and CO₂ storage and the low efficiency in the practical production test of CH₄/CO₂ replacement, studies have been extended to enhance the replacement rate and efficiency and to explore the replacement mechanism in the laboratory. In order to improve the replacement efficiency of CO₂ replacement, factors such as replacement conditions (pressure and temperature), CO₂ injection state, and sediment characteristics that may affect the replacement efficiency have been studied by many researchers [5,9,21–24]. Chen et al. [25] suggested that temperature had a great influence on CH₄/CO₂ replacement. At higher temperature, decomposition and replacement may exist simultaneously [26]. Moreover, the influence of temperature is related to the freezing point of water. For example, if the temperature is higher than the freezing point, the replacement efficiency increases with the increase of temperature; while if the temperature is lower than the freezing point, an ice layer may form on the hydrate surface, which may result in a relatively slow replacement process [27,28]. The state of CO₂ is also an essential factor affecting the replacement efficiency. At the same P-T condition, injection of gaseous CO₂, liquid CO₂, CO₂ emulsion, and supercritical CO₂ into methane hydrate results in the following replacement efficiency ranking: supercritical CO₂ > emulsion CO₂ > liquid CO₂ > gaseous CO₂ [22,29–32]. Ota et al. [33] found that the replacement reaction was promoted by an increase in pressure from 3.2 to 3.6 MPa. However, no change was observed at higher pressures because of CO₂ liquefaction. Several studies also demonstrated that injecting a certain proportion of N₂–CO₂ gas mixture could improve the replacement rate [34–36]. It was proposed that the external N₂ molecules specifically would attack the CH₄ molecules already entrapped in a small cage and play a significant role in substantially increasing the CH₄ recovery rate [34]. It was also found that minerals with small particle size (for example clay minerals) could significantly reduce the permeability of sediments, and result in lower CH₄/CO₂ replacement efficiency [9]. These studies have shown that optimizing CO₂ injection conditions can improve the displacement efficiency effectively. Moreover, researchers also studied the replacement efficiency of the combined production methods, for example, CH₄/CO₂ injection and depressurization, CH₄/CO₂ injection and heat stimulation, and injection of both CH₄/CO₂ and chemical additives (such as NaCl, surfactant, etc.). The combined production methods were found to be favorable in improving the CH₄/CO₂ replacement efficiency [37–43].

When discussing the reasons for the low replacement efficiency, it is generally believed that the CH₄/CO₂ replacement starts at the surface of methane hydrate, which hinders further diffusion of CO₂ and the occurrence of replacement. Lee et al. [16] and Bai et al. [44] proposed that the replacement rate gradually decreased as the CO₂–CH₄ mixed hydrate gradually formed, which decreased the diffusivity of the CO₂ through the preformed hydrate layer. However, this may not be the case for hydrate reservoirs. With the injection of CO₂ in sediments, they may quickly form a CO₂ hydrate layer which prevents the further penetration of gaseous CO₂. Therefore, the vertical diffusion of CO₂ in CH₄ hydrate bearing sediments is essential in determining the vertical displacement degree of CO₂, which is of theoretical significance for further understanding the displacement process. Although a number of previous CO₂ replacement experiments have been carried out to examine the factors affecting the replacement efficiency, there is still a lack of theoretical discussion on the CO₂ replacement efficiency with regard to the vertical diffusion process of CO₂ in a methane hydrate reservoir. In this study, experiments were conducted in a pressure

vessel with sea sand as sediment media. Different from previous works, the sediment samples were carefully examined layer by layer after replacement, aiming to study the vertical distribution and diffusion characteristics of CO₂ in the process of replacement, as well as the influence of factors that affect the replacement efficiency including replacement temperature and initial CH₄ hydrate saturation.

2. Materials and Methods

2.1. Experimental Apparatus

The experimental system (Figure 1) consists of a cylindrical pressure vessel, a reactant-supply module for gas injecting, a thermostatic chamber, a gas chromatograph (GC), and a data-acquisition module. The main body of the pressure vessel is made of stainless steel with a pressure tolerance of 30 MPa and equipped with two temperature sensors and one pressure sensor. The effective volume of the vessel is 120 mL. The GC (ThermoGC1100) is connected to the pressure vessel through two valves to measure the gas components in the vessel during the replacement. After replacement, the recovered gas of each sample slice is also analyzed by GC. The pressure vessel is situated in the thermostatic chamber with a temperature controlling range of $-30\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$. The temperature fluctuation during experiments is lower than $0.1\text{ }^{\circ}\text{C}$.

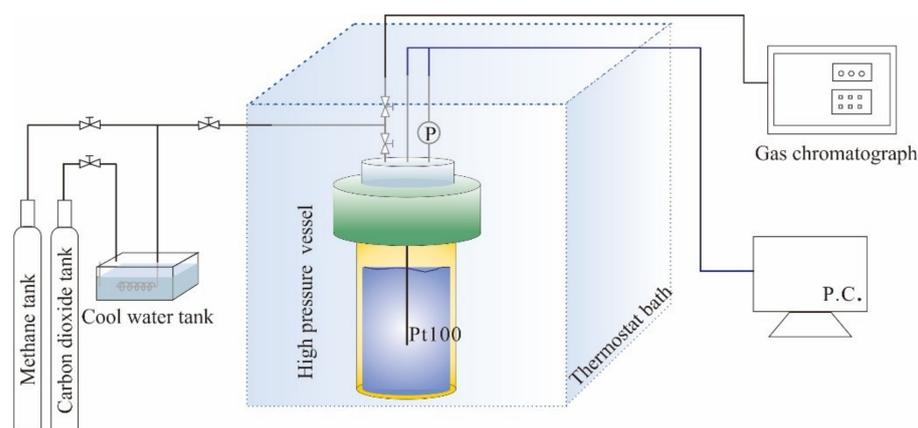


Figure 1. Schematic diagram of the experimental apparatus.

2.2. Experimental Procedure

2.2.1. Sample Preparation

The cylindrical pressure vessel and the associated inner cylinder sample holder (inner diameter 35 mm) were carefully washed with deionized water and dried. Then selected sea sand (grain size ranges from 0.15 mm to 0.25 mm) were evenly mixed with a certain amount of deionized water (water saturation is 30–35%). After that, water bearing sea sand of a total volume of 60 mL was added into the sample holder and the sample holder was placed in the pressure vessel. The pressure vessel was then sealed and put under vacuum. Based on the required hydrate saturation of a single experiment, CH₄ gas was injected into the pressure vessel to a certain pressure and maintained for 24 h. The pressure vessel was then cooled to $1.5\text{ }^{\circ}\text{C}$ to form CH₄ hydrate until the pressure remained unchanged for at least 12 h. To ensure the reliability of the experimental results, the distribution uniformity of methane hydrate in the sample before replacement was examined in the following steps. First, a methane hydrate-bearing sample was prepared with exactly the same procedure as described above. Then the sample was sliced into two pieces horizontally with the protection of liquid nitrogen, and the upper and lower parts were scanned by nano-focus X-ray computed tomography (X-CT, Phoenix X-ray v|tome|x, GE Sensing & Inspection Technologies, Wunstorf, Germany). A self-developed container with controllable temperature and pressure was used for X-CT analysis, which can maintain the stability of the hydrate during CT scanning. The X-CT data were analyzed with VG Studio MAX. The

detailed X-CT measurement and analytical method were followed exactly as that reported in Li et al. [45,46].

