Experimental investigation into methane production from hydrate-bearing clayey sediment by CO₂/N₂ replacement

Dong-Bin Pan¹,², Xiu-Ping Zhong¹,², Bing Li¹,², Xi-Tong Li¹,² and Chen Chen¹,²

Abstract
The replacement of gas hydrate in clayey sediment by a CO₂/N₂ (20:80) gas mixture injection was experimentally studied to explore the influence of clay on the gas exchange behaviours in the gas hydrate. Clay (montmorillonite) and silica sand were mixed in three different proportions (clay mass ratios of 10%, 30% and 50%) to simulate the host sediments of natural gas hydrate while pure silica sand sediment was selected for comparison. Experimental results showed that clay hindered gas diffusion during the initial replacement stage and thus reduced the methane recovery rate. In the later stage, the gas exchange between CO₂/N₂ and methane in the hydrate structure might be subject to thermodynamic inhibition and geometric constraints of the clay interlayer. Moreover, the CO₂ sequestration ratio was lowered significantly in the sediment with a 50% clay mass ratio. Therefore, it was determined that clay has an inhibitory effect on gas hydrate replacement by CO₂/N₂.

Keywords
Natural gas hydrate, clayey sediment, hydrate replacement, methane recovery, carbon dioxide sequestration

¹College of Construction Engineering, Jilin University, Changchun, China
²Key Laboratory of Drilling and Exploitation Technology in Complex Conditions, Ministry of Land and Resources, Jilin University, Changchun, China

Corresponding author:
Chen Chen, Jilin University, No. 938, Ximinzhu Street, Changchun 130026, China.
Email: chenchen@jlu.edu.cn

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Introduction

Natural gas hydrate (NGH) is a nonstoichiometric, crystalline compound formed by water and light hydrocarbons (mainly CH$_4$) under certain temperature and pressure conditions (Li et al., 2012; Sloan and Koh, 2007). NGH has great potential as a next-generation energy source due to large reserves; NGH resources are mainly stored in both clayey and sandy sediments (Boswell and Collett, 2011; Chen et al., 2019; Collett, 2002). Clayey NGH deposits are distributed worldwide and NGH resources account for more than 90% of all global hydrate resources (Johnson, 2011; Li et al., 2018b). At present, the three main methods of NGH production involve depressurization (Wang et al., 2016; Yang et al., 2018), thermal stimulation (Sun et al., 2014) and inhibitor injection (Zhao et al., 2016); all three are based on breaking down the NGH phase equilibrium through external stimulation (Chong et al., 2016; Li et al., 2016). Since NGH decomposition may cause hydrate reservoir sediment instability which can result in submarine slides or subsidence (Moridis et al., 2011), CO$_2$ replacement is recognized as a promising option for recovering natural gas without hydrate decomposition (Zhang et al., 2017). It has the added benefit of permanent CO$_2$ sequestration in the hydrate reservoir (Koh et al., 2016; Zhao et al., 2015).

The concept of NGH production with CO$_2$ replacement was first proposed by Ohgaki et al. (1996), and both its thermodynamic and kinetic feasibilities have been demonstrated (Smith et al., 2001; Uchida et al., 2010). Subsequent work utilized N$_2$ as an additional replacement media to enhance the CH$_4$-CO$_2$ replacement in NGH (Shin et al., 2008). Park et al. (2006) compared the replacement process by injecting a CO$_2$/N$_2$ gas mixture (20/80 mol% to simulate flue gas from a power plant) as well as pure CO$_2$. They found the total CH$_4$ production increased from 64% to 85% upon the addition of N$_2$ to CO$_2$. Moreover, the direct injection of a CO$_2$/N$_2$ gas mixture not only reduced CO$_2$ separation costs but also prevented CO$_2$ liquefaction and potential pipeline blockage problems as compared with the injection of pure CO$_2$ into hydrate reservoirs (Koh et al., 2015). The successful application of the replacement technique by using a binary CO$_2$–N$_2$ gas mixture on the Alaska North Slope in the United States demonstrated the feasibility of this technique in the field (Boswell et al., 2016). In order to explore the NGH replacement mechanism, the phase equilibria of CO$_2$/N$_2$, CO$_2$/CH$_4$ and CH$_4$/CO$_2$/N$_2$ gas mixtures and the distribution of the mixed gas molecules in hydrate structures were investigated (Herri et al., 2011; Lim et al., 2017; Sun et al., 2017). Additionally, extensive research efforts have focused on factors influencing CH$_4$-CO$_2$ replacement that include temperature, pressure, sediment particle size, permeability, water salinity, water saturation and hydrate saturation (Lee et al., 2014; Mu and von Solms, 2016, 2018; Sun et al., 2018; Wang et al., 2018). However, previous studies were mainly focused on gas hydrates in water or silica sand and scant attention was paid to the influence of clay on CH$_4$-CO$_2$ replacement.

