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Self-adaptive gas flow and phase change behaviors during hydrate exploitation by alternate injection of N_2 and CO_2

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ABSTRACT

Since hydrate resources play a part of the stratigraphic framework structure in sediments, establishing a safe and economic method for hydrates exploitation remains the primary challenge to this day. Among the proposed methods, the spontaneous displacement of CH_4 from hydrate cages by CO_2 seems to be a perfect mechanism to address gas production and CO_2 storage, especially in today's strong demand for carbon reduction and replacing clean energy. After extensive lab researches, in the past decade, injecting a mixture of CO_2 and small molecule gas has become a key means to enhance displacement efficiency and has great potential for application. However, there is a lack of in-depth research on gas flow in the reservoir, while the injected gas always passes through low-saturated hydrate areas with high permeability and then occurs gas channel in a short term, finally resulting in the decreases in gas production efficiency and produced gas quality. Therefore, we explored a new injection-production mode of alternate injection of N_2 and CO_2 in order to fully coordinate the advantages of N_2 in enhanced hydrate decomposition and CO_2 in solid storage and heat compensation. These alternate "taking" and "storing" processes perfectly repair the problem of the gas channel, achieving self-regulation effect of CH_4 recovery and CO_2 storage. The 3-D experimental results show that compared to the mixed gas injection, CH_4 recovery is increased by >50% and CO_2 storage is increased by >70%. Additionally, this alternate injection mode presented a better performance in CH_4 concentration of produced gas and showed outstanding N_2 utilization efficiency. Further, we analyzed its self-adaptive gas flow mechanism and proposed an application model of "one injection and multiple production". We look forward to this study accelerating the application of CO_2-CH_4 replacement technology.

1. Introduction

Unlike the conventional oil and gas resources, natural gas hydrates (NGHs) exist in solid form in the reservoirs as a part of the formation skeleton structure, which has a certain cementation effect on sediment particles (Rutqvist and Moridis, 2009; Wang et al., 2018). Therefore, NGHs exploitation process is relatively more complex, generally involving the phase transition process of hydrate decomposition into water and natural gas, which requires absorbing a lot of heat from the environment (Wang et al., 2015a, b;

Sun et al., 2022) and is accompanied by sediment skeleton shrinkage and weakened cementation (Pinkert and Grozic, 2014; Madhusudhan et al., 2019). Typically, the commonly studied methods such as depressurization, heat stimulation and inhibitor injection are all to break or change the phase equilibrium conditions of NGHs to promote the hydrate decomposition and extract natural gas (Yu et al., 2021). Meanwhile, because the submarine hydrate-bearing sediments are mostly composed of muddy silt (Wei et al., 2021), the continuous reduction of hydrates as the binder can lead to problems such as sediment fluidization (sand production) and reservoir shrinkage and collapse (Sun et al., 2016; Sun X. et al., 2019). One important reason for the forced suspension of Japan's first offshore trial production was the risk of well blockage caused by sand production (Yamamoto, 2015). In recent years, the issue of sand production during hydrate mining has

become one of the research focuses. For the latest trial production in China in 2020, it seemed that some mechanical technology could prevent sand from entering the wellbore (Wei et al., 2021), but the sediment migration and accumulation around the well was unfavorable for long-term mining of NGHs. Therefore, compared to other oil and gas resources, geological issues require special attention in the development process of hydrate resources.

In recent years, the technology of CO_2-CH_4 replacement has become a new star in NGHs exploitation. It has the advantages of CH_4 recovery, CO_2 storage, heat balance and formation stability (Yuan et al., 2012; Gambelli et al., 2019). However, the main challenges come from the slow mass transfer after initial hydrate being encapsulated by CO_2 hydrate film at the micro level and the limited CO_2 coverage in the reservoir at the macro level (Stanwix et al., 2018). Therefore, scholars have been committed to research on improving replacement efficiency, with the injection of gas mixture containing CO_2 replacing pure CO_2 being particularly prominent. As shown in Fig. 1, there are two mainstream ideas for NGHs exploitation by gas mixture injection. Park et al. (2006) and Koh et al. (2016) proposed CO_2/N_2 gas (flue gas) as an alternative to enhance replacement efficiency and assumed N_2 could replace CH_4 in small cages, thereby achieving a higher CH_4 recovery ratio. In 2012, the first field test of NGHs exploitation by gas mixture (77% N_2 + 23% CO_2) injection and depressurization was conducted in Alaska Northern Slope of USA, and totally 2.8×10^4 m^3 of natural gas was successfully produced (Schoderbek et al., 2013). However, from the perspective of displacement, this single well operation was inefficient considering that a large amount of injected gas was subsequently produced. Afterwards, Lee's team and Seo's team (Koh et al., 2012; Kang et al., 2014; Lee et al., 2014, 2017, 2020; Mok et al., 2021) in South Korea further optimized the injection rate, well spacing, and gas composition and attempted to reveal the deep mechanism of this enhanced replacement. They calculated that the recovery ratios of CO_2/N_2-CH_4 replacement for hydrates of Type I and Type II could reach 85% and 92%, respectively (Koh et al., 2015; Seo et al., 2016). Since 2013, in response to the issue of the high separation cost of CH_4 and N_2 in the produced gas when using CO_2/N_2 injection, Chen's team (Wang et al., 2017) proposed a new idea of CO_2/H_2-CH_4 replacement, as shown in Fig. 1(b). They cleverly coupled the replacement and CH_4 steam reforming technology, achieving carbon sequestration and H_2 production throughout the entire cycle. Similarly, they also have conducted extensive researches on the optimization of the gas injection-production process (Sun et al., 2018, 2021; Sun Y.F. et al., 2019; Kan et al., 2021; Cao et al., 2023), as well as the related studies on hydrate membrane morphology and thermodynamic behavior (Zhong et al., 2020; Xie et al., 2022). Here the key issue in using CO_2/H_2 mixture is how to

ensure effective recovery of H_2. Overall, although this type of replacement technology is still in the lab research stage, many experimental and numerical simulation results indicate that it has higher CH_4 recovery and mining safety compared to traditional depressurization or heat injection, as well as the pure CO_2 injection, which greatly raises its application potential (Zhong et al., 2020; Kan et al., 2021; Wang et al., 2021; Xie et al., 2022). Especially for the NGHs in the unsealed submarine area, in addition to the ability of CO_2 hydrate to repair reservoirs, the high-pressure gas can also inhibit the infiltration of peripheral water, thus significantly improving the gas-water ratio of production (Sun et al., 2021). The good experimental results have attracted many research institutions to start related research (Zhou et al., 2019; Pan et al., 2020; Li D. et al., 2021; Li S. et al., 2021; Niu et al., 2021).

