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Citation: Yun-shuang Zeng, Dong-bin Pan, Chen Chen, Yu Xie, Yang Zhou, 2026. Effect of reservoir goaf on methane recovery and carbon dioxide sequestration in sandy and clayey hydrate reservoirs: An experimental study, *China Geology*, 9, 624–634. doi: [10.31035/cg2025070](https://doi.org/10.31035/cg2025070).

View online: <https://doi.org/10.31035/cg2025070>

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Effect of reservoir goaf on methane recovery and carbon dioxide sequestration in sandy and clayey hydrate reservoirs: An experimental study

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ARTICLE INFO

Article history:

Received 9 April 2025

Received in revised form 1 August 2025

Accepted 24 December 2025

Available online 25 February 2026

Keywords:

Natural gas hydrate

Combustible ice

Clean energy

CO₂ sequestration

Hydrate exploitation

Reservoir goaf

Solid fluidization

Carbon sequestration

Carbon capture, utilization, and storage (CCUS)

ABSTRACT

Carbon dioxide (CO₂) replacement is a promising technique for extracting natural gas hydrate (NGH), a promising clean energy source, capable of promoting energy development while mitigating the greenhouse effect. However, the improvement of NGH extraction efficiency in field engineering is hindered by the difficulty of CO₂ injection and diffusion. To overcome these difficulties, this study proposes combining CO₂ replacement with the solid fluidization method for the exploitation of NGH. The effects of solid fluidization mining goaf on methane (CH₄) recovery and CO₂ sequestration were experimentally investigated. The results indicate that the presence of a goaf in a sandy hydrate reservoir improves the CH₄ recovery ratio and CO₂ storage capacity due to its ability to provide a higher replacement driving force. However, the CO₂ sequestration ratio in the goaf-containing reservoir is lower than that in the intact hydrate reservoir due to the influence of free water content. Besides increasing the replacement driving force, the goaf in the clayey hydrate reservoir can also enhance the diffusion of the replacement medium. The enhancement of CH₄ recovery and CO₂ storage amount per unit sediment volume is 5.3% and 22.8%, respectively. Moreover, the CO₂ sequestration ratio in the goaf-containing hydrate reservoir is higher than that in the intact hydrate reservoir. These results provide theoretical support for the extraction of NGH via the CO₂ replacement method.

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1. Introduction

Natural gas hydrate (NGH) is a solid crystalline substance formed by the interaction of small gas molecules such as light hydrocarbons (CH₄ is dominant in nature) and water under specific environmental conditions (usually high pressure and low temperature) (Sloan ED, 2003). NGH is commonly found in permafrost and seafloor sediments at continental margins. The global carbon reserves in NGH are approximately twice as large as the sum of conventional fossil energy sources (Makogon YF, 2010; Boswell R et al., 2016). Moreover, more than 90% of the hydrate resources are found in marine sediments (Wei N et al., 2024). The exploitation of marine NGH is of great significance for the development of the

world's oil and gas industry as well as the transformation of energy structure (Choudhary N and Phirani J, 2024; Wei N et al., 2024).

Conventional NGH extraction methods include depressurization, thermal stimulation, inhibitor injection and their combinations (Chong ZR et al., 2016; Li XS et al., 2016; Kashish et al., 2024). Depressurization and thermal stimulation are used to alter the temperature and pressure environment of the *in situ* hydrate reservoir through boreholes, causing the hydrate to decompose and thereby recovering CH₄ (Sun X et al., 2019; Yoshimoto N et al., 2023). Inhibitor injection alters the phase equilibrium conditions of the hydrate itself, to make the hydrate decompose under the original temperature and pressure. However, marine hydrate reservoirs are characterized by low sediment cementation strength (Zeng ZJ et al., 2023). The extensive decomposition of hydrate during long-term exploitation greatly weakens the mechanical strength of the reservoirs, which can easily lead to engineering geological disasters (borehole instability, submarine landslides, etc.)

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Literary editor: Li-qiong Jia

doi:10.31035/cg2025070

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(Handwerger AL et al., 2017; Chen Y et al., 2019; Song BJ et al., 2019; Chibura PE et al., 2022). Solid fluidization and CO₂ replacement are innovative hydrate extraction technologies (Zhou S et al., 2018; Ndlovu P et al., 2022). The solid fluidization technique involves breaking the NGH reservoir *in situ* into a slurry by mechanical means (mainly water jet crushing). Subsequently, a pipe conveyor is used to lift the ore slurry to the extraction platform for gas collection (Fig. 1). Finally, the hydrate reservoir forms a goaf with a certain volume. The goaf can exist stably if its size and diameter do not exceed the critical value (Wu KS et al., 2017; Mao LJ et al., 2022). In May 2017, the solid fluidization method was successfully applied in the Liwan No. 3 well of the Shenhu area in the South China Sea, confirming its feasibility in NGH extraction projects (Zhou SW et al., 2018).

The CO₂ replacement method generally uses pure CO₂ or CO₂/N₂ as the replacement medium (Chen Y et al., 2019; Mok J et al., 2025). Existing experimental studies and numerical simulation studies have indicated that the technique can remodel the hydrate cage structure during exploitation, thereby preventing a reduction in the reservoir's mechanical strength (Gajanan K et al., 2024; Gu YH et al., 2025). It can be considered that CO₂ replacement is a safe way to extract marine NGH. Moreover, this method enables the permanent storage of CO₂ through the formation of hydrate on the seafloor, and thus contributes to the reduction of the global greenhouse effect. However, the principle of NGH extraction by CO₂ replacement indicates that the efficiency of CH₄ recovery and CO₂ sequestration is severely limited by the amount of CO₂ injected into the reservoir and the extent of CO₂ diffusion (Koh DY et al., 2016; Matsui H et al., 2020). Most of the marine hydrate reservoirs around the world are rich in clay minerals (mainly montmorillonite, illite, and kaolinite) and characterized by low permeability, which makes it difficult to inject a large amount of CO₂ into the reservoir through drilling wells in the actual mining project (Boswell R et al., 2017; Wu ZR et al., 2020). Moreover, the injected CO₂ can easily react with pore water to form CO₂

hydrate, leading to the blockage of seepage channels. Therefore, the efficiency of CH₄ extraction and CO₂ sequestration in the process of hydrate extraction by CO₂ replacement method is relatively limited (Kan JY et al., 2021; Zhang YL et al., 2023; Gajanan K et al., 2024). Many Scholars have introduced the depressurization and thermal stimulation-induced process into the CO₂ replacement method, which promotes the seepage of CO₂ in the NGH reservoir, and ultimately improves the efficiency of NGH extraction to a certain extent (Chen Y et al., 2019; Wang YH et al., 2021; Zhang XM et al., 2024). However, these improved measures did not achieve the goal of massive CO₂ injection into the reservoir.

This study proposes the mining method of CO₂ replacement combined with solid fluidization. The schematic diagram is shown in Fig. 1. The formation of a goaf in the NGH reservoir after solid fluidization mining can provide a huge storage space for CO₂ or CO₂/N₂, which directly overcomes the challenge of injecting large amounts of CO₂. Meanwhile, the goaf can increase the contact area between the replacement medium and the hydrate formation, which is conducive to the penetration of the replacement medium into the NGH reservoir. Additionally, the formation of CO₂ hydrate during NGH exploitation may enhance the stability of the reservoir and goaf. Therefore, this combined mining method has the potential to realize the safe and efficient exploitation of marine NGH. To evaluate the theoretical feasibility of this combined mining technology, it is extremely important to clarify the effect of the presence of goaf on the behavior of CH₄ recovery and CO₂ sequestration.

In this study, sandy hydrate sediment samples and clayey hydrate sediment samples were employed in CO₂/N₂ replacement mining experiments for CH₄ hydrate to comprehensively investigate the effect of reservoir goaf on CH₄ recovery behavior and CO₂ sequestration behavior. Two sets of experiments in the intact reservoir (without goaf) were used for comparison. During the replacement process, the multi-component (CH₄, CO₂, and N₂) evolution in the gas and hydrate phases was analyzed by a gas chromatograph. It is hoped that this study could provide some guidance for the safe and efficient development of marine NGH.

2. Experimental section

2.1. Experimental materials and apparatus

CH₄, CO₂ and N₂ were used, each with a purity of 99.99%. N₂ was blended with CO₂ as a replacement medium to boost the efficiency of CH₄ extraction from NGH reservoirs, and a 1 : 4 molar ratio was adopted to simulate flue gas emitted by power plants. 200–400 mesh quartz sand was used to prepare sandy sediment. 1250 mesh sodium montmorillonite was used to prepare clayey sediment after mixing with quartz sand, and distilled water was used. Both quartz sand and sodium montmorillonite were purchased from Hunyuan Junhong New Material Co., Ltd. in China.