The host sediments of NGH mainly consist of fine-grained silt, clay and sand (Boswell and Collett, 2011; Koh et al., 2016); the clay content of hydrate deposits varies in different regions (Kumar et al., 2015; Liu et al., 2015). Compared to silt and sand, clay has a special structure which causes NGH behaviour to differ from gas hydrates in water or silica sand (Cygán et al., 2004; Guggenheim and van Groos, 2003); therefore, CH$_4$-CO$_2$ swapping process in NGH may be affected by clay. Moreover, clay concentration variations also affect the thermodynamic phase behaviour of NGH (Seo et al., 2009). However, only a few reports have dealt with the effects of clay on CH$_4$-CO$_2$ replacement; even though clay is one of the main components of NGH host sediments. Yang et al. (2008) investigated
CH4-CO2 replacement in silica sand and a kaolinite–sand mixture using liquid CO2. They observed a significantly lower methane recovery rate in the kaolinite–sand mixture relative to silica sand. Koh et al. (2012) compared gas replacement in pure CH4 hydrates, NGH sediments and CH4 hydrates bearing clay (montmorillonite) by injecting a CO2 and CO2/N2 gas mixture. They found that the total recovered CH4 for the all three samples were nearly identical; however, the methane recovery rate was largest in the pure CH4 hydrate, followed by the NGH sediments and finally the CH4 hydrate-bearing clay. However, those previous studies were mainly focused on CH4 recovery rates that were affected by clay. The influence of clay on CH4, CO2 and N2 variations in both gas and hydrate phases as well as CO2 sequestration, which are important for analysing the mechanism of gas hydrate replacement (Li et al., 2018a; Yang et al., 2017), have not been investigated. Thus, the influence of clay on CH4-CO2 exchange behaviours may not be well understood. In addition, although the clay concentration varies in the NGH host sediments, the effect of different clay levels on CH4-CO2 replacement has received very little attention. Therefore, it is significant to completely reveal the CO2-CH4 replacement mechanism in hydrate-bearing clayey sediments and investigate the influence of clay content on gas exchange behaviours.

In this work, replacement of CH4 hydrate in clayey sediments by a CO2/N2 gas mixture was experimentally studied and the replacement in CH4 hydrate-bearing sand sediment was analysed for comparison. The clayey sediments used in these experiments were simulated from the host sediments of NGH in the Shenhui area of the South China Sea. In that area, montmorillonite and illite are the primary clay mineral types and the clay content in the NGH reservoirs ranged from 0.4% to 30% (Li et al., 2018b; Liu et al., 2012). Thus, clay (montmorillonite) and silica sand were mixed in three different proportions (the three clay mass ratios were 10%, 30% and 50%). Montmorillonite was also chosen because it is generally the richest clay mineral in NGH bearing sediments worldwide (Zhou et al., 2011). The gas mixture of 20 mol% CO2 and 80 mol% N2 was used to simulate flue gas. During gas replacement, the evolution of CH4, CO2 and N2 in the gas phase were examined using gas chromatography (GC) to study gas exchange behaviours between the CO2/N2 and CH4 hydrate-bearing clay/sand sediments.