Compared to the pure CO_2 injection (Xu et al., 2022), the CO_2-containing gas injection seems to make the decomposition and reformation of hydrates during the replacement process more independent. The reduced CH_4 partial pressure in the sediment pores with gas flow stimulates CH_4 hydrate decomposition, while CO_2 with rising concentration forms new hydrates with water (Sun et al., 2021). From this perspective, the replacement efficiency is determined by the gas phase composition and renewal rate in the pores. On one hand, if the injected gas cannot effectively spread to a certain area or displace enough CH_4 there, it can be invalid for CH_4 hydrate decomposition. We previously found that the gas injected could easily form pathways between the gas injection well and production well, leading to a series of problems such as the decrease in CH_4 production rate and CH_4 concentration in produced gas, as well as the increase in injection-production ratio (Sun et al., 2018). Intermittent gas injection was proved to provide more spread time for the gas (Sun Y.F. et al., 2019), but this expansion via free diffusion is a relatively inefficient method. Therefore, when using the gas injection method, how to avoid gas short-circuit behavior and improve the utilization efficiency of the injected gas is a key issue. On the other hand, gas composition is the core factor affecting the equilibrium state in the pores containing hydrates (Wang et al., 2015a, b). CO_2-rich gas injection always provides a relatively higher driving force for hydrate formation (Cao et al., 2023), which will ultimately result in the so-called "shell effect" and insufficient CH_4 recovery. In contrast, although small gases, such as N_2 and H_2, can enhance CH_4 hydrate decomposition, CO_2 hydrate is also difficult to form due to the high hydrate equilibrium pressure needed and low CO_2 partial pressure (Sfaxi et al., 2012). Therefore, to achieve a real replacement process, it is crucial to solve or alleviate the mutual constraints between CH_4 recovery and CO_2 storage, which is the foundation for achieving both high CH_4 recovery and high CO_2 sequestration simultaneously. Liu et al.
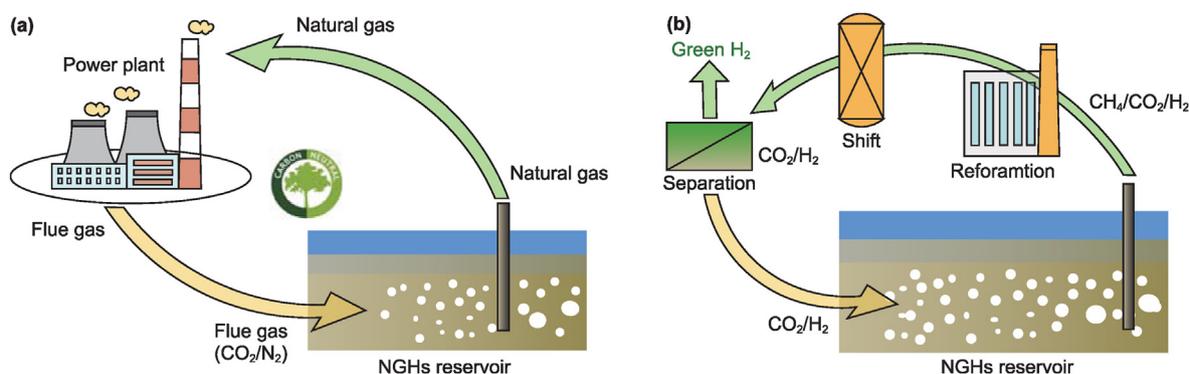

Fig. 1. Two mainstream ideas for NGHs exploitation by gas mixture injection. **(a)** Schematic diagram of flue gas injection and natural gas production from NGHs-bearing sediments. **(b)** Schematic diagram of the combined technology integrating CO_2/H_2 injection and CH_4 production, in situ steam reformation of CH_4, and gas separation of CO_2 and H_2.

(2018) have explored the CO₂ storage as a hydrate in depleted CH_4 hydrate-bearing sediments, which is the most extreme process of first CH_4 hydrate decomposition and then CO_2 hydrate formation. However, it is difficult to determine whether this "late" CO_2 can effectively repair the sediments in situ. In our previous work, we proposed an approach of CO_2/H_2 gas mixture injection with varying composition, which improved the CO_2 storage capacity on the basis of maintaining a high CH_4 recovery ratio. The advantage of this strategy also lies in its ability to keep hydrate saturation in the reservoir within a safe threshold and repair the reservoir before the occurrence of wellbore and formation damages by regulating the gas composition of the injected gas; however, nowadays regulating gas composition is relatively complex and lacks specific standards for regulation. In summary, the bottleneck of the gas injection method is how to improve the gas coverage range and optimize the gas composition.

In this work, we proposed a new gas injection strategy, that is, N_2 and CO_2 are alternately injected into the CH_4 hydrate-bearing sediments. Through this approach, the abilities of small molecule N_2 to enhance hydrate decomposition and CO_2 to repair the formation could be fully used. In addition, considering the common problem of short circuits during gas injection, we speculate that CO_2 would flow along the pores of N_2 flow and block the existing advantageous channels with the CO_2 hydrate formation, thereby forcing subsequent gases into other areas. Therefore, we designed a series of experiments to validate this idea and ultimately gained some new insights. Meanwhile, this control strategy for gas injection may provide inspiration for safe and controllable NGHs development.

2. Experimental section

2.1. Materials and experimental apparatus

In this work, the quartz sands of 20–40 mesh were used as the sediment of the simulated reservoir with a porosity of 0.46. Brine with a mass fraction of 3.33% was prepared with sodium sulfate and the experimental water was deionized. The Beijing Hepu Beifen Gas Industry Corporation (BAPB) provided CH_4 with a purity of 99.95 mol%, and N_2 and CO_2 with a purity of 99.995 mol%.