Fig. 2 shows the schematic diagram of the CO₂/N₂

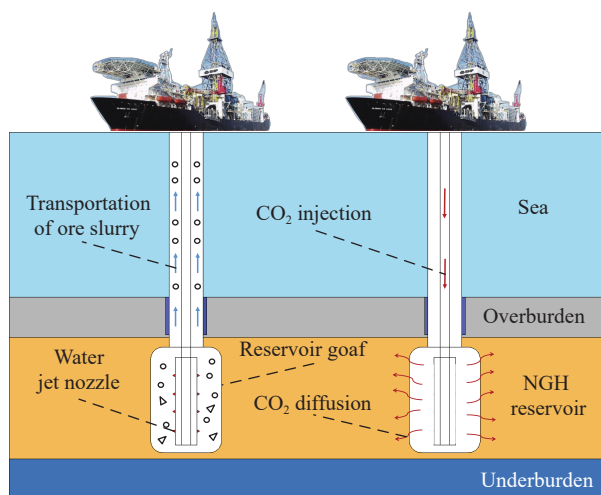


Fig. 1. Schematic diagram of CO₂ replacement combined with solid fluidization for NGH extraction.

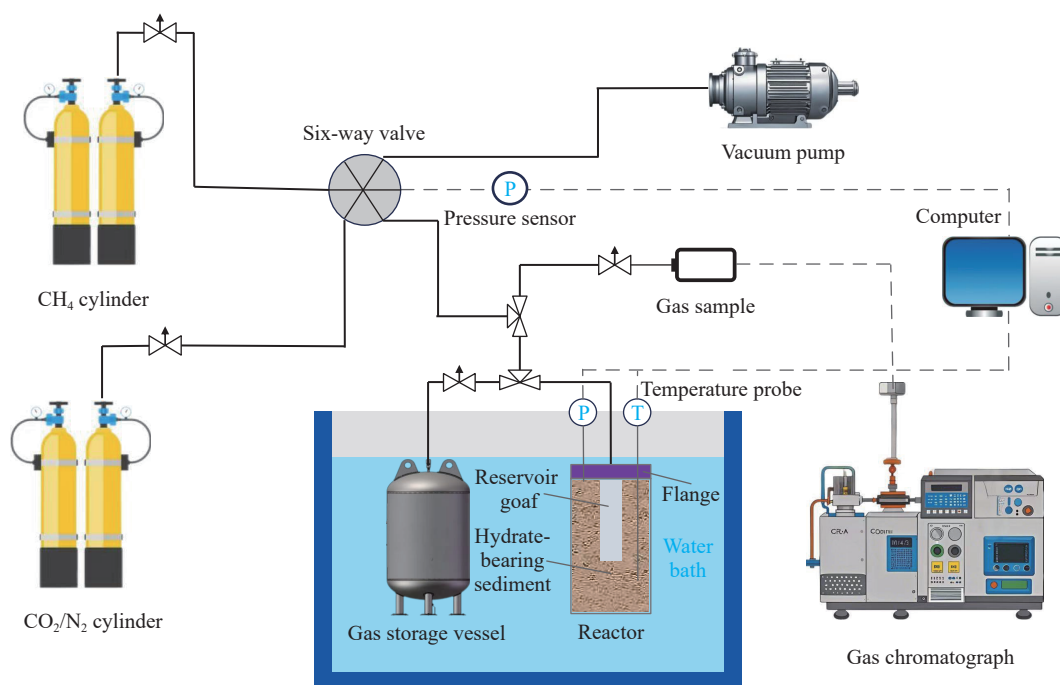


Fig. 2. Schematic diagram of the CO₂/N₂ replacement mining experimental system for natural gas hydrate.

replacement mining experiment system for CH₄ hydrate. The inner space of the reactor is cylindrical with an effective volume of 509 mL, a height of 20 cm, and an inner diameter of 6 cm. The gas storage vessel is used to store CH₄ gas during the formation of CH₄ hydrate and to store CO₂/N₂ during the replacement. The temperature range of the water bath is from 243.15 K to 373.15 K. The pressure sensor was connected to the top flange of the reactor through a pipe. A temperature probe was arranged in the hydrate-bearing sediment. The measurement errors of pressure and temperature are ± 25 kPa and ± 0.1 K, respectively. The pressure and temperature were recorded in real time by a computer during the experiment. A gas chromatograph (Agilent 7890B) was used to determine the ratio of gas components of the gas samples taken in the reactor and the gas storage vessel.

2.2. Procedure

The experimental process of this study is consistent with the proposed mining method. The specific experimental procedures are as follows.

(i) Sediment sample preparation. Firstly, a certain amount of sand and montmorillonite were dried for 72 h. Then, the dried quartz sand and montmorillonite were packed into an enclosed container according to a certain ratio (70 : 30). The mixture was shaken vigorously for 0.5 h to mix the quartz sand and montmorillonite evenly. Subsequently, distilled water was sprayed onto the sample, and the sample was mixed well by stirring.

(ii) Reactor filling. The prepared sediment sample was filled into the reactor in several layers. Each layer was compacted with a punch hammer. Subsequently, a hollow thin-walled cylindrical steel tube was used to hollow out the

center portion of the sediment. The hollowed-out hole was 3 cm in diameter and 9 cm in length, and it was used to simulate a goaf in a hydrate reservoir. It should be noted that the size of the goaf is basically the same as the size of the erosion hole formed in the previous experiment using a water jet to erode hydrate-bearing sediment (Pan DB et al., 2023). Finally, the reactor was sealed with a flange.

(iii) CH₄ hydrate formation. After the injection of CH₄, the reactor and gas storage vessel were placed in a water bath and cooled down to 274.15 K. When the reactor's temperature increased instead of decreased, it indicated that a large amount of CH₄ hydrate started to form (Fig. 3, Case 1). Finally, the hydrate synthesis is considered to be completed when the temperature is stabilized at 1°C, and the pressure is stable for 48 h. The gas storage vessel can store enough CH₄ at this stage to ensure that the required hydrate saturation can be synthesized with a single gas injection.

(iv) CO₂/N₂ injection. It has been shown that CH₄ hydrate

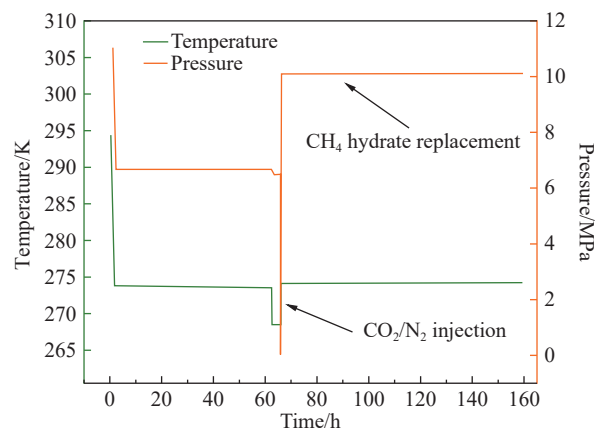


Fig. 3. Variations of pressure and temperature of hydrate synthesis and replacement reaction process in Case 1.

has a strong self-protection effect at 268.15 K, and the decomposition rate is extremely slow at this temperature (Stern LA et al., 2003). Therefore, the water bath temperature was lowered to 268.15 K after the formation of CH₄ hydrate. The remaining CH₄ in the gas storage vessel was emptied and evacuated, and then CO₂/N₂ was injected at a predetermined pressure. After that, the remaining CH₄ inside the reactor was quickly emptied, and the valve between the reactor and the vessel was opened. The CO₂/N₂ in the vessel rapidly entered the reactor, which was considered the beginning of the CH₄–CO₂/N₂ replacement reaction (replacement pressure was about 10 MPa). Finally, the water bath temperature was adjusted to 274.15 K. During the replacement, the connection between the reactor and vessel was maintained at all times. The experimental scheme of this work is illustrated in Table 1. The variations of pressure and temperature of the CH₄ synthesis and replacement reaction in Case 1 are shown in Fig. 3. This case is a typical example of all experiments in this work.

(v) Gas sampling. After the replacement reaction lasted about 90 h, there was little change in the gas phase and hydrate phase components. Therefore, the replacement reactions in all experiments were controlled within 86 h. The gas sampling intervals were set to 0.5 h, 0.5 h, 2 h, 3 h, 8 h, 24 h, 24 h, and 24 h. To ensure the accuracy of experiment results, all experimental cases were repeated three times.