**Experimental**

*Materials and apparatus*

Analytically pure (99.99%) CH4, CO2 and N2 gases used were supplied by Beifang Special Gas Industry Corporation (China). The silica sand was 200–400 mesh and the montmorillonite was 1250 mesh, both were supplied by Hunyuan Junhong New Materials Co., Ltd. (China). Double-distilled water was used. A schematic diagram of the experimental apparatus is shown in Figure 1. The experimental apparatus is composed of a reactor, three gas cylinders, a glycol bath, a GC, a set of data acquisition system and so on. The reactor is made of 316 L stainless steel, is 18 cm tall with an internal diameter of 6 cm for an effective volume of 509 mL. The temperature was measured by two secondary platinum resistance thermometers (type pt100), which were uniformly arranged in the vertical direction inside the reactor; a pressure sensor was used to monitor the reactor pressure. The small cylinder was used to store CH4 and provided a sufficient gas source for hydrate formation in the reactor, thus avoiding the secondary injection of CH4 to form a hydrate. The glycol bath
was used to regulate the reactor temperature of the reactor. The uncertainties of measured pressure and temperature are ±0.01 MPa and ±0.1 K, respectively.

**Procedures**

*CH₄ hydrate formation in clayey sediment.* At first, a certain amount of silica sand and montmorillonite were dried at 373.2 K for 72 h. Silica sand, montmorillonite and distilled water were thoroughly mixed at predetermined mass ratios and those mixtures were loaded into the reactor in small quantity batches. Each batch was compacted to remove voids in the reactor. The entire system was then evacuated and purged three times with CH₄ to vent the air completely. The reactor and the small cylinder were pressurized to approximately 9 MPa using CH₄ and set at room temperature for 24 h to monitor for leaks. When the reactor pressure stabilized, the reactor and small cylinder were put into the glycol bath at 275.2 K. The CH₄ hydrate began to form once the system temperature dropped to a certain value. The system pressure gradually decreased with hydrate formation. Finally, when the pressure and temperature stabilized for 48 h (Figure 2), CH₄ hydrate formation was assumed to be finished. Preparation of the silica sand sediment hydrate sample was consistent with the aforementioned procedure.

*CO₂/N₂ injection and CH₄ recovery.* After preparing the CH₄ hydrate sample, the glycol bath was set to 268.2 K and the small cylinder valve was closed. When the temperature and pressure of the reactor stabilized, residual CH₄ in the reactor was released through a six-way valve and the reactor was evacuated for 20 s. Afterwards, the room temperature CO₂/N₂ was injected into the reactor through a cold pipe (a 5 m pipeline placed in the glycol bath) until the pressure in the reactor reached the desired value and the initial gas sample was taken. This CO₂/N₂ injection process was also controlled by the six-way valve and lasted for
Figure 2. Variations of reactor temperature and pressure over time during CH$_4$ hydrate formation: (a) Run 4 and (b) Run 1.

Table 1. Experimental parameters for CH$_4$ hydrate replacement by CO$_2$/N$_2$.

| Runs | Clay mass ratio | T/K  | $P_i$/MPa | $P_r$/MPa | Porosity/% | Hydrate saturation/% | Water saturation/% |
|------|----------------|------|-----------|-----------|------------|----------------------|-------------------|
| 1    | 0 (silica sand)| 274.2| 8.49      | 7.90      | 58.14      | 34.49                | 3.07              |
| 2    | 10             | 274.2| 8.19      | 8.00      | 57.13      | 32.29                | 7.48              |
| 3    | 30             | 274.2| 8.25      | 8.53      | 55.52      | 24.76                | 17.71             |
| 4    | 50             | 274.2| 8.34      | 8.84      | 58.15      | 15.75                | 22.38             |

$T$ is the hydrate replacement temperature; $P_i$ is the hydrate replacement pressure just after CO$_2$/N$_2$ injection; $P_r$ is the pressure after replacement.

approximately 30 s. The reactor was sealed and the bath was set to 274.2 K for gas hydrate replacement. During replacement, a series of gas samples (100 mL, atmospheric pressure) were taken at predetermined time intervals and measured by GC. Experimental parameters for CH$_4$ hydrate replacement are shown in Table 1.
Results and discussion

CH₄ hydrate formation

Figure 2(a) shows temperature and pressure variations during hydrate formation in the clayey sediment (Run 4, clay mass ratio of 50%). The temperature and pressure evolution in Run 4 was similar to Runs 2 and 3 and was selected to represent typical results of CH₄ hydrate formation. As shown in Figure 2(a), the trend of temperature 1 and temperature 2 is almost the same, which indicates that the hydrate is formed evenly in the clayey sediment. Meanwhile, both temperature and pressure decreased linearly after the reactor is placed in the bath. After approximately 2 h, the pressure dropped sharply, but the temperature increased suddenly and reached a maximum of 281.4 K, which indicated the rapid formation of hydrate. The pressure stabilized after ~5 h, indicating the end of hydrate formation.