The experimental apparatus used in this work was indicated in Fig. 2 and the whole setup consisted of a gas injection system, a reaction system, a production system and the monitor and control generated system (MCGS). The injection system was mainly composed of gas cylinders, pressure relief valves and a flow meter to realize the preparation of hydrate sample and the alternate injection operation. As the core of the experimental device, the reaction system took a cylindrical reactor as the significant part, which had an effective volume of 10.6 L (Φ 300 × 150 mm) and a safe operating pressure of 25 MPa. In total, 54 thermocouples with a precision of 0.1 °C were evenly distributed in the reactor, and a constant temperature water tank was used to simulate the ambient temperature. The hydrate replacement behavior, fluid flow, as well as the variations of temperature and pressure discussed in this work all occurred in this reactor. The produced gas was collected by the production system and there was almost no water production in this work. MCGS was used to record the temperature and pressure during the experiment and its recording interval was once per minute. Additionally, the determination of gas composition in the reactor and production gas cylinder was done by a gas chromatograph (Agilent 7890B).

2.2. Experimental procedure

2.2.1. Preparation of hydrate-bearing sediments

The preparation method of the hydrate reservoir was similar to our previous studies (Sun et al., 2018). To ensure the consistency of properties, the preparation of hydrate samples was strictly as follows: (1) Quartz sand pre-cooled to −15 °C and 0.1 °C brine were fully mixed and filled into the reactor with manual compaction in the water tank at 1 °C. The reactor was then sealed and evacuated for 10 min (2) CH_4 gas was injected into the reactor to about 8.6 MPa. Hydrate formation caused the pressure in the reactor to drop, and when the pressure was lower than the experimental set value, adjust the temperature of the water bath to make the temperature in the reactor reach 2 °C. When the temperature and pressure in the reactor were stabilized for more than 6 h, it could be considered that the simulated hydrate reservoir had been prepared. The final properties of the reservoir samples are shown in Table 1 in detail. The detailed calculation method of the saturations of gas, water and hydrate can be referenced in our previous work (Sun et al., 2018).

2.2.2. Gas injection-production procedure

The continuous injection-production mode was adopted in this study (Sun et al., 2018). After the experiment started, N_2 and CO_2 were sequentially injected into the reactor, and one N_2 injection and subsequent one CO_2 injection were recorded as one round. The specific alternate operation design is shown in Table 2. We made Run 1–3 correspond to 1 round, 2 rounds, and 3 rounds of alternate operations, respectively. As a comparison, the continuous injection-production process of CO_2/N_2 mixture was applied in Run 4, and the operation times were adjusted in Run 5. The total duration of each experiment was controlled at 240 min, while the injection rate of N_2, CO_2 or CO_2/N_2 mixture was regulated to 3 SLM. Therefore, the total injection amounts of N_2 and CO_2 in Runs 1–5 were almost the same. During these continuous injection-production processes, the production pressure remained constant at 3.7 MPa. The gas compositions in the reactor and production gas cylinder were measured by a gas chromatograph (Agilent 7890B).

3. Results and discussion

3.1. CH_4 recovery and CO_2 storage

As shown in Fig. 3, we first compared the overall evolutions of CH_4 recovery ratio for Runs 1–5. Here the CH_4 produced included the free gas and release gas from hydrate in the simulated reservoir. Compared to the continuous injection-production mode we had established in the past (Sun et al., 2018), the alternate injection of N_2 and CO_2 mode achieved a higher CH_4 recovery ratio. Under the condition of this study, the final CH_4 recovery ratio increased from 43% to 62%–72% at 240 min, with the growth ratio of 44%–67.5%. It should be emphasized again that the total amount of N_2 and CO_2 used in the five Runs remained basically the same, indicating that the injected gas had higher efficiency in enhancing CH_4 recovery, which is very important to practical application. We believe that this enhancement effect arose from the better utilization of the functions of N_2 and CO_2. Due to the extremely high pressure (~37 MPa at 2.1 °C) required for N_2 to form hydrate (Yi et al., 2019), N_2 injection could generate a significant driving force for CH_4 hydrate decomposition after displacing pore CH_4 gas, thus leading to intense hydrate decomposition. Yet the local overpressure caused
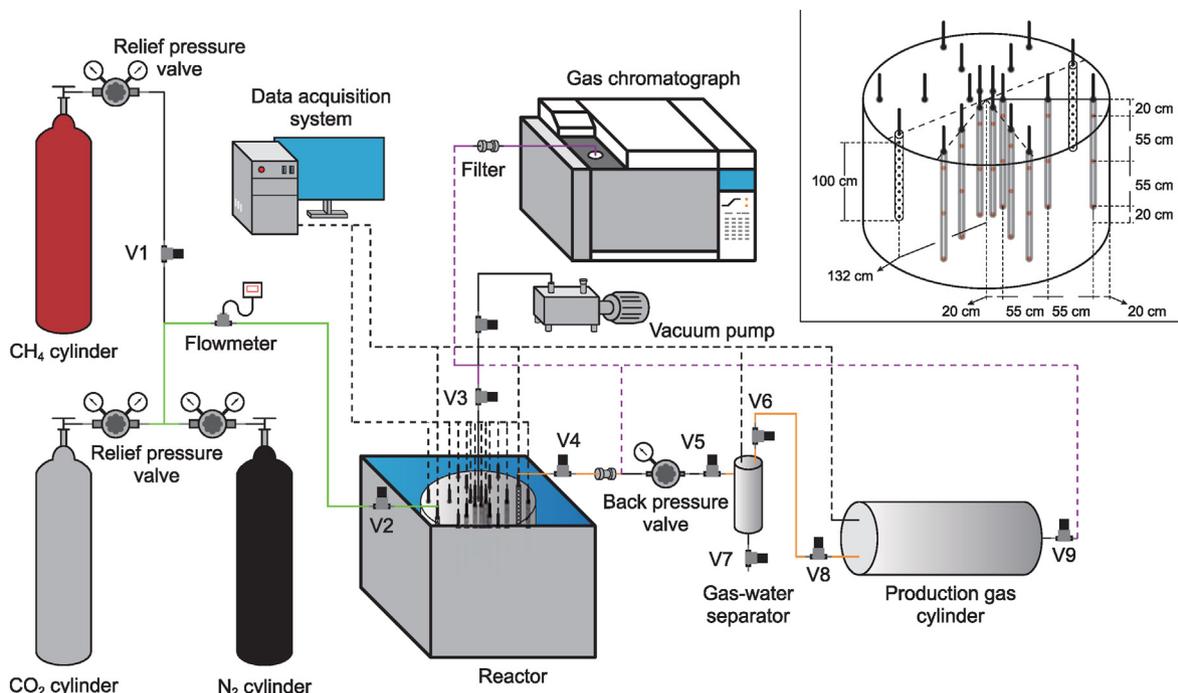
Fig. 2. Schematic diagram of experimental apparatus.