2.2.2. CH₄/CO₂ Replacement

- (1) CO₂ injection: After the formation of CH₄ hydrate, the pressure vessel was cooled down to $-20\text{ }^{\circ}\text{C}$ and held for at least 1 h. CH₄ gas in the vessel was released within 10 s and CO₂ was re-injected until the pressure reached $\sim 3.5\text{ MPa}$. To avoid hydrate dissociation, CO₂ was precooled in the cold-water buffer tank before injection. Then the vessel was heated to a certain temperature, and this specific point in time was recorded as the start of the replacement process.
- (2) In situ analysis: Straight after the re-injection of CO₂, the valves between the pressure vessel and the GC were opened and closed in turn to allow a small volume of gas (less than 0.2% *v/v* of the pressure vessel) in the pressure vessel to be sampled, so that the initial gas composition in the pressure vessel could be determined. The same method was conducted to obtain the gas composition in the pressure vessel every 24 h until the end of the experiments, which lasted for 12 days.
- (3) Sample slicing: After replacement, hydrate-bearing sample in the pressure vessel was taken out and sliced into four pieces horizontally under the protection of liquid nitrogen (Figure 2). The composition of the decomposed gas for each sample piece was collected and analyzed by GC.

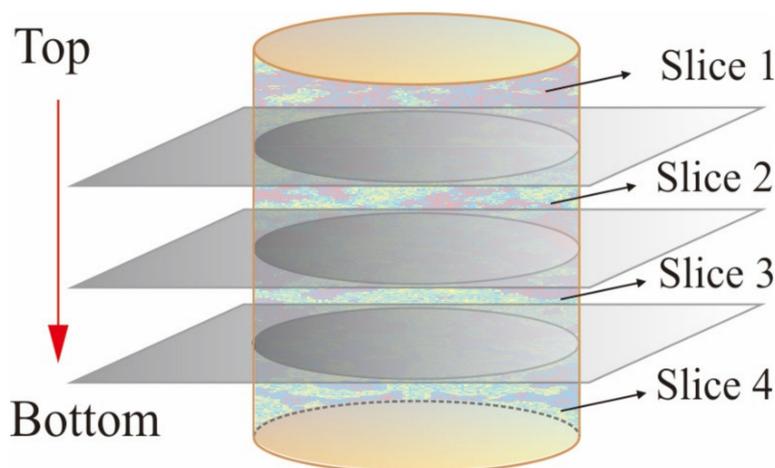


Figure 2. Schematic diagram of the sample slices.

The replacement conditions are summarized in Table 1 below.

Table 1. Experimental conditions of individual CO₂ replacement.

	Run1	Run2	Run3	Run4	Run5	Run6	Run7	Run8
Replacement Temperature (T)	1.5	2.5	3.5	5.0	2.5	2.5	2.5	2.5
Initial hydrate saturation (S_h)	46.5	46.9	45.8	46.2	10.8	26.7	42.1	55.2
Pressure of CO ₂ injection	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0

2.3. Calculation Methods

2.3.1. Hydrate Saturation

The amount of formed methane hydrate in our experiments was determined according to the amount of methane gas consumed in the process of hydrate formation. Assuming that the density of methane hydrate is the same as the value reported previously [47], then

the saturation of hydrate can be calculated by using the porosity of the sediments. The formula to calculate the saturation of hydrate is shown in Equation (1):

$$S_h = \frac{\left(\frac{P_1}{Z_1 T} - \frac{P_2}{Z_2 T}\right) \times \frac{V_g}{R} \times M_h}{\rho_h V_p} \quad (1)$$

where S_h is the saturation of gas hydrate (the volume ratio of gas hydrate and pore space) in our sample prepared in the pressure vessel; M_h is the molar mass of gas hydrate, taking CH_4 hydrate for example, the value of M_h is 122.02 g/mol if the hydration index of methane hydrate is 5.89; ρ_h is the density of gas hydrate, which is 0.91 g/mL in the current calculation; V_p is the total volume of pore space of the sediment sample; V_g is the volume of gas phase in the reactor; T is the replacement temperature; P_1 is the initial pressure of the system; P_2 is the pressure after hydrate formation; R is the ideal gas constant, which is 8.314 J/(mol·K); Z_1 and Z_2 are the gas compressibility factors at P_1 and P_2 , respectively.

2.3.2. Replacement Efficiency

The replacement efficiency γ is calculated by the following formula:

$$\gamma = \frac{n_{\text{CH}_4}}{n_{\text{CH}_4, \text{Hydrate}}} \quad (2)$$

where n_{CH_4} is the mole number of methane in the gaseous phase in the pressure vessel; $n_{\text{CH}_4, \text{Hydrate}}$ is the mole number of methane in the hydrate phase before replacement.

3. Results and Discussion

3.1. Distribution of Methane Hydrate before Replacement

Since the CO_2/CH_4 replacement can be highly affected by the spatial distribution of methane hydrate in sediments, the study of the vertical distribution of CO_2 requires an even distribution of methane hydrate in the sediment sample. Therefore, to ensure the reliability of the experimental results, the distribution of methane hydrate in our sample before replacement was examined. The spatial distribution of methane hydrate in the prepared sediment sample is shown in Figure 3. Since the methane hydrate was formed in the selected sea sand, it was mainly formed in the pore space of the sample and was unlikely to form relatively larger clumps (Figure 3). We used the sediment porosity and hydrate saturation as criteria to examine the distribution uniformity of methane hydrate. Through three-dimensional data reconstruction and gray threshold segmentation of the scanned CT image, the gray ranges of gas, water, hydrate, and sediment were obtained [46]. Then, by calculating the volume proportion of each component, the porosity and hydrate saturation of the sample were estimated. The X-CT image analysis results showed that the porosity and the hydrate saturation of the upper and lower slice were 38.2%, 44.6% and 38.4%, 43.2%, indicating uniform spatial distribution of methane hydrate in the sediment sample. Therefore, it was reasonable for us to use the hydrate-bearing sample to study the influence factors of CH_4/CO_2 replacement and the distribution characteristics of CO_2 .