Figure 2(b) shows temperature and pressure data during hydrate formation in silica sand sediment. Temperature and pressure variations over time in Run 1 agreed with those from Run 4; however, the pressure drop in Run 1 was much larger than Run 4. The pressure drop difference between the two runs was ~1.75 MPa, indicating that hydrate formation in silica sand was significantly larger than clayey sediment. This is attributed to the high water absorption and expansion characteristics of clay. When water was mixed with clayey sediment, a number of water molecules were orderly adsorbed and incorporated into the interlayer space of clay sheets (Uchida et al., 2004). During hydrate formation, the ordered water structure of clay inter-layer promoted CH₄ hydrate nucleation (Seo et al., 2009; Uchida et al., 2004), but growth of the hydrate crystal was limited due to the water activity reduction caused by geometrical constraints (Uchida et al., 2002). Furthermore, the pore size in clayey sediment is smaller than silica sand sediment since clay particles swell after absorbing water; that swelling hinders hydrate formation outside the clay inter-layers.

Variation of gas compositions in the gas phase

Direct component determination by GC is helpful for quantitative analysis of the gas phase in the reactor. Based on gas-phase analysis and the gas equation of state, mole percent variations CH₄, N₂ and CO₂ in the gas phase before sampling during replacement were obtained (Figure 4). Runs 1–4 all showed similar gas phase trends, CH₄ increased with time, while N₂ and CO₂ decreased. That indicated CH₄ was recovered from the hydrate in the reactor after injection of the CO₂/N₂ gas mixture. In particular, for all four runs, the mole content of CH₄ initially increased rapidly but decreased with time. Using Run 2 as an example, from 0 to 4 h (Stage 1), the mole percentage of CH₄ increased from 0 to 9.65%, but over the next 274 h (Stage 2), the mole percentage increased by 21.35 mol%. The CH₄ recovery rate of Run 2 in Stage 1 was 32 times higher than that in Stage 2. This observation is likely due to the reduction of driving forces over time during hydrate replacement. Previous studies have shown that the driving force of gas hydrate replacement is the chemical potential gradient between the hydrate phase and the gas phase (Schicks et al., 2011).
Figure 3. The mole ratio of initial CH$_4$ conversion to hydrate in silica sand and clayey sediment during the hydrate formation.

Figure 4. Variation of CH$_4$, CO$_2$ and N$_2$ mole percentages in gas phase with time during hydrate replacement: (a) Run 1; (b) Run 2; (c) Run 3; and (d) Run 4.
With the progress of the hydrate replacement by CO₂/N₂ gas mixture, the recovered CH₄ will gradually dilute the CO₂/N₂ gas mixture, which reduces the gradient of the chemical potential between the hydrate phase and the gas phase.

Table 2 presents the average recovery rate of CH₄ at Stages 1 and 2. For all four runs, the average recovery rate of CH₄ in Stage 1 was more than 30 times higher than that in Stage 2. However, it should be noted that in Stage 1, the average recovery rate in silica sand was higher than clayey sediment. This is attributed to the different diffusion ranges of CO₂/N₂ in silica sand and clayey sediments. For the CH₄ hydrate in silica sand, after CO₂/N₂ injection, the mixed gas diffuses rapidly in the void space of the sediment system and then contacts the hydrate for CH₄ recovery. But the clayey sediment has smaller pore sizes than silica sand due to expansion of the clay particles which hinders diffusion of the CO₂/N₂ gas mixture in the void space and results in a smaller gas diffusion range.