2.3. Calculation formulas

During the replacement reaction, different gas components (CH₄, CO₂, and N₂) exist only in the gas phase or the hydrate phase. The calculation process of the molar amounts of different gas components in the gas phase and hydrate phase is as follows (Eqs. 1–6):

$$n_{i,j,\text{gas}} = \frac{PV}{ZTR} \cdot y_{i,j} + \sum_{i=1} \Delta n_{i,j} \quad (1)$$

where i is the serial number of gas sampling times; j represents the three gas components: CH₄, CO₂ and N₂; $n_{i,j,\text{gas}}$ is the molar amount of gas component j in the gas phase of the reactor at the moment before collecting the i -th gas sample; P is the pressure (Pa) in the reactor during the replacement; V is the total gas volume (m³) in the reactor, which is determined after the formation of CH₄ hydrate and can be obtained by subtracting the volume of internal sediments from the effective volume of the reactor; R is the molar gas constant; T is the value of temperature (K) measured by temperature probe; Z is the compression factor of the mixed gases (CH₄,

CO₂ and N₂) in the reactor, which can be calculated by the gas state equation; $y_{i,j}$ is the ratio of the molar amount of gas component j to the total molar amount of all gas components in the i -th gas sample of the reactor, which can be measured by a gas chromatograph; $\Delta n_{i,j}$ is the molar amount of gas component j in the i -th gas sample of the reactor.

$$n_{i,j,\text{gas}}^c = \frac{PV_{\text{vessel}}}{Z^c T^c R} \cdot y_{i,j}^c + \sum_{i=1} \Delta n_{i,j}^c \quad (2)$$

where $n_{i,j,\text{gas}}^c$ is the molar amounts of gas component j in the gas phase of the gas storage vessel at the moment before collecting the i -th gas sample; V_{vessel} is the effective internal volume of the gas storage vessel; T^c is the temperature in the gas storage vessel; Z^c is the compression factor of the mixed gases (CH₄, CO₂, and N₂) in the gas storage vessel; $y_{i,j}^c$ is the ratio of the molar amount of gas component j to the total molar amount of all gas components in the i -th gas sample of the gas storage vessel; $\Delta n_{i,j}^c$ is the molar amount of gas component j in the i -th gas sample of the gas storage vessel.

$$\sum_j n_{i,j,\text{hyd}} = n_{i,\text{CH}_4,\text{hyd}} + n_{i,\text{CO}_2,\text{hyd}} + n_{i,\text{N}_2,\text{hyd}} \quad (3)$$

where $n_{i,j,\text{hyd}}$ is the molar amount of gas component j in the hydrate phase of the reactor at the moment before collecting the i -th gas sample.

$$n_{i,\text{CH}_4,\text{hyd}} = \Delta n_{\text{CH}_4} - (n_{i,\text{CH}_4,\text{gas}} + n_{i,\text{CH}_4,\text{gas}}^c) \quad (4)$$

where Δn_{CH_4} is the total molar amount of synthesized CH₄ hydrate.

$$n_{i,\text{CO}_2,\text{hyd}} = n_{\text{initial},\text{CO}_2,\text{gas}} - (n_{i,\text{CO}_2,\text{gas}} + n_{i,\text{CO}_2,\text{gas}}^c) \quad (5)$$

where $n_{\text{initial},\text{CO}_2,\text{gas}}$ is the total molar amount of injected CO₂.

$$n_{i,\text{N}_2,\text{hyd}} = n_{\text{initial},\text{N}_2,\text{gas}} - (n_{i,\text{N}_2,\text{gas}} + n_{i,\text{N}_2,\text{gas}}^c) \quad (6)$$

The CH₄ recovery ratio is defined as the ratio of the molar amount of CH₄ in the gas phase during the replacement reaction to the total molar amount of synthesized CH₄ hydrate. The small amount of CH₄ generated during the injection of CO₂/N₂ is removed. The calculation formula is as follows (Eq. 7):

$$\text{CH}_4 \text{ recovery ratio} = \frac{(n_{i,\text{CH}_4,\text{gas}} + n_{i,\text{CH}_4,\text{gas}}^c) - (n_{1,\text{CH}_4,\text{gas}} + n_{1,\text{CH}_4,\text{gas}}^c)}{\Delta n_{\text{CH}_4}} \times 100\% \quad (7)$$

The CO₂ sequestration ratio is defined as the ratio of the molar amount of CO₂ consumed in the reactor during the

Table 1. Experimental scheme for CO₂/N₂ replacement mining of CH₄ hydrate.

Cases	Sediment type	Clay mineral mass fraction/%	Goaf setting	Replacement temperature/K	Replacement pressure/MPa	Porosity/%	CH ₄ hydrate saturation/%	Water saturation/%
1	S	0	none	274.2	10.6	51.1	30.4	19.7
2	S	0	one goaf	274.2	10.4	50.5	31.0	20.7
3	M+S	30	none	274.2	10.5	50.9	30.8	20.2
4	M+S	30	one goaf	274.2	10.5	50.7	30.6	21.2

Note: S is quartz sand, and M is sodium montmorillonite.

replacement reaction to the total molar amount of injected CO_2 . The calculation formula is as follows (Eq. 8):

$$\text{CO}_2 \text{ sequestration ratio} = \frac{n_{\text{initial,CO}_2,\text{gas}} - (n_{i,\text{CO}_2,\text{gas}} + n_{i,\text{CO}_2,\text{gas}}^c)}{n_{\text{initial,CO}_2,\text{gas}}} \times 100\% \quad (8)$$

The CO_2 storage amount per unit sediment volume (S_c) is defined as the ratio of the molar amount of CO_2 hydrate formed in the reactor ($n_{i,\text{CO}_2,\text{hyd}}$) to the volume of hydrate-bearing sediment (V_{sediment}). The calculation formula is as follows (Eq. 9):

$$S_c = \frac{n_{i,\text{CO}_2,\text{hyd}}}{V_{\text{sediment}}} \quad (9)$$

3. Results and discussion

3.1. Evolution of CH_4 , CO_2 and N_2 in gas and hydrate phases

In all experiments, variations in gaseous components within the hydrate reservoir are detected by gas chromatography. Then, the variations of hydrate phase components can be obtained based on the R–K gas equation of state (Redlich O and Kwong JNS, 1949). Fig. 4 and Fig. 5 show the evolution of the molar percentages of CH_4 , CO_2 , and N_2 in the gas and hydrate phases, respectively, during the replacement reaction. The CO_2 and N_2 contents in the gas phase both decrease gradually with time, and the CH_4 content

increases gradually. Correspondingly, the CO_2 and N_2 contents in the hydrate phase gradually increase with time, and the CH_4 content gradually decreases. These phenomena indicate that molecular exchange between CO_2/N_2 and CH_4 hydrate occurs in different types of reservoirs. Moreover, regardless of the presence or absence of a goaf in the hydrate reservoir, the CO_2 and N_2 contents in the hydrate phase increase rapidly in the first period (0–3 h) of the replacement reaction and slowly in the later period (3–86 h), and the CH_4 content decreases rapidly in the first period and slowly in the later period. Two factors lead to this phenomenon: (1) The driving force of the replacement reaction decreases over time due to the continuous consumption of CO_2/N_2 ; (2) the difficulty of molecular exchange between CO_2/N_2 and CH_4 hydrate particles increases in the later stages due to the gradual thickening of the CO_2/N_2 hydrate film. Considering that the molar percentage of CH_4 at the end of the replacement reaction is at a low level (less than 10%) in all experiments and that the CO_2/N_2 consumed during the replacement reaction in the reactor is replenished by CO_2/N_2 in the gas storage vessel, factor 2 may be the main reason for the slow change of CH_4 , CO_2 , and N_2 content at the late stage of the replacement reaction.