Table 1
Properties of prepared CH_4 hydrate sediments for Runs 1−5.

Run	1	2	3	4	5
Quartz sand, mesh	20−40	20−40	20−40	20−40	20−40
Temperature[a], °C	2.1	2.1	2.0	2.1	2.0
Pressure[b], MPa	3.655	3.650	3.614	3.653	3.617
Hydrate saturation, %	24.61	23.47	23.37	23.55	23.87
Water saturation, %	23.47	24.71	24.79	24.65	24.39

[a] Average temperature after hydrate formation was complete.
[b] Average pressure during the gas injection-production stage.

by CH_4 release could accelerate the flow and production of CH_4. When CO_2 was injected, the local high CO_2 concentration provided sufficient driving force for CO_2 hydrate reformation, while releasing a large amount of heat to fill the temperature drop during N_2 injection. On the other hand, the phase equilibrium pressure corresponding to the gas mixture used in Run 4 was close to the reservoir pressure, and CH_4 hydrate decomposition and CO_2 hydrate formation may occur simultaneously during gas injection. However, the CO_2-CH_4 hydrate shell formed in the early stage was undoubtedly an obstacle to deep displacement, so the corresponding gas production efficiency was relatively low.

Based on this step-by-step synergistic effect of N_2 injection and CO_2 injection, the storage capacity of CO_2 has also been improved compared to the continuous CO_2/N_2 mixture injection. As shown in Fig. 4, under the condition of this study, the final CO_2 sequestration ratio increased from 40% to 66%−83% at 240 min, with the growth ratio of 65.0%−107.5%. After N_2 injection for a period of time, CO_2 sequestration ratio could present a rapid linear increase once again. The primary reason was that pure CO_2 could provide a greater driving force for CO_2 hydrate formation. In addition, we suggested that CO_2 tended to enter the main flow channels established during N_2 injection, which contained more free water and was at a relatively lower temperature, providing a favorable environment for the growth of CO_2 hydrates. In our experiment, we also attempted to block these short-circuited channels through the generation of CO_2 hydrates, so that the subsequent injected gas could spread to a wider area. But unfortunately, when we tried to further optimize with higher frequency alternating operations, the results showed that increasing the number of alternating rounds would lead to a light decrease in both CH_4 production and CO_2 sequestration. Intuitively, the premature CO_2 injected hinders the subsequent CH_4 recovery to a certain extent, and the N_2 entering the reservoir subsequently brings out a portion of the unsettled CO_2 in the reservoir. Nevertheless, this alternating gas injection mode still
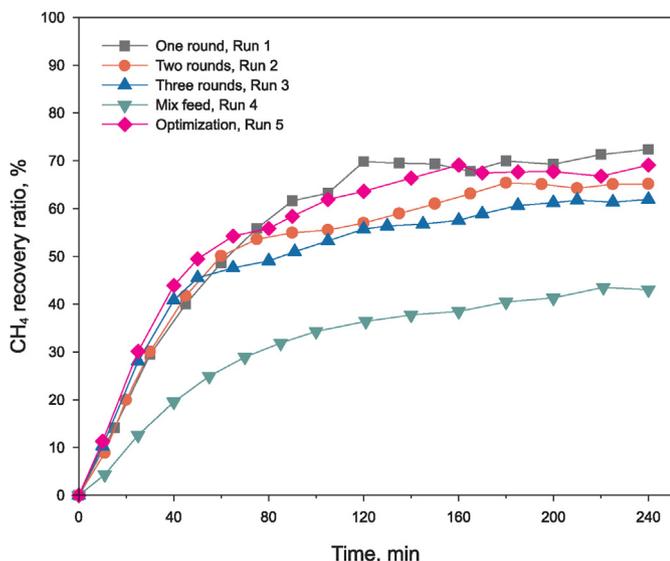
Table 2
Operation of gas injection for Runs 1−5.

Run	Alternate injection of N_2 and CO_2		
	Round number	Duration of each round, min	Gas injection rate, L/min
1	1	120 (N_2) + 120 (CO_2)	3
2	2	60 (N_2) + 60 (CO_2)	3
3	3	40 (N_2) + 40 (CO_2)	3
4	/	240 (N_2/CO_2)	3
5	2	40 (N_2) + 40 (CO_2) in Round 1 and 80 (N_2) + 80 (CO_2) in round 2	3

Fig. 3. Performance of CH_4 recovery for Runs 1–5. The solid and dashed lines represent the processes of N_2 injection and CO_2 injection, respectively.
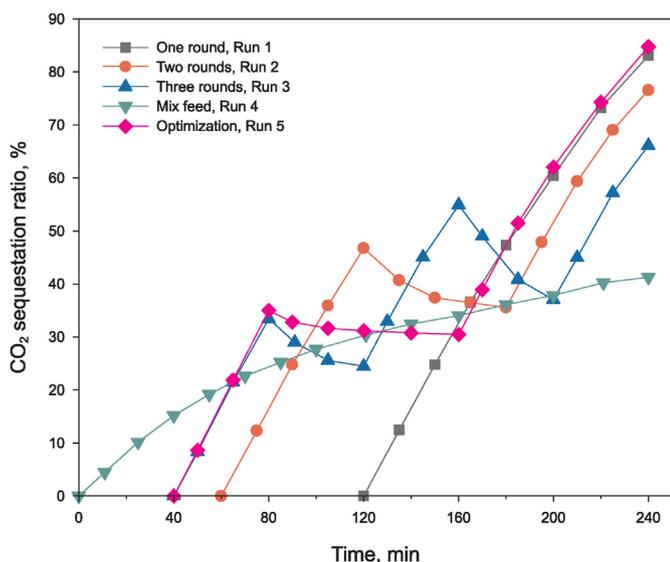

Fig. 4. Performance of CO_2 sequestration for Runs 1–5. The solid and dashed lines represent nitrogen and carbon dioxide injection stages respectively.

achieved a win-win goal of high CH_4 recovery and high CO_2 storage on the original basis, and of course, there is still a large room for improvement in gas control.