Therefore, as the clay mass ratio increases, gas diffusion is hindered and lowers the average CH₄ recovery rate. However, as listed in Table 2, the recovery rate in Run 4 was higher than Runs 2 and 3, although the clay mass ratio in Run 4 was the largest. This abnormal observation could be associated with CH₄ hydrate saturation in Run 4. An analysis suggested that an increase in hydrate saturation reduced the void space in the porous media system and restricted diffusion of the replacement gas. As shown in Table 1, the hydrate saturation in Run 4 was 15.75%, significantly lower than the other runs. Despite the clay particle expansion that leads to a void space reduction in the porous media system of Run 4, the low-hydrate saturation partially offsets this and increases the diffusion range of the injected CO₂/N₂ gas mixture.

Variation of gas compositions in the hydrate phase

Figure 5 illustrates the mole percent variation CH₄, N₂ and CO₂ in the hydrate phase before gas sampling in the replacement process. As can be seen from Figure 5, the trend of variations for all runs was similar; the mole content of CH₄ in the hydrate phase decreased with time, while N₂ and CO₂ increased. This indicated that gas exchange occurred between the CO₂/N₂ and the CH₄ hydrate. Furthermore, this phenomenon was also observed during early research on gas hydrate replacement using a CO₂/N₂ gas mixture or pure CO₂ (Li et al., 2018a; Sun et al., 2018).

### Table 2. The average recovery rate of CH₄ at Stage 1 and Stage 2 during replacement.

| Experiment | Clay mass ratio (%) | Stage | Average recovery rate (10⁻⁴ mol/h) |
|------------|---------------------|-------|----------------------------------|
| Run 1      | 0                   | 1     | 218.3                            |
|            |                     | 2     | 6.6                              |
| Run 2      | 10                  | 1     | 171.4                            |
|            |                     | 2     | 5.3                              |
| Run 3      | 30                  | 1     | 154.2                            |
|            |                     | 2     | 4.1                              |
| Run 4      | 50                  | 1     | 187.7                            |
|            |                     | 2     | 2.1                              |
In Figure 5, for Run 1, the mole percent of CO₂ in the hydrate phase was nearly identical to the mole percent of N₂ at the end of Stage 1 (0–4 h); however, the CO₂ mole percent was higher than N₂ for Runs 2–4. In particular, the CO₂ mole percent in Run 4 maximized at the end of Stage 1 (16.03%). This observation could be related to the formation of mixed gas hydrate after CO₂/N₂ injection. The equilibrium pressure of CO₂/N₂ binary hydrate in all experimental runs was ~7 MPa at the experimental temperature. The pressures in Runs 1–4 during replacement were higher than this phase equilibrium pressure, indicating the formation of a CO₂/N₂ binary hydrate could occur after gas injection. For ease of analysis, the CO₂ to N₂ molar ratio in the hydrate phase is referred to as the Sequestration Ratio (C/N).

Figure 6 shows C/N variations over time for all four runs. At 4 h, the C/N was 3.18 when the clay mass ratio was 50%, close to the theoretical consumption ratio of CO₂/N₂ (3:1) (Seo et al., 2015). This means that gas exchange between the CO₂/N₂ mixture and the CH₄ hydrate was dominant in Stage 1 compared to formation of the mixed gas hydrate. Moreover, the value C/N at 4 h decreased with the decreasing clay content in the clayey sediment and was lowest in the silica sand sediment; this indicated that the extent of mixed hydrate formation in Stage 1 was largest for silica sand sediment and decreased as the clay content increased. This analysis suggested the difference in the extent of mixed hydrate formation between the silica sand sediment and the clayey sediment was due to the difference in the amount of free water (water unabsorbed by clay) in the system. As mentioned, clay has a strong water absorption capacity and many water molecules were adsorbed into the clay inter-layer system. The amount of free water in the system decreased as the clay
content increased, thus causing gas exchange to dominate in Run 4. Meanwhile, the free water content in Run 1 was higher due to the weak water absorption capacity of silica sand which favoured formation of the CO₂/N₂ binary hydrate in the silica sand sediment relative to the clayey sediment. It should be noted that the diffusion range of the CO₂/N₂ gas mixture in Stage 1 may also affect the extent of mixed hydrate formation in the system. In addition, C/N remains low after 40 h and is related to the distinct gas exchange behavior of CO₂ and N₂.