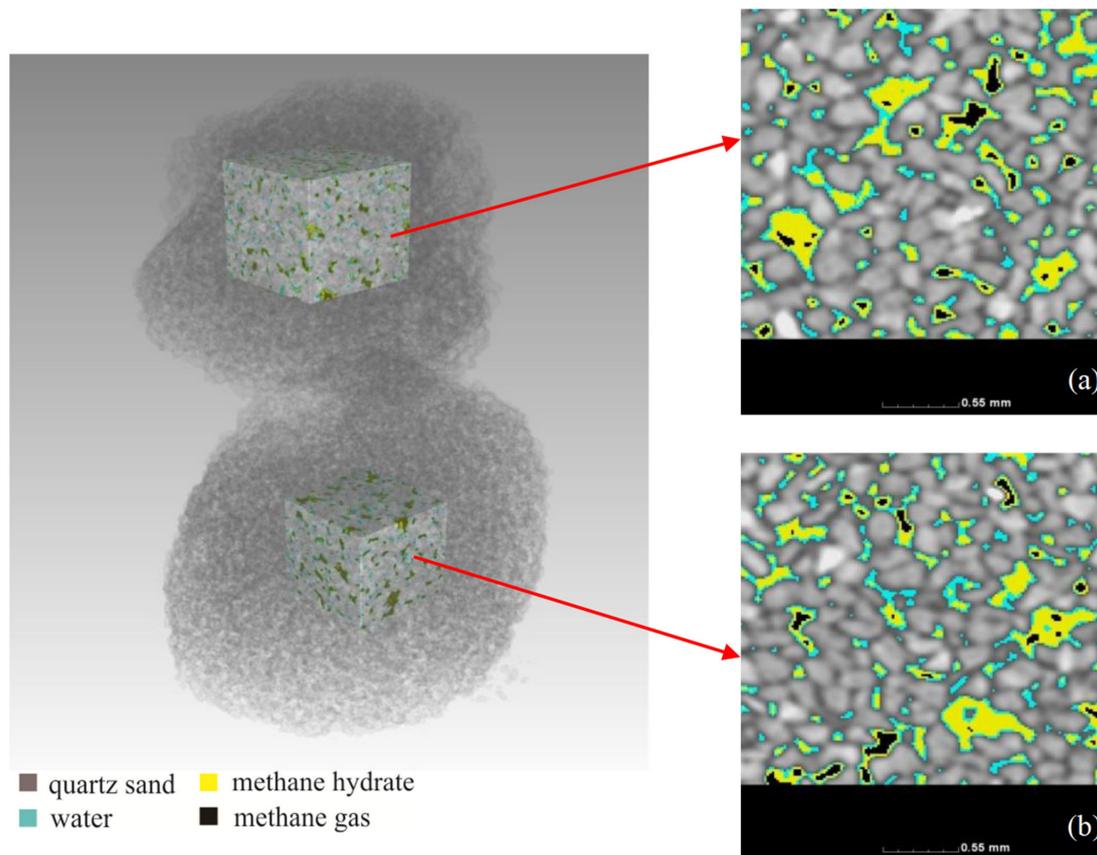


Figure 3. X-CT images of hydrate-bearing sediment sample: (a) upper slice, (b) lower slice.

3.2. Influencing Factor of Replacement Efficiency

3.2.1. Temperature

Based on the results of GC measurement; the CO_2/CH_4 replacement percentages during experiments with similar initial hydrate saturation were calculated and are shown in Figure 4. For all the four experiment runs; the replacement process can be divided into two stages according to the replacement rate. The first stage starts from the beginning of the experiment and lasts for about 3 days. The replacement percentage reached over 80% of the final replacement percentage. The second stage begins from Day 4 to Day 12; when the replacement percentage showed quite a slight increase. This two-stage replacement process has been reported in many previous studies [21,48]. The rapid reaction stage refers to fast surface reactions; and the second stage with low reaction rate was due to the hinderance of CO_2 diffusion by the formation of the mixed $\text{CO}_2\text{-CH}_4$ hydrate layer on the surface of methane hydrate.

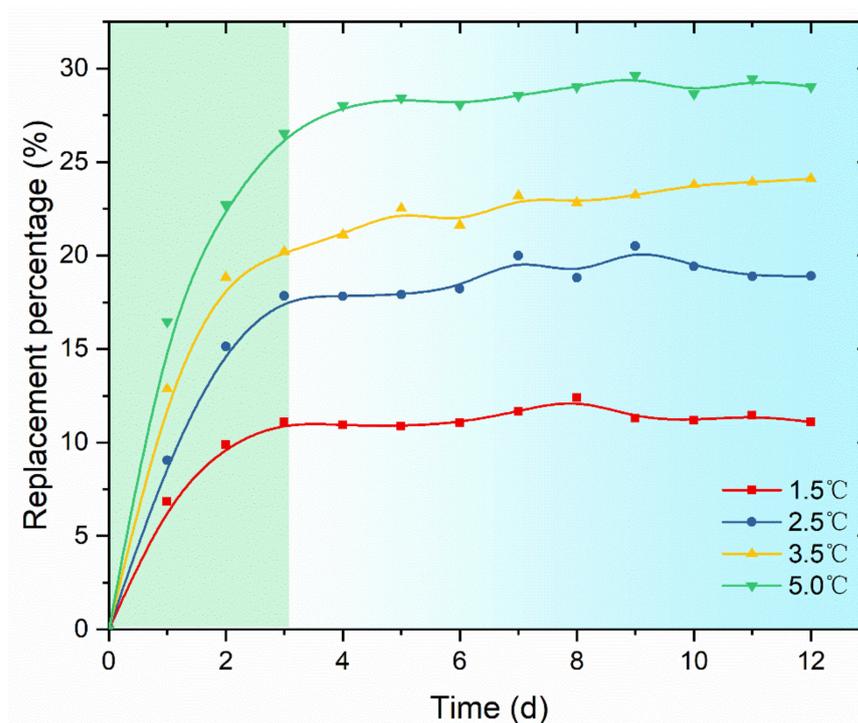


Figure 4. Time evolution of the replacement percentage during CH₄/CO₂ replacement with different experimental temperatures.

At the end of the replacement experiment, the overall replacement percentages were 11.1%, 18.9%, 24.1%, and 29.0% at 1.5 °C, 2.5 °C, 3.5 °C, and 5.0 °C, respectively. Higher temperature results in relatively higher replacement percentage. Our results are consistent with previous studies of the effect of thermal stimulation on CH₄/CO₂ replacement [25,26]. Noting that the replacement P-T conditions of all our experiments were below the equilibrium point of methane hydrate, the replacement reaction would inevitably be accompanied by the dissociation of methane hydrate. Previous experiments [16] have shown that CO₂/CH₄ replacement always occurred with the dissociation of methane hydrate, then the released methane gas could mix with CO₂ and reform CO₂-CH₄ hydrate. Since higher temperature is favorable for methane hydrate to dissociate and release methane gas, the higher dissociation rate resulting by higher temperature would benefit CO₂/CH₄ replacement and eventually lead to higher replacement percentage.

3.2.2. Initial Hydrate Saturation

The variation of CO₂ replacement percentage with time for different initial methane hydrate saturations is shown in Figure 4. Similar with the temperature-controlled experiments, the replacement process can also be divided into fast stage and slow stage at the same time point (72 h). The replacement percentage of the experiment also reached about 80% of the final value. Meanwhile, the increasing rate of the replacement percentage is negatively correlated with the initial hydrate saturation (Figure 5). Samples with lower initial hydrate saturation result in greater replacement percentage. After 12 days' replacement, the CO₂ replacement percentages corresponding to 10.8%, 26.7%, 42.1%, and 55.1% initial hydrate saturation are 27.2%, 22.0%, 18.9%, and 10.1%, respectively. Such a trend in replacement percentage has also been reported by Yuan et al. [49]. Although they performed replacement experiments with liquid CO₂ at relatively higher pressure, the experimental results also showed an increasing replacement percentage of CH₄ hydrate with the decrease of hydrate saturation and the increase of water saturation.