On the other hand, a portion of N_2 and CO_2 was also produced along with CH_4, which affected the quality of the produced gas. Therefore, we further analyzed the changes in CH_4 concentration in the collector. As shown in Fig. 5, the CH_4 concentration of all runs continued to decrease. By comparison, the final cumulative CH_4 concentrations were 35%–45%, which were larger than that obtained by injecting N_2/CO_2 mixture directly in Run 4 (27%). This effect could undoubtedly reduce the subsequent cost of gas separation.
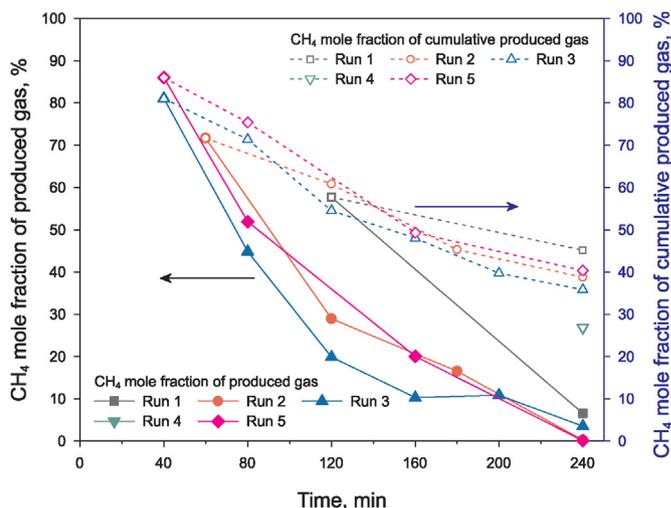

Fig. 5. CH_4 mole concentrations of produced gas in each round and their accumulation in the collector.

3.2. Gas flow and temperature response

In this work, we further confirmed the flow pattern of N_2 and CO_2 in the reservoir through the spatiotemporal evolution characteristics of temperature field. Here, the most representative result of Run 2 was selected for illustration, as shown in Fig. 6. When N_2 was injected for 11 min, temperatures at the bottom region of the simulated reservoir decreased to 0–1 °C, and there was a significant temperature difference compared to the middle and upper regions. Clearly, this was due to the rapid decomposition of CH_4 hydrate under the action of N_2, indicating that the injected N_2 in round 1 first flowed through the reservoir bottom region. In the following time, the low-temperature region kept moving upward, which meant that more N_2 gradually spread upward and stimulated the hydrate decomposition in the corresponding regions. Theoretically, N_2 flow was dominated by local regions with high permeability, and this difference in N_2 flux in different regions and relatively slow gas diffusion between these regions led to the hydrate decomposition sequence. Overall, before switching to CO_2 injection at 60 min, the CH_4 recovery ratio was close to 50%, and the hydrate decomposition regions were mainly concentrated in the bottom layer and the central parts of the middle and upper layers of the reservoir. Then, at the 15th minute after CO_2 injection, there was a significant temperature rise in the bottom region of the reservoir, with a contour similar to the temperature drop region during N_2 injection at 11 min, but slightly tilted towards the injection well. During this process, the sensible heat brought in by CO_2 injection could not cause this degree of temperature rise, so it was caused by a large amount of heat released from hydrate reformation. At the end of the first round of CO_2 injection, the temperature rise region also covers the middle and upper regions. At this stage, less than 0.3 mol of CO_2 was produced, only accounting for 6% of the injection amount. Although it was difficult to calculate the proportion of CO_2 present in the form of solid hydrates, we found that CO_2 did not experience serious leakage due to local short circuits like N_2. On the contrary, CO_2 hydrates formation reduced reservoir permeability, which promoted CO_2 diffusion around the injection well. Meanwhile, the sealing effect of CO_2 hydrates formation also affected the
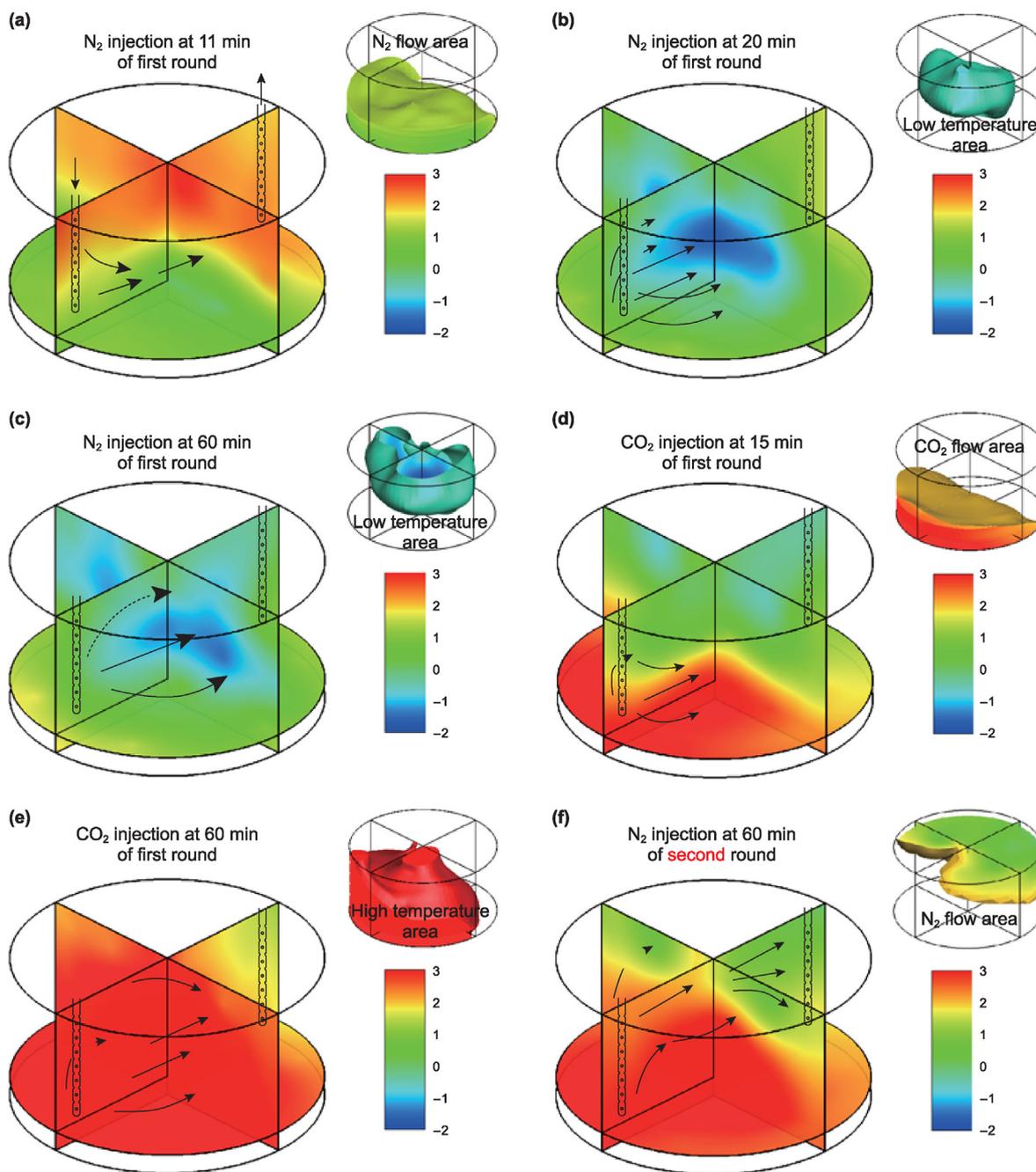
Fig. 6. The spatiotemporal evolution of reservoir temperatures in Run 2. The arrows describe the main regions of gas flow based on the temperature analysis. The contours of the regions with relatively low temperature or high temperature are separately outlined in the upper right corner of each graph, which represent the main regions of N₂ or CO₂ flow.