Figure 7 shows water consumption at 4, 40 and 280 h for all four runs during replacement. Water consumption in Run 1 was significantly higher than Runs 2–4 over 4 h, which further supports the aforementioned observation and analysis. Furthermore, water consumption at 40 h was slightly less than that at 280 h, indicating that after 40 h, the amount of mixed hydrate formation in Runs 1–4 was very small and all experimental runs were dominated by gas exchange between the replacement gas and the CH₄ hydrate. Combining results from Figures 5 and 8, after 40 h, the increase in CO₂ mole percent slowed considerably while the N₂ mole percent continued to increase; meanwhile, the ratio of the N₂ increments in the hydrate phase to the CH₄ reductions in hydrate phase from 40 to 280 h was between 0.8 and 0.9. This indicated that after 40 h, the gas exchange amount between N₂ and CH₄ molecules in the hydrate structure was significantly higher than for CO₂ molecules. These observations are attributed to the stronger diffusibility of N₂ relative to CO₂ molecules. Since N₂ is smaller than CO₂ (Liu et al., 2016), N₂ molecules migrate deeper into the hydrate layer to recover CH₄ molecules occupied in water cavities. Therefore, all experimental runs were dominated by the gas exchange between N₂ and CH₄ the hydrate from 40 to 280 h.

The percentage increase of N₂ in the hydrate phase for Runs 1–4 after 40 h is also illustrated in Figure 8. As can be seen, the percentage of N₂ in silica sand sediment was higher than clayey sediment and the increased percentage of N₂ decreased as the clay mass ratio increased in the clayey sediment. This indicated the replacement extent in silica sand
sediment after 40 h was higher than clayey sediment since the gas exchange between the N$_2$ and CH$_4$ hydrate dominates all experimental runs. This may be due to difficulties in replacing CH$_4$ of the clay inter-layer with N$_2$. As the replacement process proceeds in the clayey sediment, N$_2$ molecules penetrate the clay inter-layer to extract CH$_4$ molecules; however, since the thermodynamic stability of the CH$_4$ hydrate in the clay inter-layer exceeds the pure
hydrate (Park and Sposito, 2003; Seo et al., 2009), CH₄ extraction in the clay inter-layer might be thermodynamically inhibited. Additionally, N₂ migration in the clay inter-layer is likely to be restricted due to geometric constraints resulting in lower N₂ penetration depths in the hydrate layer of clayey sediment relative to the hydrate layer of silica sand.

**CO₂ sequestration and hydrate replacement efficiency**

**CO₂ sequestration.** The CO₂ sequestration ratio is defined as the molar quantity of consumed CO₂ in the gas phase to the initial molar quantity of CO₂ after gas mixture injection. CO₂ sequestration rates and CO₂ sequestration ratios are shown in Table 3. The CO₂ sequestration rate in silica sand sediment was highest and the sequestration rate in Run 4 was higher than Runs 2 and 3 despite the elevated clay mass ratio for Run 4. Remarkably, CO₂ sequestration rates for the four runs agreed with H₄ recovery rates discussed in Variation of gas compositions in the gas phase section. As a consequence, the different CO₂ sequestration rates for all four runs was mainly due to the difference in gas diffusion ranges caused by the interaction between clay expansion and CH₄ hydrate saturation. Moreover, it should be noted that a part of the CO₂ consumption rate in Stage 1 was contributed by mixed hydrate formation. On the other hand, as listed in Table 3, 80.4%, 73.1%, 69.5% and 49.6% of the initial CO₂ in the gas phase were captured and retained in the hydrates in Runs 1–4, respectively. These results demonstrate that CO₂ sequestration capacity of silica sand sediment surpassed clayey sediment. This is understandable because the amount of free water in the clayey sediment is limited and CO₂ migration into the clay inter-layer is difficult to replace CH₄ in the hydrate structure. Accounting for the sharp slope change of CO₂ sequestration in the clayey sediment with a 50% clay mass ratio, it suggested the hydrate reservoirs with high clay content are not conducive to CO₂ capture and storage by CO₂/N₂ injection.