3.2. CH_4 recovery and CO_2 sequestration in sandy hydrate reservoir

The CH_4 recovery ratio is an important metric for

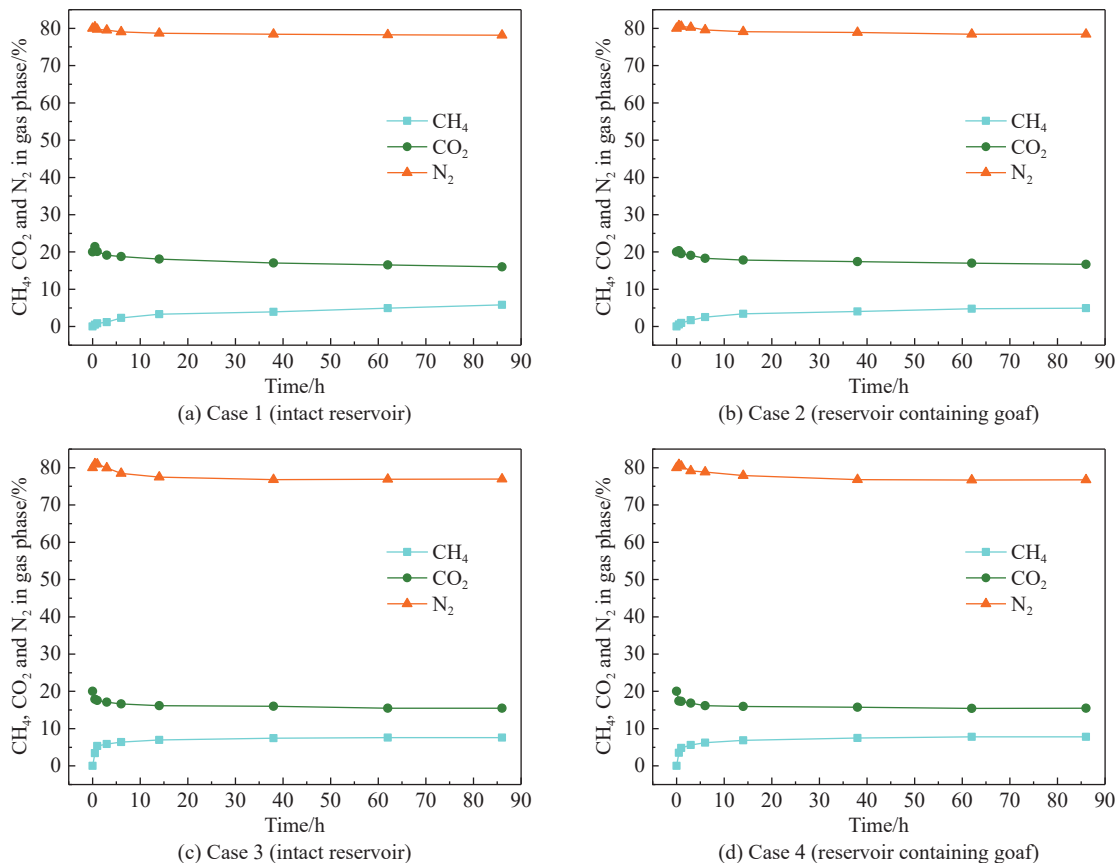


Fig. 4. Variation of CH_4 , CO_2 and N_2 in gas phase during hydrate exploitation.

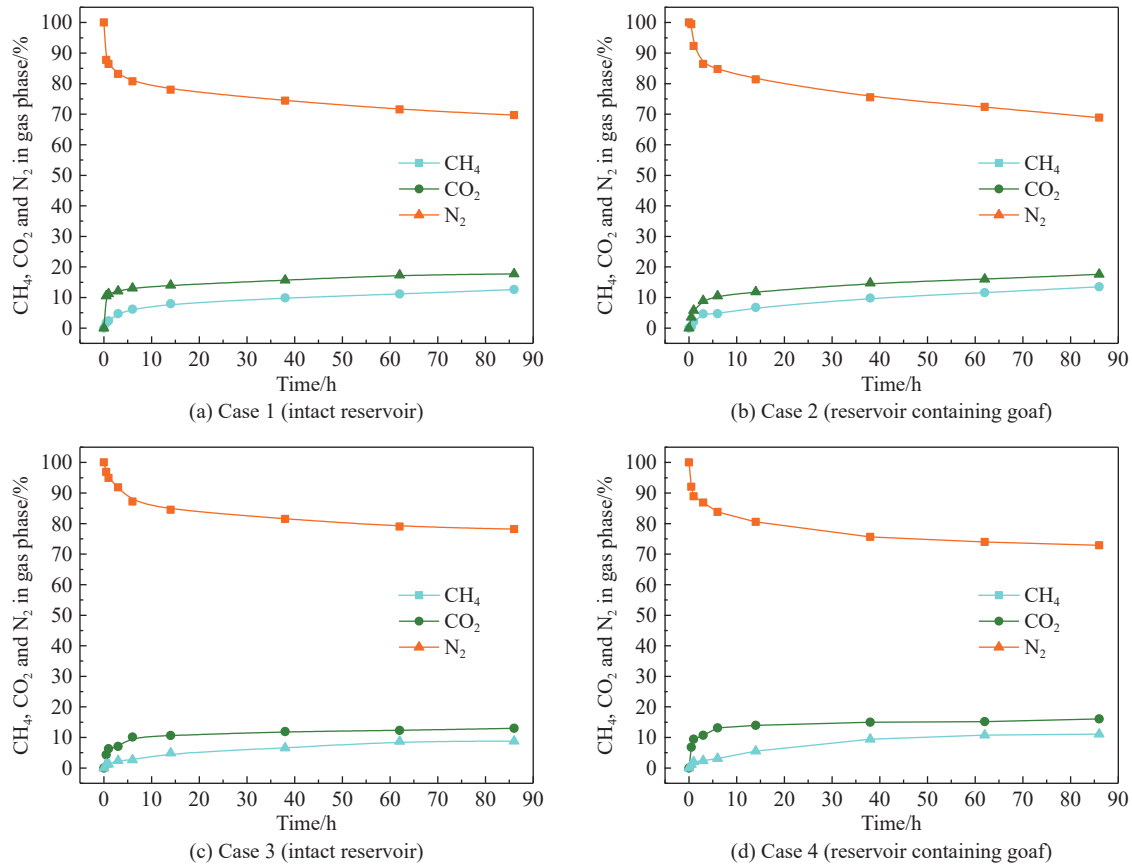


Fig. 5. Variation of CH₄, CO₂ and N₂ in hydrate phase during hydrate exploitation.

evaluating the extent of NGH exploitation. The evolution of the CH₄ recovery ratio in the sandy reservoir during hydrate extraction is shown in Fig. 6. It is found that the CH₄ recovery ratios gradually increase in both the intact reservoir and the reservoir containing goaf. Moreover, they increase rapidly in the early stage of hydrate mining (the first 3 h) and gradually stabilize in the later stage. It should be noted that the variation of the two curves show little difference in the early stage, with almost the same increment. However, as the replacement reaction proceeds, the CH₄ recovery ratio of the reservoir containing goaf is larger than that of the intact reservoir, and the difference between the two gradually increases. For Case 2, the values of the CH₄ recovery ratio at 3 h and the end of the replacement reaction are 5.2% and 19.7%, respectively. For Case 1, the values of the CH₄ recovery ratio at 3 h and the end of the replacement reaction are 3.9% and 14.2%, respectively. These phenomena indicate that in a sandy reservoir, the presence of a goaf can significantly improve the degree of CH₄ production in the late stage. However, it has little effect on the CH₄ production in the early stage. These results are associated with the injected CO₂/N₂ molar amount. The previous study has confirmed that the diffusion of CO₂/N₂ in sandy reservoirs during hydrate extraction is almost unimpeded (Pan DB et al., 2020). In Cases 1, 2, when the gas storage vessel is connected to the reactor, CO₂/N₂ can diffuse rapidly into all the pores of the hydrate reservoir and contact CH₄ hydrate particles for the replacement reaction. The presence of the vessel does not affect CO₂/N₂ diffusion.

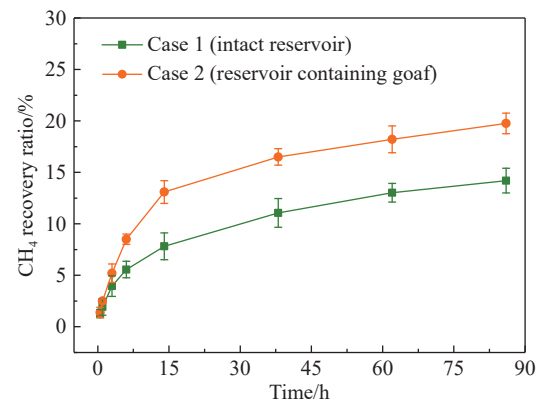


Fig. 6. Evolution of CH₄ recovery ratio in Cases 1, 2 during hydrate exploitation.

However, compared to an intact reservoir, a goaf provides additional storage space for CO₂/N₂. The difference in CO₂/N₂ gas content between the intact reservoir and the reservoir containing goaf is the root cause of the difference in the CH₄ recovery ratio.

In this study, the molar ratio of injected CO₂/N₂ to initial CH₄ hydrate was used to quantify the difference in replacement gas content in the reservoir. As shown in Table 2, the molar ratios of Case 1 and Case 2 are 3.26 and 3.78, respectively. In the early stage of the replacement reaction, both the intact reservoir and the reservoir containing goaf have sufficient CO₂/N₂ content, which can maintain a large

driving force for replacement. Thus, the values of the CH₄ recovery ratio of the two reservoirs increase synchronously by the same amount. As the replacement reaction proceeds, the formation of a mixed hydrate layer on the surface of CH₄ hydrate particles hinders molecular exchange. However, higher CO₂/N₂ content can maintain a greater driving force for the replacement reaction, and the growth rate of the CH₄ recovery ratio decreases more slowly. As a result, the CH₄ recovery ratio in the reservoir containing goaf is higher than that in the intact reservoir at the later stage.