flow of the injected gas in round 2. From the temperature distribution after the second N₂ injection, the low-temperature areas were concentrated at the upper layer and close to the side of the production well. That is, after a round of alternating injection of N₂ and CO₂, the dominant channels for gas flow in the simulated reservoir moved from the bottom to the top, mainly because the hydrates reformation changed the local permeability of the reservoir.

Based on the above analysis, we think that this alternate gas injection mode has an idealized characteristic, that is, CO₂ hydrate can block the dominant channel of gas flow in the previous N₂ injection stage, thereby promoting the subsequent injection of N₂ to spread to other regions. As shown in Fig. 7, we describe the fluid flow and hydrate evolution during alternate gas injection based on the above understanding. N₂ is like an excavator that digs new channels for CO₂ storage, while CO₂ is the reinforcement and new resident in these channels in the form of CO₂ hydrate. In theory, their synergism may effectively prevent a serious decline in gas production efficiency when gas shortcut occurs. Therefore, compared to continuous injection of gas mixture, this method
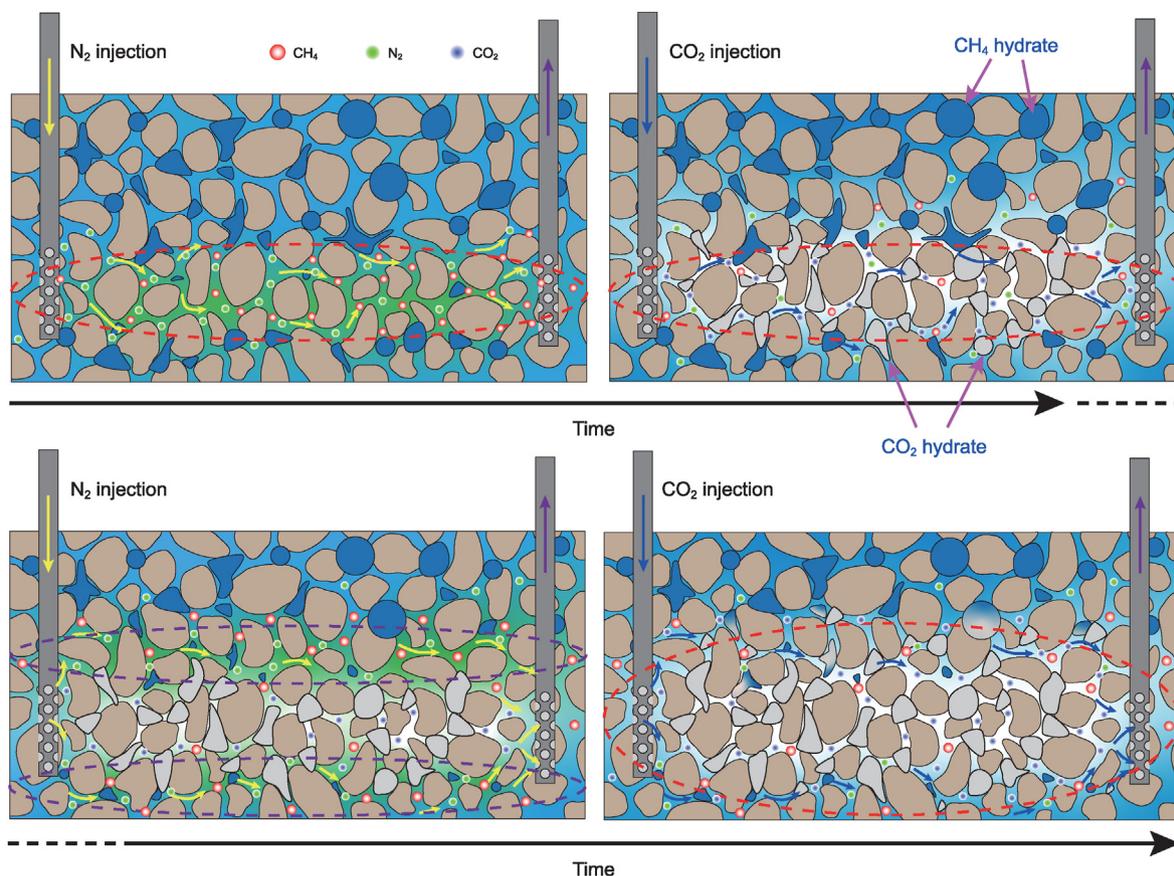
Fig. 7. The illustration of gas flow and hydrate evolution.

essentially changes the migration routes of injected gases, thereby expanding the mining range. In addition, compared to the semi-continuous injection-production mode that utilized gas diffusion (Sun Y.F. et al., 2019), this improved method applied to continuous injection-production mode is undoubtedly more efficient. However, the high-frequency switch of injected gas did not result in higher CH_4 recovery in our work, and we speculated that this was mainly due to the insufficient simulation volume in this work. N_2 can infiltrate most of the reservoir extensively during the first injection, but in numerical simulations for an actual reservoir (Kan et al., 2021), the injected gas often flows from a narrow channel between the injection well and production well. In such a vast environment, this forced change in gas flow trajectory may become a key means to improve gas utilization efficiency, thereby increasing CH_4 concentration and gas injection-production ratio.