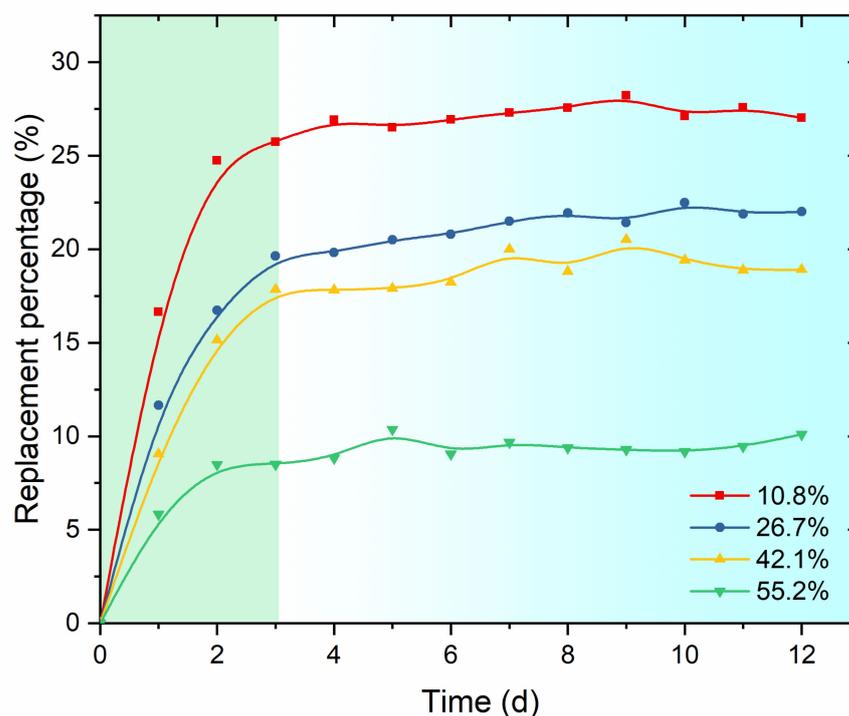


Figure 5. Time evolution of the replacement percentage during CH_4/CO_2 replacement with different initial hydrate saturations.

Despite the highest replacement percent, the CO_2/CH_4 replacement experiment conducted with lowest hydrate saturation generated the lowest amount of CH_4 production. Previous studies [16] have shown that the fast reaction stage of replacement is closely related with the surface reaction. Therefore, surface area (i.e., hydrate– CO_2 contact area) would probably act as an important factor in determining the amount of produced CH_4 in the fast reaction stage. In the current study, methane hydrate was formed in the porous sand media. With increasing hydrate saturation in the sediment sample, there must be a bottleneck in the growth of the hydrate surface area with this increasing hydrate saturation (shown in Figure 6). This is probably the reason why the amount of recovered CH_4 gas did not linearly increase with the initial hydrate saturation. When the initial methane hydrate saturation exceeded $\sim 42\%$ in our experiments, the overall area of hydrate–gas interface probably became smaller owing to the agglomeration of hydrate particles in the pore space. As a result, the total amount of recovered CH_4 gas in the experiment with highest initial hydrate saturation was not the largest.

3.3. Vertical Distribution of CO_2

As discussed in Section 3.1, methane hydrate in our samples before replacement was evenly distributed in the pore space. In addition, the injection of CO_2 was performed on top of the sediment sample. Therefore, the pore structure of the hydrate-bearing sample may affect the distribution of CO_2 and CH_4 along the direction of CO_2 permeation. The vertical distribution characteristics of CO_2 and CH_4 for each sample after replacement are shown in Figures 7 and 8. For most experiments, the CO_2 molar percentage gradually decreased and the CH_4 molar percentage gradually increased with the increase of sediment depth. When comparing the gas contents in slices at the same sample location in different experiments, the contents of CO_2 increase with higher temperature and lower initial hydrate saturation, whereas the contents of CH_4 decrease with higher temperature and lower initial hydrate saturation. The above distribution character is consistent with the penetration order of CO_2 through the sample. With the injection of CO_2 , hydrate in the upper part of the sample started to react first. The dissociation of methane hydrate and reformation of

the mix CO₂/CH₄ have a chance to reduce the sediment porosity and permeability, and subsequently slow down the CH₄/CO₂ replacement rate in the lower sediment layers. However, such a hinderance seems not strong enough to prevent the penetration of CO₂ through the sediments completely. This phenomenon is probably caused by both the relatively larger pore size and the smaller vertical height of the sediment sample.

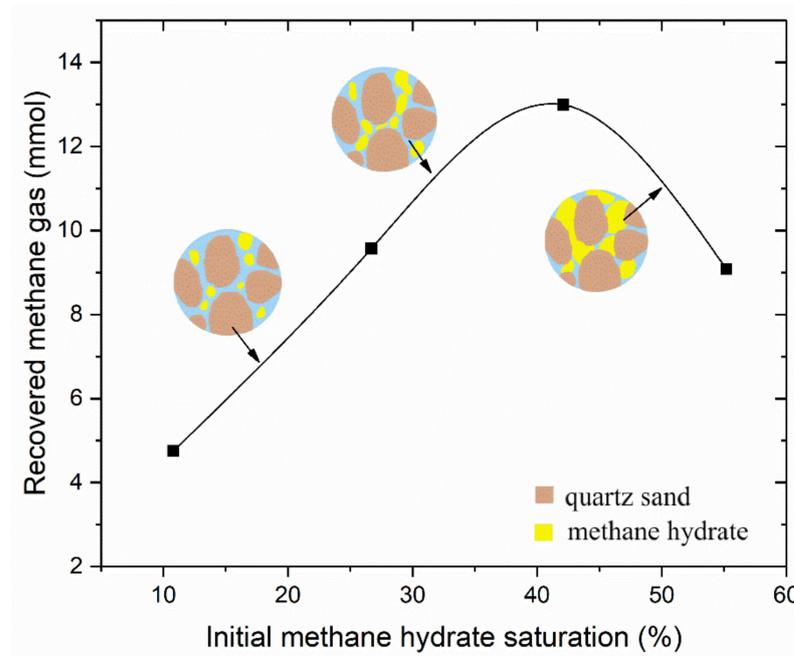


Figure 6. The total amounts of recovered methane gas in experiments with different initial hydrate saturation.