Additionally, the average CH₄ production rate during hydrate extraction is shown in Table 2. For Case 1, the values in the early and later stages are 102.4×10^{-4} mol/h and 8.4×10^{-4} mol/h, respectively. For Case 2, the average CH₄ production rates in the early and later stages are 99.2×10^{-4} mol/h and 9.4×10^{-4} mol/h, respectively. The CH₄ production rates in the early stage of the replacement reaction are significantly higher than those in the later stage. Moreover, the average CH₄ production rate during the late stage in the intact reservoir is lower than that in a reservoir containing goaf, which is attributed to the lower CO₂/N₂–CH₄ hydrate molar ratio in the intact reservoir. However, the total amount of CH₄ hydrate in the intact reservoir is larger than that in the reservoir containing goaf. Therefore, a larger area of CO₂/N₂–CH₄ hydrate replacement reaction occurs in the intact reservoir. Hence, the average CH₄ production rate of the early stage in the intact reservoir is higher than that in the goaf-containing reservoir.

The CO₂ sequestration ratio is used to research the behavior of CO₂ geologic sequestration in the NGH reservoir. Fig. 7 shows the evolution of the CO₂ sequestration ratio in the hydrate mining process. The values of Case 1 and Case 2 both increase rapidly in the early stage and stabilize gradually in the later stage. Meanwhile, the variation of water consumption (Fig. 8) in the cases is similar to that of the CO₂ sequestration ratio. Given this, it can be considered that, in addition to the consumption of CO₂ in the gas phase by replacement reaction, the formation of mixed hydrate by the interaction of CO₂/N₂ and free water (pore water) in the reservoir also plays an important role in CO₂ sequestration. On the other hand, it is observed from Fig. 7 that the CO₂ sequestration ratio of reservoir containing goaf is smaller than that of intact reservoir throughout the replacement process, which differs from the results of the comparison of CH₄

Table 2. Average CH₄ production rate and the molar ratio of injected CO₂/N₂ to initial CH₄ hydrate in sandy hydrate reservoir.

Case	Reservoir type	Molar ratio of injected CO ₂ /N ₂ to initial CH ₄ hydrate	Stage of replacement reaction	Average CH ₄ production rate/(10 ^{−4} mol/h)
1	Intact reservoir	3.26	early stage (0–3 h)	102.4
			late stage (3–86 h)	8.4
2	Reservoir containing goaf	3.78	early stage (0–3 h)	99.2
			late stage (3–86 h)	9.4

recovery ratios in the two kinds of reservoirs. At the end of the hydrate extraction, the CO₂ sequestration ratios in the reservoir containing goaf and the intact reservoir are 25.8% and 27.1%, respectively. Two factors contribute to these phenomena. First, although the degree of hydrate replacement is more extensive in the reservoir containing goaf than that in the intact reservoir, the total amount of CH₄ hydrate in the reservoir containing goaf is smaller than that in the intact reservoir. This results in a smaller surface area for CO₂/N₂–CH₄ hydrate replacement reaction, unfavorable for carbon sequestration. Second, the free water content of the reservoir containing goaf is also smaller than that of the intact reservoir, leading to the formation of smaller amounts of CO₂/N₂ mixed hydrate in it. This is evidenced by the comparison of water consumption in Fig. 8. This is also detrimental to carbon sequestration.

It should be noted that the lower CO₂ sequestration ratio in the goaf-containing reservoir compared to the intact reservoir does not imply that the goaf-containing reservoir has a weaker CO₂ storage capacity. In this study, the CO₂ storage amount per unit sediment volume (*S_c*) is defined as the ratio of the molar amount of CO₂ hydrate formed in the NGH reservoir to the volume of hydrate-bearing sediment, and it is used to evaluate the CO₂ storage capacity of the reservoir. The evolution of *S_c* of Cases 1, 2 is illustrated in Fig. 7. It is found that the values of *S_c* of Cases 1, 2 both increase rapidly

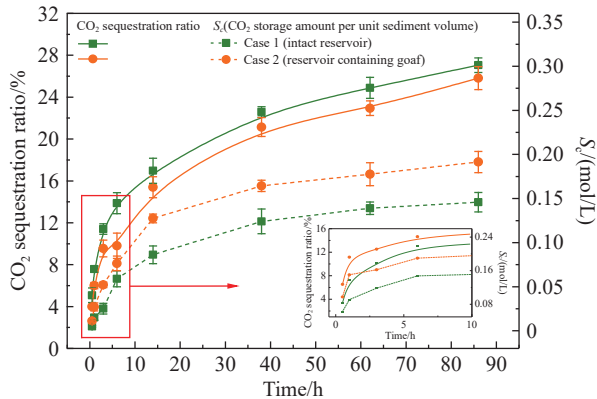


Fig. 7. CO₂ sequestration ratio and CO₂ storage amount per unit sediment volume in sandy hydrate reservoir.

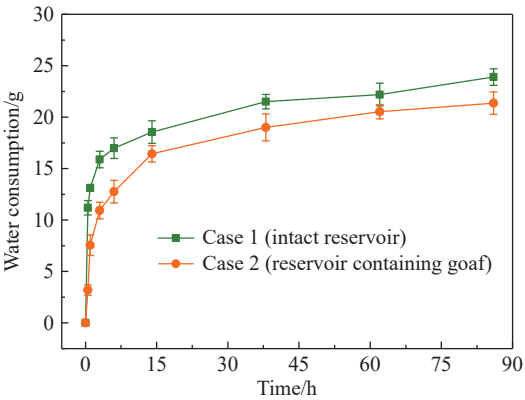


Fig. 8. Evolution of water consumption in Cases 1, 2 during hydrate exploitation.

in the early stage and stabilize gradually in the later stage. Under the influence of mixed hydrate formation and molecular exchange between CO_2/N_2 and CH_4 hydrate, the S_c of Case 1 is always smaller than that of Case 2 during hydrate production. After hydrate production, the S_c of Case 2 is higher than that of Case 1 by 31.2%. These results demonstrate that the presence of a goaf can improve the CO_2 storage capacity of a sandy hydrate reservoir.

In general, it can be concluded that for sandy hydrate reservoir, the presence of a goaf can enhance CH_4 production and S_c in the hydrate extraction process. Since the diffusion of the replacement medium in such a reservoir is not much hindered, the beneficial effect of the goaf is reflected in the enhancement of the amount of replacement medium injected during hydrate extraction.

3.3. CH_4 recovery and CO_2 sequestration in clayey hydrate reservoir

The evolution of the CH_4 recovery ratio in the clayey reservoir during hydrate extraction is shown in Fig. 9. Similar to Cases 1, 2, the CH_4 recovery ratios in Cases 3, 4 all increase gradually as hydrate extraction proceeds. Moreover, it increases rapidly in the first 3 h, and the variation gradually stabilizes in the later stage. However, different from Cases 1, 2, the gap between the two curves for Cases 3, 4 remained consistently large throughout the replacement reaction period. Meanwhile, the CH_4 recovery ratio in the reservoir containing goaf is continuously greater than that in the intact reservoir, and the gap between the two increases gradually. For Case 4, the CH_4 recovery ratios at 3 h and at the end of hydrate exploitation are 12.0% and 25.1%, respectively. For Case 3, the CH_4 recovery ratios at 3 h and at the end of hydrate exploitation are 7.2% and 19.8%, respectively. These phenomena indicate that in a clayey hydrate reservoir, the presence of a goaf can significantly improve the degree of CH_4 production throughout the replacement reaction period. It is related not only to the molar ratio of injected CO_2/N_2 to initial CH_4 hydrate but also to the diffusion of CO_2/N_2 . On the one hand, for Cases 3, 4, the diffusion of CO_2/N_2 from the gas vessel into the reactor is impeded due to the expansion of

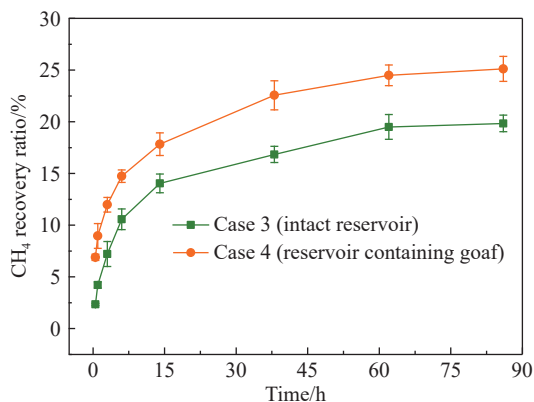


Fig. 9. Evolution of CH_4 recovery ratio in Cases 3, 4 during hydrate exploitation.