For the actual reservoir, the mode of single-well injection and multi-well production seems more suitable for practical application scenario for the lower injection costs, as shown in Fig. 8. The gas enters the reservoir through the central injection well and flows around, and the differences in flowability in different directions may cause the gas to lean more towards a particular production well, or even cause a gas short-cut. As the degree of hydrate decomposition increases, this bias may become more severe. If CO_2 is injected after N_2 breakthrough and rapid production in a certain line, it can be able to block the gas channel by forming hydrates

based on this experimental result. After that, the next N_2 injection can spread in other directions, accelerating the gas production efficiency of other produced wells. For the production well completed high-speed gas recovery, it can be used for both CH_4 recovery or for CO_2 sequestration according to the mining situation. Therefore, we expect that when gas injection is used for hydrate exploitation, this method of alternating injection of N_2 and CO_2 can be applied to solve the problem of injection gas bias.

3.3. Formation remediation

NGHs is one of the components of the hydrate-bearing reservoir matrix (Song et al., 2014; Zhu et al., 2019), and hydrate saturation is a significant parameter controlling the geomechanical strength of the sediments (Yoneda et al., 2015; Zhang et al., 2016). Some studies suggest that the cementation of hydrate plays an important role in maintaining the mechanical strength of sedimentary layers, and some mechanical properties, such as bulk modulus and shear cohesion, always increase linearly with hydrate saturation (Rutqvist and Moridis, 2009; Zhang et al., 2017), which also explains the reasons for sediments settlement and formation shear failure during conventional depressurization and heat/inhibitor investigation (Li et al., 2016). It is obvious that maintaining the hydrate saturation has a positive effect on maintaining the cementation and the shrinkage of solid volume, reducing sediment
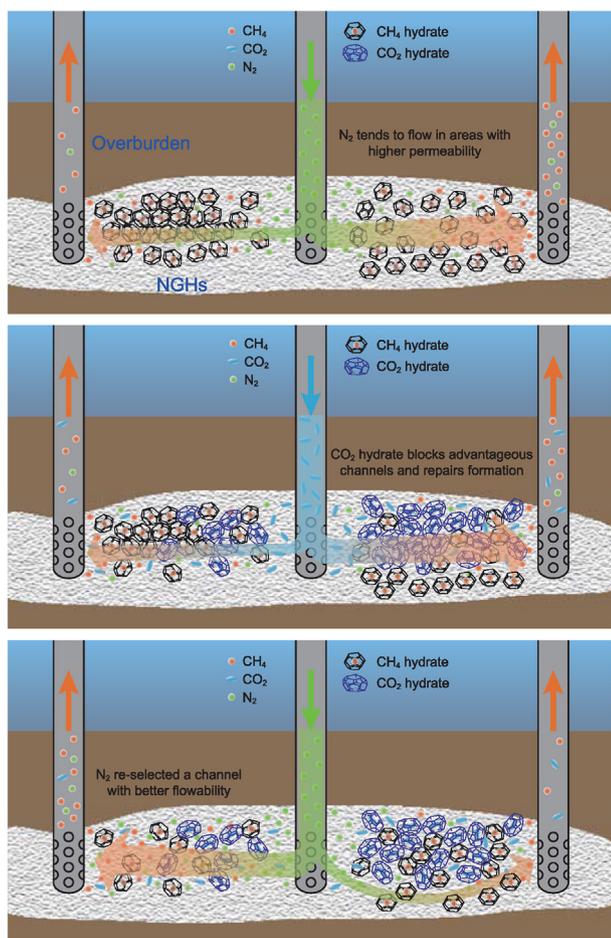
Fig. 8. Application scenario: single-well injection and multi-well production.

of 75%. The direct consequence of this excessive hydrate decomposition was a significant shrinkage of nearly 950 mL of the solid phase volume for the formation, corresponding to the solid shrinkage ratio of 14%. Although CO_2 injection brought the hydrate saturation back to its initial level in our experiment, excessive formation deformation was usually irreparable during actual mining processes. At this point, increasing the frequency of gas alternation demonstrated an advantage in repairing hydrate-bearing sediments earlier than formation damage. For the two and three rounds of alternating injection (Runs 2 and 3), the hydrate saturations after the first round of N_2 injection reached their minimum values of 9.7% and 12.5%, respectively. The corresponding saturation variation amplitude decreased to 58.3% and 46.0%, respectively. Due to the maintenance of hydrate saturation, the maximum solid shrinkage volume of the reservoir also decreased to 524–667 mL, and the shrinkage ratios were 9.8% and 7.7%. Delightfully, the reservoir was almost restored to its initial level at the end of each experiment, manifested in the recovery of hydrate saturation and formation volume. Although it was difficult for our reactor with fixed internal space to reflect the actual deformation of the reservoir, the results still largely demonstrated the potential of this method in formation remediation. We can even ensure the amplitude of formation deformation by adjusting the frequency of N_2 and CO_2 injection.

4. Conclusions

In this work, to enhance CH_4 hydrate mining and in-situ CO_2 storage in the form of solid hydrate, we proposed a new injection-production mode of alternate injection of N_2 and CO_2. The performances of alternate injection and mixed injection of N_2/CO_2 were systematically compared in CH_4 recovery, CO_2 storage and formation stability. Compared with the continuous CO_2/N_2 mixture injection, the results show that this alternate injection mode could fully utilize the respective capabilities of N_2 and CO_2, thereby achieving a higher CH_4 recovery ratio from 40% to 60%–70% and CO_2 storage ratio from 40% to 65%–85%. Due to the influence of confined space, increasing the number of alternating rounds resulted in a slight decrease in CH_4 production and CO_2 sequestration. Nevertheless, this alternate mode achieved the win-win goal of relatively high CH_4 recovery and high CO_2 storage to a certain extent. More importantly, we noticed that the alternate injection mode had an idealized feature, that is, CO_2 always entered the dominant gas channel in the previous N_2 injection round and formed hydrate to change the local permeability of the reservoir. This showed good performance in repairing reservoir stability; meanwhile, increasing the number of alternate rounds could reduce the maximum volumetric deformation of the formation from 14.08% to 7.71%. Interestingly, this repair ability could promote the diffusion of subsequent N_2 injection to other undeveloped areas and in turn produce a series of enhancement effects. Based on this characteristic, we have envisioned an application scenario of single-well injection and multi-well production. To sum up, the injection-production mode of alternate injection of N_2 and CO_2 preliminary breaks the mutual constraints between CH_4 recovery and CO_2 storage to a certain extent. It provides a new idea for the safe and efficient development of gas hydrates.