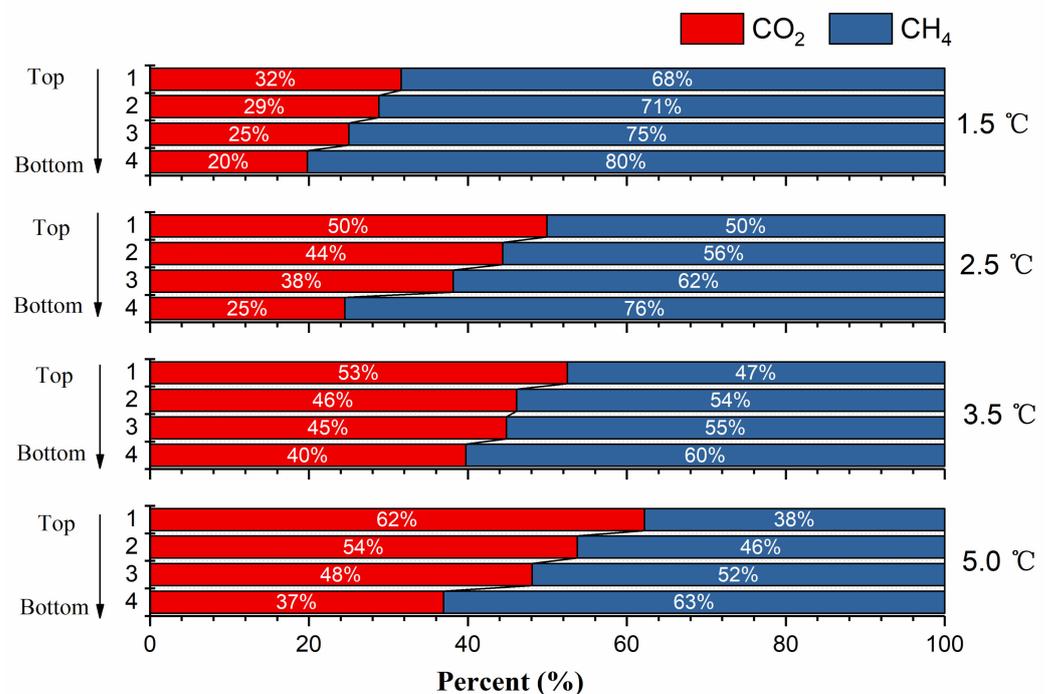


Figure 7. Relative contents of CH₄ and CO₂ in sample slices with different temperatures.

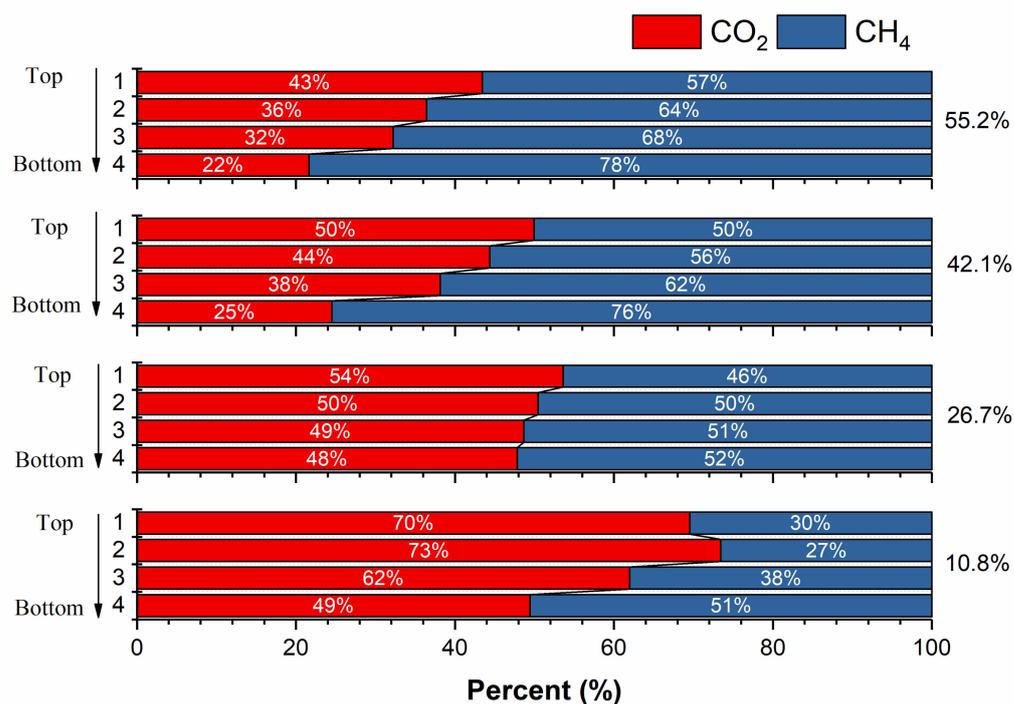


Figure 8. Relative contents of CH₄ and CO₂ in sample slices with different initial hydrate saturation.

3.4. The Excess Consumption of CO₂

For CH₄/CO₂ replacement experiments, the consumed gaseous CO₂ and the recovered CH₄ should be equal in molar number if the effect of gas solubility is excluded. In such circumstance, the pressure in the vessel should remain constant throughout the replacement process if the compressibility factors of CH₄ and CO₂ are assumed equal. However, we observed an obvious pressure drop for all our experiments. Taking the saturation-controlled experiments for example, the pressure decreased about 0.1–0.3 MPa after replacement (Figure 9). Although the CH₄/CO₂ replacement is an exothermic process, the relatively slow reaction rate and the small amount of released heat would probably result in a tiny heat fluctuation. Moreover, the discrepancy in the compressibility factor of CO₂ and CH₄ is quite small. Therefore, it can be deduced that the distinct pressure drop during the replacement was probably caused by the excess consumption of CO₂ in the gaseous phase.

The process of methane hydrate formation in the sample preparation was inadequate in consuming all the water in the pore space. Moreover, the replacement P-T condition used in our experiments was above the equilibrium condition of CO₂ hydrate. Thus, the formation of CO₂ hydrate could inevitably occur at the same time of CH₄/CO₂ replacement. This implication can be further verified by the sharp pressure decrease in the experiment with 10.8% initial hydrate saturation (red line in Figure 9). Lower initial hydrate saturation indicates higher contents of free water in the sample, which is favorable in CO₂ hydrate formation. Thus, the pressure drop right after the onset of the particular replacement experiment was relatively fast in comparison with other experiments. Based on the GC data, the relative percentage of hydrate forming-CO₂ and replacement-CO₂ were calculated. Figure 10 shows the variation of CO₂ consumed in the two processes in one particular experiment. It is shown that the consumption of CO₂ in CH₄ recovery almost stopped after three days reaction, whereas the consumption rate of CO₂ by CO₂-hydrate formation was almost steady. The continuous formation of CO₂ hydrate throughout the whole experiment implied that the migration of CO₂ gas probably could not be interrupted by either the formation of CO₂ hydrate or the CH₄/CO₂ replacement. Under current experimental conditions and duration, it is deduced that the permeability of the sediments during replacement remained feasible for the diffusion of the gaseous phase. Therefore, the major

hinderance of CH₄ recovery should be the diffusion of CO₂ through the mix CH₄-CO₂ layer formed at the surface of methane hydrate.

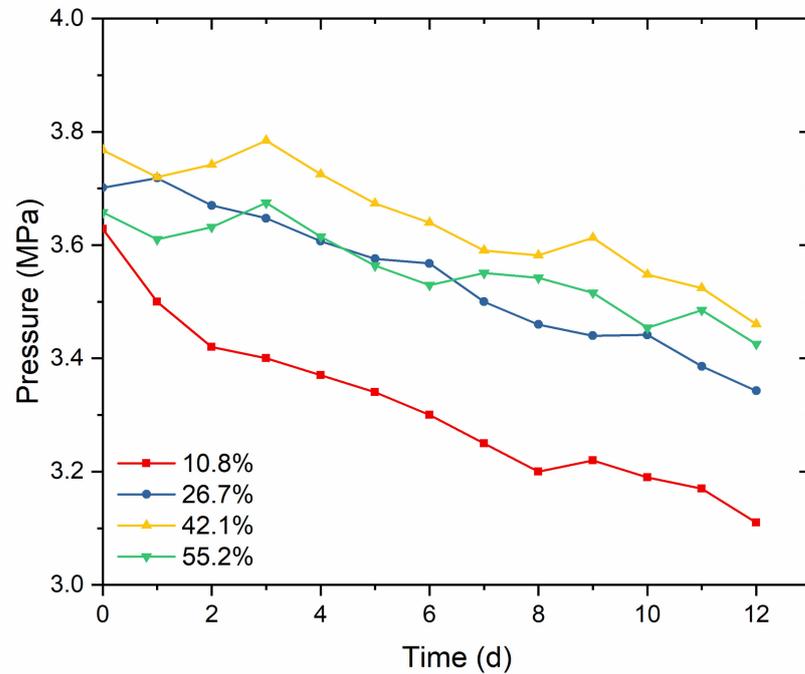


Figure 9. Evolution of pressure during initial hydrate saturation-controlled experiments.