montmorillonite in the reservoir, which reduces the pore space. However, in the case of a reservoir containing goaf, the presence of the goaf enlarges the contact area between CO_2/N_2 and hydrate-bearing sediment, which improves the diffusion of CO_2/N_2 in the reservoir to a certain extent. Therefore, the promotion effect of the goaf is reflected in the fact that the CH_4 recovery ratio of the reservoir containing goaf is significantly higher than that of the intact reservoir in the early stage. On the other hand, as shown in Table 3, the molar ratio of injected CO_2/N_2 to initial CH_4 hydrate in the intact reservoir and the reservoir containing goaf is 3.37 and 3.97, respectively. A relatively high ratio maintains a greater driving force for the replacement reaction, which is more favorable for increasing the CH_4 recovery ratio. Thus, in the combination of these two factors, the CH_4 recovery ratio of the reservoir containing goaf is higher than that of the intact reservoir during the whole replacement reaction.

Additionally, the average CH_4 production rates of Cases 3, 4 during hydrate extraction are also shown in Table 3. For Case 3 and Case 4, the average CH_4 production rates in the early stage are 161.8×10^{-4} mol/h and 196.6×10^{-4} mol/h, respectively. The CH_4 production rate in the intact reservoir is significantly lower than that in the reservoir containing goaf, which is contrary to the comparison of CH_4 production rates in Cases 1, 2 (see Table 2). This result suggests that the replacement reaction area of CO_2/N_2 - CH_4 hydrate in the clayey reservoir containing goaf is larger than that in the clayey intact reservoir. Moreover, it proves that the presence of goaf contributes to the diffusion of CO_2/N_2 .

Fig. 10 shows the evolution of the CO_2 sequestration ratio in the hydrate mining process. The variations of CO_2 sequestration ratios in Cases 3, 4 are similar to those in Cases 1, 2 (see Fig. 7). They all increase rapidly in the early stage (0–3 h) and stabilize gradually in the later stage (3–86 h). Given that most of the free water in clayey sediment is absorbed by clay particles, the formation degree of CO_2/N_2 mixed hydrate is low (as reflected by the water consumption curve shown in Fig. 11). After hydrate production, the water consumption of the intact reservoir and the reservoir containing goaf is low, both of which are not greater than 4 g. It can be concluded that the replacement reaction of CO_2/N_2 with CH_4 hydrate plays a dominant role in carbon sequestration. As shown in Fig. 10, it is also found that the difference between the two curves vary in both the early and

Table 3. Average CH_4 production rate and the molar ratio of injected CO_2/N_2 to initial CH_4 hydrate in clayey hydrate reservoir.

Case	Reservoir type	Molar ratio of injected CO_2/N_2 to initial CH_4 hydrate	Stage of replacement reaction	Average CH_4 production rate/(10^{-4} mol/h)
3	Intact reservoir	3.37	early stage (0–3 h)	161.8
			late stage (3–86 h)	11.2
4	Reservoir containing goaf	3.97	early stage (0–3 h)	196.6
			late stage (3–86 h)	10.1

late stages. The CO_2 sequestration ratio in the early stage of the reservoir containing goaf is significantly higher than that of the intact reservoir. For example, the sequestration ratios of Case 4 and Case 3 at 3 h are 12.5% and 10.1%, respectively, and then the difference gradually decreases. The CO_2 sequestration ratio of Case 4 is slightly higher than that of Case 3 at the end of hydrate extraction, and the CO_2 sequestration ratios of Case 4 and Case 3 are 18.5% and 17.8%, respectively. These phenomena should be related to the diffusion behavior of CO_2/N_2 in clayey sediment. In the early stage, the degree of CO_2/N_2 diffusion in the reservoir containing goaf is greater than that in the intact reservoir, resulting in a larger reaction surface area in the reservoir containing goaf. Therefore, the reservoir containing goaf is more favorable for CO_2 sequestration. Subsequently, the replacement medium gradually penetrates the reservoir. As the total amount of CH_4 hydrate in the intact reservoir is greater, the surface area of the replacement reaction in the intact reservoir is larger than that in the reservoir containing goaf. Therefore, the intact reservoir is more favorable for CO_2 sequestration, even though the extent of replacement reaction is greater in the reservoir containing goaf (as shown by the higher CH_4 recovery ratio in Case 4 than in Case 3). Therefore, the difference in the CO_2 sequestration ratio between the two cases at the end of the replacement reaction is small.

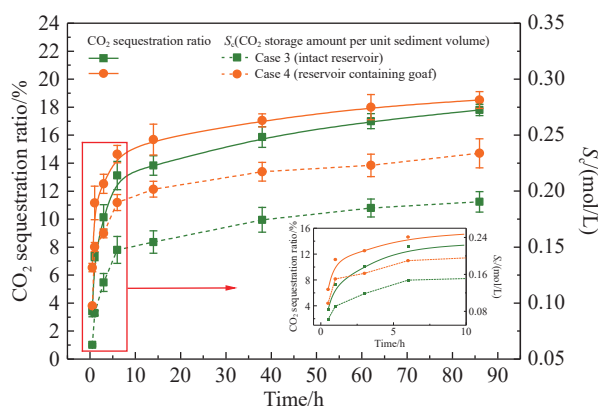


Fig. 10. CO_2 sequestration ratio and CO_2 storage amount per unit sediment volume in clayey hydrate reservoir.

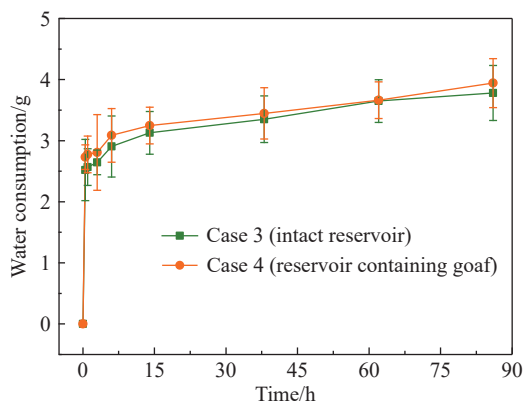


Fig. 11. Evolution of water consumption in Cases 3, 4 during hydrate exploitation.

The evolution of S_c of Cases 3, 4 is also illustrated in Fig. 10. It is found that the values of S_c of Cases 3, 4 increase rapidly in the early stage and stabilize gradually in the later stage. Under the effect of molecular exchange between CO_2/N_2 and CH_4 hydrate, the S_c of Case 3 is always smaller than that of Case 4 during hydrate production. After hydrate production, the S_c of Case 4 is higher than that of Case 3 by 22.8%. These results demonstrate that the presence of a goaf can also improve the CO_2 storage capacity of clayey hydrate reservoir.

In general, it can be concluded that for a clayey hydrate reservoir, the presence of a goaf can enhance CH_4 production and CO_2 sequestration in the hydrate extraction process. The beneficial effect of the goaf is reflected in the increasing degree of diffusion of the replacement medium and the growing amount of replacement fluid injected during hydrate extraction.

3.4. Comparison of CH_4 recovery and CO_2 sequestration in reservoirs

Fig. 12 illustrates the values of CH_4 recovery ratio, CO_2 sequestration ratio, and S_c in all cases after hydrate extraction. It is found that the CH_4 recovery ratio in clayey reservoir is greater than that in sandy reservoir, regardless of the presence or absence of a goaf. This result is caused by the formation of CO_2/N_2 mixed hydrate. During hydrate replacement mining, a large amount of free water in a sandy reservoir forms a mixed hydrate layer on the surface of CH_4 hydrate particles after contact with injected CO_2/N_2 . It increases the difficulty of CH_4 substitution from the water molecule cages. This result is also confirmed in the study of Matsui H et al. (2020) and Yuan Q et al. (2013). However, most of the free water in the clayey reservoir is absorbed by montmorillonite, and the formation of CO_2/N_2 mixed hydrate is greatly reduced (as shown by comparing the water consumption in Fig. 8 with Fig. 11), which contributes to the escaping of CH_4 from the water molecule cages. Admittedly, it is undeniable that the water-absorbing swelling of montmorillonite can inhibit the gas transportation in the reservoir (Ren JJ et al., 2022, 2024), which is unfavorable to CH_4 recovery to some extent.