migration and formation deformation. In this work, the formation of CO_2 hydrate was also a means of reservoir remediation after the decomposition of CH_4 hydrate, so we further analyzed the changes in hydrate saturation and solid volume to reflect the reservoir remediation ability upon gas injection control, as shown in Fig. 9. The two outcomes were directly related, that is, the manifestation of the hydrate saturation change was the contraction $(-)$ and expansion $(+)$ of the solid volume of the formation. This net change of solid volume here was not directly equivalent to the degree of formation deformation, but they must be a positive correlation. It was worth noting that although the indexes such as CH_4 recovery and CO_2 storage of Run 4 were mediocre, it was outstanding in maintaining the hydrate saturation with a maximum change amplitude of $+15.04$. Its specific manifestation is that the final expansion ratio of formation volume was $+2.53\%$ after a small initial volume shrinkage of -1.59%, so we called it a non-destructive mining technique. However, for actual mining, achieving high efficiency while ensuring mining safety is the key point. By comparison, for the single round alternating injection-production (Run 1) getting the best performance on CH_4 recovery and CO_2 storage, the hydrate saturation continuously decreased to ~7% during N_2 injection, corresponding to a saturation change ratio
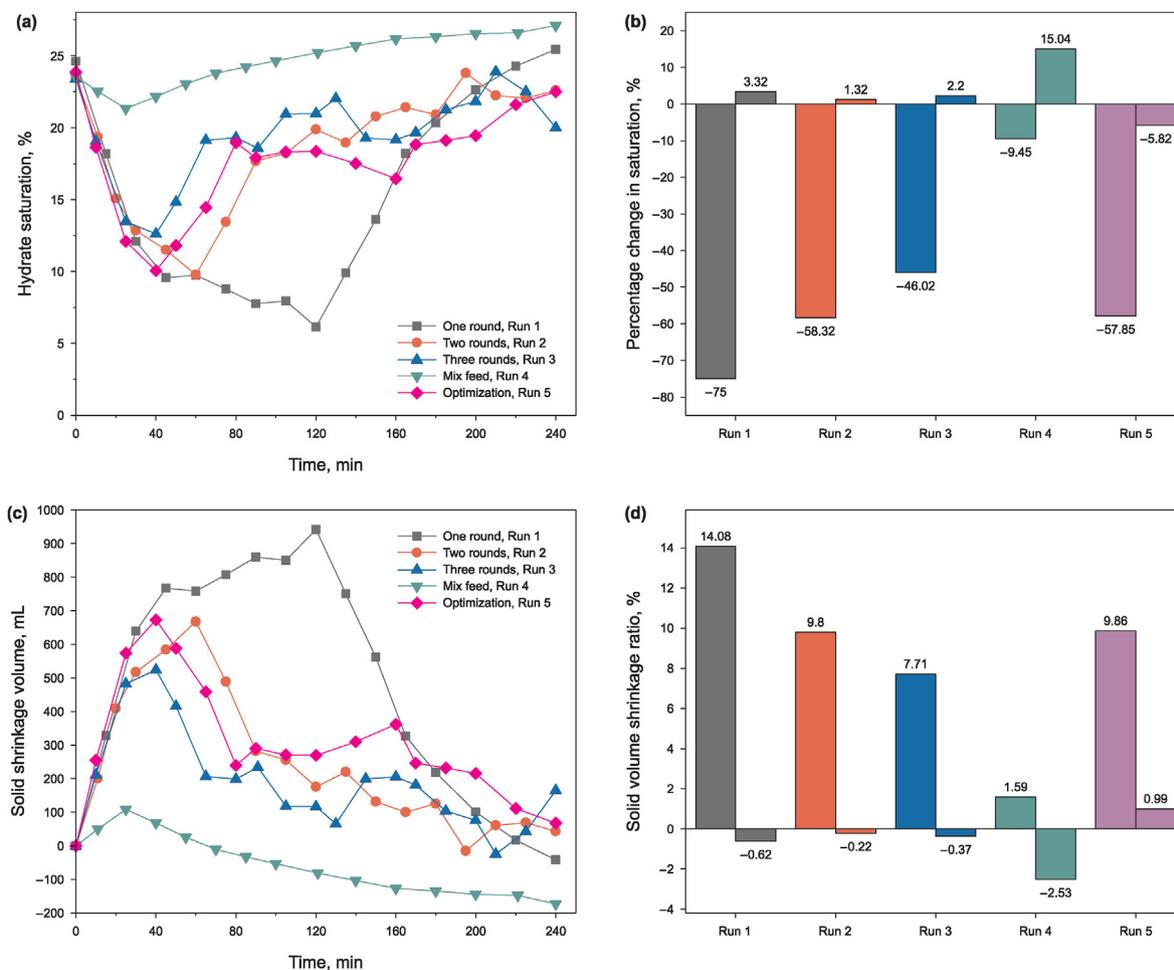
Fig. 9. Comprehensive performance of formation remediation for Runs 1–5. The solid and dashed lines represent the injection stages N_2 and CO_2, respectively. **(a)** Hydrate saturation changes with time due to the unequal CH_4 hydrate decomposition and CO_2 hydrate formation. **(b)** Formation remediation abilities for the different gas injection strategies. **(c)** Variation of solid shrinkage volume with time. **(d)** The maximum and minimum solid shrinkage volume ratio.

CRediT authorship contribution statement

Bo-Jian Cao: Investigation, Writing – original draft. **Yi-Fei Sun:** Funding acquisition, Investigation, Supervision, Writing – review & editing, Methodology. **Hong-Nan Chen:** Investigation. **Jin-Rong Zhong:** Validation. **Ming-Long Wang:** Investigation. **Ming Wang:** Investigation. **Chang-Yu Sun:** Resources, Supervision. **Guang-Jin Chen:** Funding acquisition, Resources, Supervision.

Declaration of competing interest

The authors declare there are no conflicts of interest.

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