**Hydrate replacement efficiency.** Replacement efficiency is defined as the ratio of the molar quantity of CH₄ in the gas phase to the initial molar quantity of CH₄ in the hydrate phase. Figure 9 illustrates replacement efficiencies of Runs 1–4 over time. Initially, replacement efficiencies for all four runs increased rapidly (0–4 h). This increase was attributed to the initially high fugacity between the gas phase and the hydrate phase. Figure 10 shows the replacement efficiencies after hydrate replacement and the mole ratios of injected CO₂/N₂ to the initial CH₄ hydrate before replacement for all four runs. In Runs 2–4, the replacement efficiency order was Run 4 > Run 3 > Run 2, which agreed with the mole ratio order of injected CO₂/N₂ to the initial CH₄ hydrate. This analysis indicated that a higher mole ratio maintained a higher partial fugacity of the CO₂/N₂ which promoted gas exchange between

| Experiment | Clay mass ratio | CO₂ sequestration rate (10⁻⁴ mol/h) | CO₂ in the gas phase (10⁻³ mole) | CO₂ sequestration ratio (%) |
|------------|-----------------|-----------------------------------|---------------------------------|-----------------------------|
| 1          | 0               | 170                               | 2                               | 149.8 29.4 80.4            |
| 2          | 0.1             | 124.5                             | 1.8                             | 133.5 35.9 73.1            |
| 3          | 0.3             | 117.2                             | 1.4                             | 137.9 42.1 69.5            |
| 4          | 0.5             | 144.2                             | 0.6                             | 142.2 71.7 49.6            |

Table 3. CO₂ sequestration rate and sequestration ratio during replacement.
the gas phase and the hydrate phase and resulted in higher replacement efficiency. This phenomenon is consistent with Sun’s finding that the replacement efficiency of the hydrate increased with the CO2 fluid mole ratio increase to the initial hydrate before replacement (Sun et al., 2018). However, it should be noted that the replacement efficiency of Run 1 was

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**Figure 9.** Variations of replacement efficiencies in Runs 1–4 over time during hydrate replacement.

**Figure 10.** Replacement efficiencies after the hydrate replacement and the mole ratios of injected CO2/N2 to initial CH4 hydrate before the replacement reaction in Run 1–4.
higher than Runs 2 and 3, although the mole ratio in Run 1 was lower than Runs 2 and 3. This anomalous result indicated the restrictive effects of clay on replacement efficiency. This is understandable since CH₄ extraction in the clay inter-layer might be thermodynamically inhibited and N₂ migration in the clay inter-layer is likely to be restricted due to geometric constraints. In conclusion, even though higher clay content has a stronger inhibitory effect on CH₄ recovery, increasing the amount of CO₂/N₂ injected into hydrate reservoirs is advantageous for improving hydrate replacement efficiency.

Conclusions

The replacement reaction occurring in clayey sediments containing CH₄ hydrates with a CO₂/N₂ mixture was examined and the replacement in hydrate-bearing sand sediment was analysed for comparison. The following conclusions were drawn:

1. Increased levels of clay in sediments inhibited hydrate formation. This was due to limited hydrate crystal growth in clay inter-layer by water activity reduction caused by geometrical constraints as well as the reduced pore space outside the clay inter-layer which resulted from clay particle expansion.
2. During the initial stage of hydrate replacement, the CH₄ recovery rate in clayey sediment was lower than silica sand but minor hydrate saturation reduced the diffusion barriers of the replacement gas; this improved the recovery rate. Moreover, the clay diminishes the free water content in sediment due to its strong water absorption capacity which reduced the extent of mixed hydrate formation during replacement.
3. Additional analysis of compositional evolution in the hydrate phase indicated that the clay was not conducive to hydrate replacement in latter stages, since CH₄ extraction in the clay inter-layer might be thermodynamically inhibited and gas migration was likely restricted due to geometric constraints of the clay interlayer.
4. It was also found that the CO₂ sequestration capacity of clayey sediment is lower than silica sand and the hydrate reservoirs with high clay content are not beneficial for CO₂ capture and storage by CO₂/N₂ injection. Furthermore, clay has an inhibitory effect on hydrate replacement efficiency but increasing the amount of CO₂/N₂ injected into hydrate reservoirs is advantageous for improving replacement efficiency.

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ORCID iD

Chen Chen https://orcid.org/0000-0003-0101-233X
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