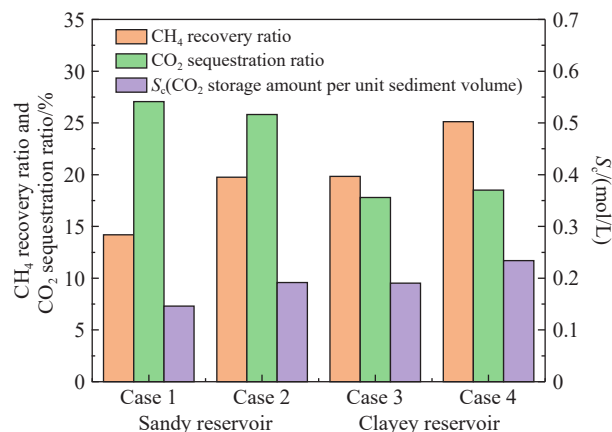


Fig. 12. Comparison of CH_4 recovery ratio, CO_2 sequestration ratio, and CO_2 storage amount per unit sediment volume in all cases.

However, the negative effect caused by the swelling of montmorillonite is not prominent under the experimental conditions in this work. It can be seen from Fig. 12 that the CO₂ sequestration ratio of Cases 1, 2 is greater than that of Cases 3, 4, regardless of the presence or absence of a goaf. This result suggests that the formation of CO₂/N₂ mixed hydrate in a sandy reservoir makes a significant contribution to the geological sequestration of CO₂. However, given that the S_c in Cases 1, 2 is lower than that in Cases 3, 4, it can be considered that the CO₂ storage capacity of the sandy hydrate reservoir is lower than that of the clayey hydrate reservoir.

4. Conclusions

Comparative experiments were conducted on the extraction of NGH using CO₂/N₂ replacement in the intact reservoir and the reservoir containing goaf. The conclusions drawn from analyzing the experimental results are as follows.

(i) Multicomponent evolution in gas and hydrate phases shows that replacement reaction can occur in the reservoir regardless of the presence or absence of a goaf.

(ii) In a sandy hydrate reservoir, the presence of a goaf results in a higher CO₂/N₂-CH₄ hydrate molar ratio, thereby increasing the CH₄ recovery ratio. Due to the higher free water content in an intact reservoir, its CO₂ sequestration ratio is higher than that of a reservoir containing a goaf. However, in terms of CO₂ storage amount per unit sediment volume, a reservoir with a goaf has increased by 31.2% compared to an intact reservoir.

(iii) In a clayey hydrate reservoir, the existence of a goaf not only increases the CO₂/N₂-CH₄ hydrate molar ratio but also promotes the diffusion of CO₂/N₂, thus enhancing the CH₄ recovery ratio. In such a reservoir, the molecular replacement between CO₂/N₂ and CH₄ hydrates dominates the CO₂ sequestration process. As a result, the CO₂ sequestration ratio of a reservoir with a goaf is higher than that of an intact reservoir, and the CO₂ storage amount per unit sediment volume has increased by 22.8% compared to an intact reservoir.

In future work, the influence of the goaf on the process of CH₄ hydrate extraction via CO₂ replacement under larger experimental scales will be investigated. Meanwhile, factors such as the heterogeneity of hydrate reservoirs and the geometric dimensions of the goaf will be considered.

CRediT authorship contribution statement

Yun-shuang Zeng contributed to formal analysis and writing-original draft. Dong-bin Pan contributed to conceptualization, methodology, writing-review and editing. Chen Chen contributed to methodology. Yu Xie contributed to formal analysis, data curation. Yang Zhou contributed to data curation.

Declaration of competing interest

The authors declare no conflicts of interest.

Acknowledgment

This work was jointly supported by the National Natural Science Foundation of China (42562030), Jiangxi Provincial Natural Science Foundation (20252BAC240263), High-level Talent Project of Jiangxi University of Science and Technology (205200100560) and Jiangxi Provincial Key Laboratory of Environmental Pollution Prevention and Control in Mining and Metallurgy (2023SSY01071).

References

- Boswell R, Schoderbek D, Collett TS, Ohtsuki S, White M, Anderson BJ. 2017. The Ignik sikumi field experiment, Alaska north slope: Design, operations, and implications for CO₂-CH₄ exchange in gas hydrate reservoirs. *Energy & Fuels*, 31(1), 140–153. doi: [10.1021/acs.energyfuels.6b01909](https://doi.org/10.1021/acs.energyfuels.6b01909).
- Boswell R, Shipp C, Reichel T, Shelander D, Saeki T, Frye M, Shedd W, Collett TS, McConnell DR. 2016. Prospecting for marine gas hydrate resources. *Interpretation*, 4(1), SA13–SA24. doi: [10.1190/int-2015-0036.1](https://doi.org/10.1190/int-2015-0036.1).
- Chen Y, Gao YH, Chen LT, Wang XR, Liu K, Sun BJ. 2019. Experimental investigation of the behavior of methane gas hydrates during depressurization-assisted CO₂ replacement. *Journal of Natural Gas Science and Engineering*, 61, 284–292. doi: [10.1016/j.jngse.2018.11.015](https://doi.org/10.1016/j.jngse.2018.11.015).
- Chen Y, Sun BJ, Gao YH, Liu K, Li H, Zhao XX. 2019. Pressure effects on heat transfer in hydrate-bearing deposit with drilling fluid invasion by lab simulation. *International Journal of Green Energy*, 16(10), 770–777. doi: [10.1080/15435075.2019.1641104](https://doi.org/10.1080/15435075.2019.1641104).
- Chibura PE, Zhang W, Luo AJ, Wang JJ. 2022. A review on gas hydrate production feasibility for permafrost and marine hydrates. *Journal of Natural Gas Science and Engineering*, 100, 104441. doi: [10.1016/j.jngse.2022.104441](https://doi.org/10.1016/j.jngse.2022.104441).
- Chong ZR, Yang SHB, Babu P, Linga P, Li XS. 2016. Review of natural gas hydrates as an energy resource: Prospects and challenges. *Applied Energy*, 162, 1633–1652. doi: [10.1016/j.apenergy.2014.12.061](https://doi.org/10.1016/j.apenergy.2014.12.061).
- Choudhary N, Phirani J. 2024. Uncertainty propagation in predicting recovery from gas hydrate reservoirs: From reservoir characteristics to performance analysis. *Energy & Fuels*, 38(5), 4021–4030. doi: [10.1021/acs.energyfuels.3c04695](https://doi.org/10.1021/acs.energyfuels.3c04695).
- Gajanan K, Ranjith PG, Yang SQ, Xu T. 2024. Advances in research and developments on natural gas hydrate extraction with gas exchange. *Renewable and Sustainable Energy Reviews*, 190, 114045. doi: [10.1016/j.rser.2023.114045](https://doi.org/10.1016/j.rser.2023.114045).
- Gu YH, Liu XJ, Li Y, Lu HF, Xu CL, Ren JF, Chen GJ, Linga P, Zhao JZ, Yin ZY. 2025. Feasibility analysis of liquid CO₂ injection and sequestration as hydrates in South China Sea marine sediments over 100 years. *Applied Energy*, 380, 125068. doi: [10.1016/j.apenergy.2024.125068](https://doi.org/10.1016/j.apenergy.2024.125068).
- Handwerger AL, Rempel AW, Skarbek RM. 2017. Submarine landslides triggered by destabilization of high-saturation hydrate anomalies. *Geochemistry, Geophysics, Geosystems*, 18(7), 2429–2445. doi: [10.1002/2016gc006706](https://doi.org/10.1002/2016gc006706).
- Kan JY, Sun YF, Dong BC, Yuan Q, Liu B, Sun CY, Chen GJ. 2021. Numerical simulation of gas production from permafrost hydrate deposits enhanced with CO₂/N₂ injection. *Energy*, 221, 119919. doi: [10.1016/j.energy.2021.119919](https://doi.org/10.1016/j.energy.2021.119919).
- Kashish, Yusuf M, Beg M, Kamyab H, Muzammil K, Ahmad M, Gupta M, Kumar S, Rezaia S, Ibrahim H. 2024. Natural gas hydrates: A review of various inhibitors and respective mechanisms. *Journal of Molecular Liquids*, 403, 124809. doi: [10.1016/j.molliq.2024.124809](https://doi.org/10.1016/j.molliq.2024.124809).