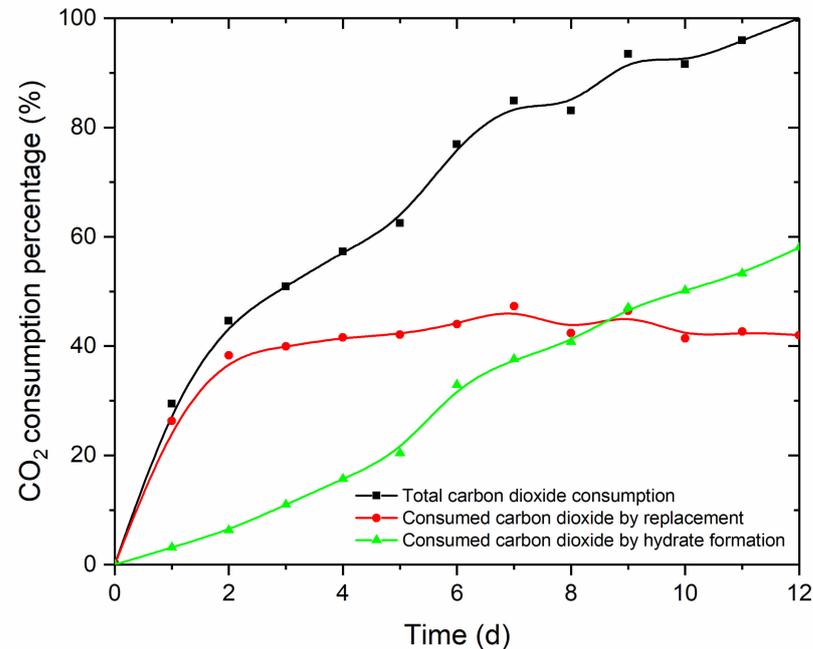


Figure 10. The consumption of CO₂ by different processes of Run 2.

Based on the above discussion, the CH₄/CO₂ replacement process in our experiments can be summarized by the following steps (Figure 11): (1) after the injection of gaseous CO₂, CO₂ diffused into the sediment sample; (2) replacement occurred at the surface of methane hydrate particles in the pore space with a relatively fast rate, meanwhile, CO₂ gas hydrate also formed in the pore space with diffused CO₂ gas and pore water; (3) after 3 days replacement, almost all the methane hydrate particles were isolated by both the mixed CH₄-CO₂ hydrate and CO₂ hydrate, so that the replacement was nearly stopped. However,

the formation of CO₂ hydrate in the pore space was unlikely to prevent the diffusion of CO₂ under our experimental conditions; as a result, CO₂ hydrate was synthesized at a steady rate throughout the whole experiment.

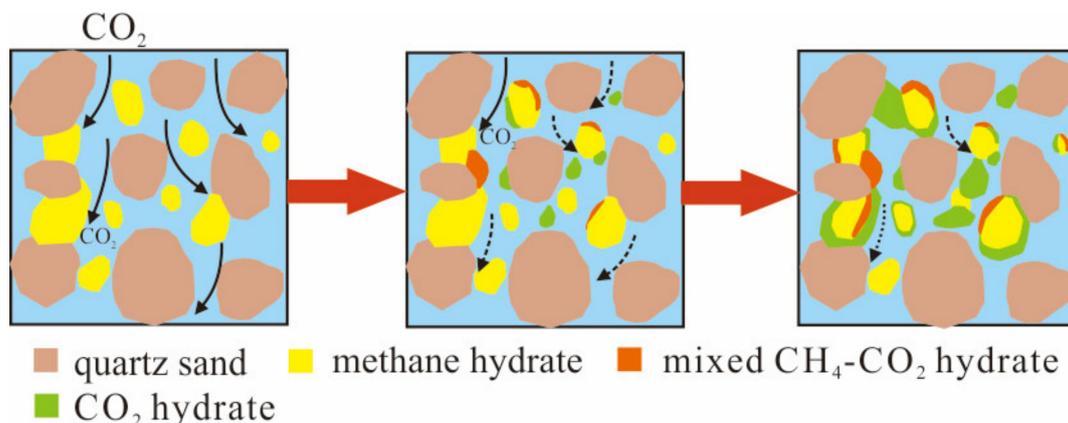


Figure 11. Schematic diagrams of the CH₄/CO₂ replacement process.

4. Conclusions

In this work, we performed CH₄/CO₂ replacement experiments in hydrate-bearing sediments. The distribution characteristics of gaseous phases and the replacement percentages during the experiments were examined. Our simulation experiments yielded the following results:

- (1) Based on the replacement rates, the replacement process can be divided into a fast stage and a slow stage, which represent two different reaction processes. At the fast stage, replacement mainly occurred at the gas-hydrate interface, while at the slow stage, the occurrence of the replacement relied on the diffusion of CO₂ and CH₄ through the hydrate phase. Although the fast stage only lasted for about 3 days, the overall replacement percentage was mainly determined at this stage.
- (2) Higher replacement temperature and lower initial methane hydrate saturation resulted in higher overall CO₂ replacement percentage. Meanwhile, the CO₂ content decreased, and the methane content increased with the increase of sediment depth. At the same sediment depth, the variation of the relative CO₂/CH₄ contents showed an increasing trend with the increase of experimental temperature/initial methane hydrate saturation.
- (3) The CH₄/CO₂ replacement reaction mainly occurs in the fast reaction stage while the CO₂ hydrate formation by CO₂ and pore water almost runs through the whole experimental cycle at almost the same rate. Under current experimental conditions and duration, the permeability of the sediments during replacement remained feasible for the diffusion of the gaseous phase. The major hinderance of CH₄ recovery should be the diffusion of CO₂ through the mix CH₄-CO₂ layer formed at the surface of methane hydrate.

It is worth noting that, before being applied, the CH₄/CO₂ replacement process must be carefully evaluated and all the variables which affect the overall efficiency must be considered and analyzed in future investigations.

Author Contributions: Conceptualization, J.S.; Data curation, X.H.; Investigation, Q.C.; Methodology, J.S. and C.L. (Chengfeng Li); Project administration, N.W.; Supervision, N.W., Y.L., L.H. and Q.B.; Validation, C.L. (Changling Liu) and Q.M.; Writing—original draft, J.S.; Writing—review & editing, X.H. All authors have read and agreed to the published version of the manuscript.