- Koh DY, Kang H, Lee JW, Park Y, Kim SJ, Lee J, Lee JY, Lee H. 2016. Energy-efficient natural gas hydrate production using gas exchange. *Applied Energy*, 162, 114–130. doi: [10.1016/j.apenergy.2015.10.082](https://doi.org/10.1016/j.apenergy.2015.10.082).
- Li XS, Xu CG, Zhang Y, Ruan XK, Li G, Wang Y. 2016. Investigation into gas production from natural gas hydrate: A review. *Applied Energy*, 172, 286–322. doi: [10.1016/j.apenergy.2016.03.101](https://doi.org/10.1016/j.apenergy.2016.03.101).
- Makogon YF. 2010. Natural gas hydrates—A promising source of energy. *Journal of Natural Gas Science and Engineering*, 2(1), 49–59. doi: [10.1016/j.jngse.2009.12.004](https://doi.org/10.1016/j.jngse.2009.12.004).
- Mao LJ, Cai MJ, Liu QY, Zhang Y. 2022. Parameter optimization for solid fluidization exploitation of natural gas hydrate in South China Sea. *Engineering Computations*, 39(3), 1051–1079. doi: [10.1108/ec-09-2020-0535](https://doi.org/10.1108/ec-09-2020-0535).
- Matsui H, Jia JH, Tsuji T, Liang YF, Masuda Y. 2020. Microsecond simulation study on the replacement of methane in methane hydrate by carbon dioxide, nitrogen, and carbon dioxide–nitrogen mixtures. *Fuel*, 263, 116640. doi: [10.1016/j.fuel.2019.116640](https://doi.org/10.1016/j.fuel.2019.116640).
- Mok J, Lee J, Choi W, Seo Y. 2025. Complementary and competitive dynamics of CO₂ and N₂ in CH₄–Flue gas replacement within natural gas hydrates. *Renewable and Sustainable Energy Reviews*, 207, 114971. doi: [10.1016/j.rser.2024.114971](https://doi.org/10.1016/j.rser.2024.114971).
- Ndlovu P, Babae S, Naidoo P. 2022. Review on CH₄–CO₂ replacement for CO₂ sequestration and CH₄/CO₂ hydrate formation in porous media. *Fuel*, 320, 123795. doi: [10.1016/j.fuel.2022.123795](https://doi.org/10.1016/j.fuel.2022.123795).
- Pan DB, Yang L, Chen C, Li XT. 2023. Experimental investigation into the erosion performance of water jets on marine hydrate-bearing sediment. *Journal of Marine Science and Engineering*, 11(1), 228. doi: [10.3390/jmse11010228](https://doi.org/10.3390/jmse11010228).
- Pan DB, Zhong XP, Zhu Y, Zhai LH, Zhang H, Li XT, Wang YF, Chen C. 2020. CH₄ recovery and CO₂ sequestration from hydrate-bearing clayey sediments via CO₂/N₂ injection. *Journal of Natural Gas Science and Engineering*, 83, 103503. doi: [10.1016/j.jngse.2020.103503](https://doi.org/10.1016/j.jngse.2020.103503).
- Redlich O, Kwong JNS. 1949. On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chemical Reviews*, 44(1), 233–244. doi: [10.1021/cr60137a013](https://doi.org/10.1021/cr60137a013).
- Ren JJ, Liu XH, Niu MY, Yin ZY. 2022. Effect of sodium montmorillonite clay on the kinetics of CH₄ hydrate-implication for energy recovery. *Chemical Engineering Journal*, 437, 135368. doi: [10.1016/j.cej.2022.135368](https://doi.org/10.1016/j.cej.2022.135368).
- Ren JJ, Yin ZY, Lu HF, Xu CL, Kuang ZG, Deng W, Liu YT, Linga P. 2024. Effects of South China Sea clayey-silty sediments on the kinetics and morphology of CH₄ hydrate: Implication on energy recovery. *Applied Energy*, 367, 123399. doi: [10.1016/j.apenergy.2024.123399](https://doi.org/10.1016/j.apenergy.2024.123399).
- Sloan ED. 2003. Fundamental principles and applications of natural gas hydrates. *Nature*, 426(6964), 353–359. doi: [10.1038/nature02135](https://doi.org/10.1038/nature02135).
- Song BJ, Cheng YF, Yan CL, Han ZY, Ding JP, Li Y, Wei J. 2019. Influences of hydrate decomposition on submarine landslide. *Landslides*, 16(11), 2127–2150. doi: [10.1007/s10346-019-01217-4](https://doi.org/10.1007/s10346-019-01217-4).
- Stern LA, Circone S, Kirby SH, Durham WB. 2003. Temperature, pressure, and compositional effects on anomalous or “self” preservation of gas hydrates. *Canadian Journal of Physics*, 81(1–2), 271–283. doi: [10.1139/p03-018](https://doi.org/10.1139/p03-018).
- Sun X, Luo TT, Wang L, Wang HJ, Song YC, Li YH. 2019. Numerical simulation of gas recovery from a low-permeability hydrate reservoir by depressurization. *Applied Energy*, 250, 7–18. doi: [10.1016/j.apenergy.2019.05.035](https://doi.org/10.1016/j.apenergy.2019.05.035).
- Wang YH, Lang XM, Fan SS, Wang SL, Yu C, Li G. 2021. Review on enhanced technology of natural gas hydrate recovery by carbon dioxide replacement. *Energy & Fuels*, 35(5), 3659–3674. doi: [10.1021/acs.energyfuels.0c04138](https://doi.org/10.1021/acs.energyfuels.0c04138).
- Wei N, Pei J, Li HT, Zhou SW, Zhao JZ, Kvamme B, Coffin RB, Zhang LH, Zhang Y, Xue J. 2024. Classification of natural gas hydrate resources: Review, application and prospect. *Gas Science and Engineering*, 124, 205269. doi: [10.1016/j.jgsce.2024.205269](https://doi.org/10.1016/j.jgsce.2024.205269).
- Wu KS, Wang YN, Zhao JZ, Zhou SW, Chen KJ, Shen JD, Zheng, LJ. 2017. Safety evaluation on the solid fluidized goaf zone in marine non-diagenetic hydrate reservoirs. *Natural Gas Industry*, 37(12), 81–86 (in Chinese with English abstract). doi: [10.3787/j.issn.1000-0976.2017.12.012](https://doi.org/10.3787/j.issn.1000-0976.2017.12.012).
- Wu ZR, Liu WG, Zheng JN, Li YH. 2020. Effect of methane hydrate dissociation and reformation on the permeability of clayey sediments. *Applied Energy*, 261, 114479. doi: [10.1016/j.apenergy.2019.114479](https://doi.org/10.1016/j.apenergy.2019.114479).
- Yoshimoto N, Wu Q, Fujita K, Kajiyama S, Nakata Y, Hyodo M. 2023. Hydrate dissociation and mechanical properties of hydrate-bearing sediments under local thermal stimulation conditions. *Gas Science and Engineering*, 116, 205045. doi: [10.1016/j.jgsce.2023.205045](https://doi.org/10.1016/j.jgsce.2023.205045).
- Yuan Q, Sun CY, Liu B, Wang X, Ma ZW, Ma QL, Yang LY, Chen GJ, Li QP, Li S, Zhang K. 2013. Methane recovery from natural gas hydrate in porous sediment using pressurized liquid CO₂. *Energy Conversion and Management*, 67, 257–264. doi: [10.1016/j.enconman.2012.11.018](https://doi.org/10.1016/j.enconman.2012.11.018).
- Zeng ZY, Kong L, Zhao YP, Sang SK, Niu G, Liu JQ, Wang N. 2023. Mechanical properties of gas hydrate-bearing sediments influenced by multiple factors: A comprehensive review of triaxial tests. *Energy & Fuels*, 37(21), 16190–16220. doi: [10.1021/acs.energyfuels.3c02623](https://doi.org/10.1021/acs.energyfuels.3c02623).
- Zhang XM, Zhang SL, Yuan Q, Liu QQ, Huang TT, Li JP, Wu QB, Zhang P. 2024. Gas production from hydrates by CH₄–CO₂ replacement: Effect of N₂ and intermittent heating. *Energy*, 288, 129965. doi: [10.1016/j.energy.2023.129965](https://doi.org/10.1016/j.energy.2023.129965).
- Zhang YL, Cui M, Xin GM, Li DX. 2023. Microscopic insights on the effects of flue gas components on CH₄–CO₂ replacement in natural gas hydrate. *Gas Science and Engineering*, 112, 204947. doi: [10.1016/j.jgsce.2023.204947](https://doi.org/10.1016/j.jgsce.2023.204947).
- Zhou SW, Zhao JZ, Li QP, Chen W, Zhou JL, Wei N, Guo P, Sun WT. 2018. Optimal design of the engineering parameters for the first global trial production of marine natural gas hydrates through solid fluidization. *Natural Gas Industry B*, 5(2), 118–131. doi: [10.1016/j.ngib.2018.01.004](https://doi.org/10.1016/j.ngib.2018.01.004).