Funding: This study is financially supported by the National Natural Science Foundation of China (Grant No. 41976205 & 41906189), and Marine Geological Survey Program (DD20221704).

Data Availability Statement: The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Koh, C.A.; Sloan, E.D.; Sum, A.K.; Wu, D.T. Fundamentals and applications of gas hydrates. *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 237–257. [[CrossRef](#)]
2. Ye, J.; Qin, X.; Xie, W.; Lu, H.; Ma, B.; Qiu, H.; Liang, J.; Lu, J.A.; Kuang, Z.; Lu, C.; et al. Main progress of the second gas hydrate trial production in the South China Sea. *Geol. China* **2020**, *47*, 557–568.
3. Dallimore, S.R.; Collett, T.S. *Scientific Results from the Mallik 2002 Gas Hydrate Production Research Well Program, Mackenzie Delta, Northwest Territories, Canada*; Geological Survey of Canada: Vancouver, BC, Canada, 2005.
4. Dubreuil-Boisclair, C.; Gloaguen, E.; Bellefleur, G.; Marcotte, D. Non-Gaussian gas hydrate grade simulation at the Mallik site, Mackenzie Delta, Canada. *Mar. Pet. Geol.* **2012**, *35*, 20–27. [[CrossRef](#)]
5. Judith, M.S. From lab to field, from micro to macro—Test of technologies for the production of hydrate bonded CH₄ via CO₂ sequestration in hydrates. In Proceedings of the 9th International Conference on Gas Hydrates, Denver, CO, USA, 25–30 June 2017.
6. Ebinuma, T. Washington, DC: U.S. Patent and Trademark Office. U.S. Patent No. 5,261,490, 11 May 1993.
7. Geng, C.Y.; Wen, H.; Zhou, H. Molecular simulation of the potential of methane reoccupation during the replacement of methane hydrate by CO₂. *J. Phys. Chem. A* **2009**, *113*, 5463–5469. [[CrossRef](#)]
8. Jadhawar, P.; Yang, J.H.; Chapoy, A.; Tohidi, B. Subsurface carbon dioxide sequestration and storage in methane hydrate reservoirs combined with clean methane energy recovery. *Energy Fuel* **2021**, *35*, 1567–1579. [[CrossRef](#)]
9. Pan, D.; Zhong, X.; Zhu, Y.; Zhai, L.; Zhang, H.; Li, X.; Wang, Y.; Chen, C. CH₄ recovery and CO₂ sequestration from hydrate-bearing clayey sediments via CO₂/N₂ injection. *J. Nat. Gas Sci. Eng.* **2020**, *83*, 103503. [[CrossRef](#)]
10. Panda, D.; Saini, C.; Singh, S.K.; Kumar, E.A. In situ casting of rice husk ash in metal organic frameworks induces enhanced CO₂ capture performance. *Sci. Rep.* **2020**, *10*, 20219. [[CrossRef](#)] [[PubMed](#)]
11. de Kleijne, K.; Hanssen, S.V.; van Dinteren, L.; Huijbregts, M.A.; van Zelm, R.; de Coninck, H. Limits to Paris compatibility of CO₂ capture and utilization. *One Earth* **2022**, *5*, 168–185. [[CrossRef](#)]
12. Ohgaki, K.; Takano, K.; Sangawa, H.; Matsubara, T.; Nakano, S. Methane exploitation by carbon dioxide from gas hydrates-Phase equilibria for CO₂-CH₄ mixed hydrate system. *J. Chem. Eng. Jpn.* **1996**, *29*, 478–483. [[CrossRef](#)]
13. Uchida, T.; Ikeda, I.Y.; Takeya, S.; Kamata, Y.; Ohmura, R.; Nagao, J.; Zatsepina, O.Y.; Buffett, B.A. Kinetics and stability of CH₄-CO₂ mixed gas hydrates during formation and long-term storage. *Chem. Phys. Chem.* **2005**, *6*, 646–654. [[CrossRef](#)]
14. Smith, D.H.; Seshadri, K.; Wilder, J.W. Assessing the thermodynamic feasibility of the conversion of methane hydrate into carbon dioxide hydrate in porous media. In Proceedings of the First National Conference on Carbon Sequestration, Washington, DC, USA, 14–17 May 2001; pp. 1–16.
15. Yezdimer, E.M.; Cummings, P.T.; Chialvo, A.A. Determination of the Gibbs free energy of gas replacement in SI clathrate hydrates by molecular simulation. *J. Phys. Chem.* **2002**, *106*, 7982–7987. [[CrossRef](#)]
16. Lee, Y.; Deusner, C.; Kossel, E.; Choi, W.; Seo, Y.; Haeckel, M. Influence of CH₄ hydrate exploitation using depressurization and replacement methods on mechanical strength of hydrate-bearing sediment. *Appl. Energy* **2020**, *277*, 115569. [[CrossRef](#)]
17. Jung, J.; Ryou, J.E.; Al-Raoush, R.I.; Alshibli, K.; Lee, J.Y. Effects of CH₄-CO₂ replacement in hydrate-bearing sediments on S-wave velocity and electrical resistivity. *J. Nat. Gas Sci. Eng.* **2020**, *82*, 103506. [[CrossRef](#)]
18. Schoderbek, D.; Farrell, H.; Howard, J.; Raterman, K.; Silpngarnlert, S.; Martin, K.; Smith, B.; Klein, P. *ConocoPhillips Gas Hydrate Production Test*; ConocoPhillips Co.: Houston, TX, USA, 2013.
19. Kvamme, B. Feasibility of simultaneous CO₂ storage and CH₄ production from natural gas hydrate using mixtures of CO₂ and N₂. *Can. J. Chem.* **2015**, *10*, 21–30. [[CrossRef](#)]
20. Sun, J.Y.; Liu, L.L.; Wang, X.W.; Wang, F.F.; Liu, C.L. Experimental study on the process of CO₂ replacement of CH₄ from methane hydrate in sediments. *Nat. Gas Ind.* **2015**, *35*, 56–62.
21. Ota, M.; Morohashi, K.; Abe, Y.; Watanabe, M.; Smith, R.L., Jr.; Inomata, H. Replacement of CH₄ in the hydrate by use of liquid CO₂. *Energy Convers. Manag.* **2005**, *46*, 1680–1691. [[CrossRef](#)]
22. Mok, J.; Choi, W.; Lee, J.; Seo, Y. Effects of pressure and temperature conditions on thermodynamic and kinetic guest exchange behaviors of CH₄-CO₂+N₂ replacement for energy recovery and greenhouse gas storage. *Energy* **2022**, *239*, 122153. [[CrossRef](#)]
23. Le, Q.D.; Rodriguez, C.T.; Legoix, L.N.; Pirim, C.; Chazallon, B. Influence of the initial CH₄-hydrate system properties on CO₂ capture kinetics. *Appl. Energy* **2020**, *280*, 115843. [[CrossRef](#)]
24. Chen, Y.; Gao, Y.; Zhao, Y.; Chen, L.; Dong, C.; Sun, B. Experimental investigation of different factors influencing the replacement efficiency of CO₂ for methane hydrate. *Appl. Energy* **2018**, *228*, 309–316. [[CrossRef](#)]
25. Li, S.; Zhang, G.; Dai, Z.; Jiang, S.; Sun, Y. Concurrent decomposition and replacement of marine gas hydrate with the injection of CO₂-N₂. *Chem. Eng. J.* **2021**, *420*, 129936. [[CrossRef](#)]
26. Zhang, X.; Li, Y.; Yao, Z.; Li, J.; Wu, Q.; Wang, Y. Experimental study on the effect of pressure on the replacement process of CO₂-CH₄ hydrate below the freezing point. *Energy Fuels* **2018**, *32*, 646–650. [[CrossRef](#)]

27. Xie, Y.; Zhu, Y.J.; Zheng, T.; Yuan, Q.; Sun, C.Y.; Yang, L.Y.; Chen, G.J. Replacement in CH₄-CO₂ hydrate below freezing point based on abnormal self-preservation differences of CH₄ hydrate. *Chem. Eng. J.* **2021**, *403*, 126283. [[CrossRef](#)]
28. Zhou, X.; Fan, S.; Liang, D.; Du, J. Replacement of methane from quartz sand-bearing hydrate with carbon dioxide-in-water emulsion. *Energy Fuels* **2008**, *22*, 1759–1764. [[CrossRef](#)]
29. Yuan, Q.; Wang, X.H.; Dandekar, A.; Sun, C.Y.; Li, Q.P.; Ma, Z.W.; Liu, B.; Chen, G.J. Replacement of methane from hydrates in porous sediments with CO₂-in-water emulsions. *Ind. Eng. Chem. Res.* **2014**, *53*, 12476–12484. [[CrossRef](#)]
30. Ota, M.; Abe, Y.; Watanabe, M.; Smith, R.L.; Inomata, H. Methane recovery from methane hydrate using pressurized CO₂. *Fluid Phase Equilib.* **2005**, *228*, 553–559. [[CrossRef](#)]
31. McGrail, B.P.; Zhu, T.; Hunter, R.B. A new method for enhanced production of gas hydrates with CO₂. In Proceedings of the AAPG Hedberg Conference, Vancouver, BC, Canada, 12–16 September 2004.
32. Ota, M.; Saito, T.; Aida, T.; Watanabe, M.; Sato, Y.; Smith, R.L., Jr.; Inomata, H. Macro and Microscopic CH₄-CO₂ Replacement in CH₄ Hydrate Under Pressurized CO₂. *Environ. Energy Eng. AIChE J.* **2007**, *53*, 2715–2721. [[CrossRef](#)]
33. Park, Y.; Kim, D.Y.; Lee, J.W.; Huh, D.G.; Park, K.P.; Lee, J.; Lee, H. Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 12690–12694. [[CrossRef](#)]
34. Lee, Y.; Kim, Y.; Lee, J.; Lee, H.; Seo, Y. CH₄ recovery and CO₂ sequestration using flue gas in natural gas hydrates as revealed by a micro-differential scanning calorimeter. *Appl. Energy* **2015**, *150*, 120–127. [[CrossRef](#)]
35. Mok, J.; Choi, W.; Seo, Y. The dual-functional roles of N₂ gas for the exploitation of natural gas hydrates: An inhibitor for dissociation and an external guest for replacement. *Energy* **2021**, *232*, 121054. [[CrossRef](#)]
36. Chen, Y.; Gao, Y.; Chen, L.; Wang, X.; Liu, K.; Sun, B. Experimental investigation of the behavior of methane gas hydrates during depressurization-assisted CO₂ replacement. *J. Nat. Gas Sci. Eng.* **2019**, *61*, 284–292. [[CrossRef](#)]
37. Zhang, L.; Yang, L.; Wang, J.; Zhao, J.; Dong, H.; Yang, M.; Liu, Y.; Song, Y. Enhanced CH₄ recovery and CO₂ storage via thermal stimulation in the CH₄/CO₂ replacement of methane hydrate. *Chem. Eng. J.* **2017**, *308*, 40–49. [[CrossRef](#)]
38. Gambelli, A.M.; Rossi, F. Natural gas hydrates: Comparison between two different applications of thermal stimulation for performing CO₂ replacement. *Energy* **2019**, *172*, 423–434. [[CrossRef](#)]
39. Ouyang, Q.; Fan, S.; Wang, Y.; Lang, X.; Wang, S.; Zhang, Y.; Yu, C. Enhanced Methane Production Efficiency with In Situ Intermittent Heating Assisted CO₂ Replacement of Hydrates. *Energy Fuels* **2020**, *34*, 12476–12485. [[CrossRef](#)]
40. Lv, J.; Cheng, Z.; Duan, J.; Wang, S.; Xue, K.; Liu, Y.; Mu, H. Enhanced CH₄ recovery from hydrate-bearing sand packs via CO₂ replacement assisted thermal stimulation method. *J. Nat. Gas Sci. Eng.* **2021**, *96*, 104326. [[CrossRef](#)]
41. Gambelli, A.M.; Rossi, F. The use of sodium chloride as strategy for improving CO₂/CH₄ replacement in natural gas hydrates promoted with depressurization methods. *Arab. J. Geosci.* **2020**, *13*, 898. [[CrossRef](#)]
42. Pandey, J.S.; Karantonidis, C.; Karcz, A.P.; Solms, N. Enhanced CH₄-CO₂ Hydrate Swapping in the Presence of Low Dosage Methanol. *Energies* **2020**, *13*, 5238. [[CrossRef](#)]
43. Lee, B.R.; Koh, C.A.; Sum, A.K. Quantitative measurement and mechanisms for CH₄ production from hydrates with the injection of liquid CO₂. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14922–14927. [[CrossRef](#)]
44. Bai, D.; Zhang, X.; Chen, G.; Wang, W. Replacement mechanism of methane hydrate with carbon dioxide from microsecond molecular dynamics simulations. *Energy Environ. Sci.* **2012**, *5*, 7033–7041. [[CrossRef](#)]
45. Li, C.; Hu, G.; Ye, Y.; Liu, C.; Cheng, J.; Zhang, L.; Zheng, R. Microscopic distribution of gas hydrate in sediment determined by X-ray computerized tomography. *J. Optoelectron. Laser* **2013**, *24*, 551–557.
46. Li, C.; Liu, C.; Hu, G.; Sun, J.; Hao, X.; Liu, L.; Meng, Q. Investigation on the multi-parameter of hydrate-bearing sands using nano-focus X-ray computed tomography. *J. Geophys. Res. Solid Earth* **2019**, *124*, 2286–2296. [[CrossRef](#)]
47. Sloan, E.D.; Koh, C. *Clathrate Hydrates of Natural Gases*; CRC Press: Boca Raton, FL, USA, 2007.
48. Zhao, J.; Zhang, L.; Chen, X.; Zhang, Y.; Liu, Y.; Song, Y. Combined replacement and depressurization methane hydrate recovery method. *Energy Explor. Exploit.* **2016**, *34*, 129–139. [[CrossRef](#)]
49. Yuan, Q.; Sun, C.-Y.; Liu, B.; Wang, X.; Ma, Z.-W.; Ma, Q.-L.; Yang, L.-Y.; Chen, G.-J.; Li, Q.-P.; Li, S.; et al. Methane recovery from natural gas hydrates in porous sediment using pressurized liquid CO₂. *Energy Convers Manag.* **2013**, *67*, 257–264. [[CrossRef](#)]