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Full Length Article

Critical parameters influencing mixed CH$_4$/CO$_2$ hydrates dissociation during multistep depressurization

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A R T I C L E   I N F O

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A B S T R A C T

Early studies show that multistep depressurization of CH$_4$/CO$_2$ mixed hydrates generates additional CH$_4$ while storing CO$_2$ in hydrate-bearing sediments. There are many critical factors that could affect the production and storage efficiency of this method. However, it is unclear how to achieve high efficiency in both CH$_4$ production and CO$_2$ storage by controlling these critical parameters. In this experimental work, we identified three critical parameters (CH$_4$/CO$_2$ ratio in mixed hydrates, residual water saturation ($S_{rw}$), and shut-in period) and investigated their effects on production parameters (CH$_4$ molar fraction in the gas phase (X$_{CH_4}$), CH$_4$ recovery percentage (RCH$_4$), and CO$_2$ storage ratio (SCO$_2$)). Experiments were performed on sandstone cores using a high-pressure core flooding system equipped with pressure, temperature, and electrical resistivity measurements. Gas composition was analyzed by gas chromatography. The results showed that the optimal production parameters were determined at low $S_{rw}$ of 43.7–47.4% and higher CH$_4$/CO$_2$ ratio of 1.76–2.06 in CH$_4$/CO$_2$ mixed hydrates. The optimized values were obtained at the equilibrium pressure of CH$_4$/CO$_2$ hydrate system at a specific reservoir temperature without water production during pressure release. In addition, the period between two pressure releases had a direct effect on the production and storage performances, and the most efficient production and storage was measured at 4-hour shut-in period of pressure release. The measured percent changes in normalized resistivity ($\Delta NR_2$) were dependent on $S_{rw}$ and shut-in period. Positive increase of $\Delta NR_2$ indicated increased hydrate saturation or improved water gas distribution in the sediment during multistep depressurization. The results demonstrated the importance of three critical parameters in designing an effective production and storage scheme after CO$_2$ injection into CH$_4$ hydrates.

1. Introduction

Natural gas hydrates (NGHs) are solid-crystalline compounds consisting of host water molecules and gas molecules (CH$_4$, C$_2$H$_6$, CO$_2$ and H$_2$). Cage-like structures are formed by hydrogen-bonded water with gas molecules stabilizing inside under low temperature and high pressure [1]. NGHs are widely recognized as promising clean hydrocarbon energy for abundant reserves in marine sediments (0–110 m below seabed) and permafrost regions (130–500 m below underground) [2,3]. The total amount of global hydrate-bonded CH$_4$ reserve is reported to be within the scale of 10$^{15}$-10$^{19}$ standard cubic meters (ST m$^3$), exceeding the known amount of conventional oil and gas resources [4–6]. Furthermore, noted that CH$_4$ is a kind of high-density energy with the combustion heat of approximately 890 kJ/mol and therefore regarded as one of the most excellent alternative energy sources in the 21st century [7]. Due to the vast reserve and high energy density of NGHs, an increasing number of researches have been conducted on NGHs exploitation in recent years.

Exploitation methods refer to those that recover natural gas (the majority are CH$_4$) from NGHs within reservoir, which mainly include depressurization [8,9], thermal stimulation [10,11], inhibitor injection [12,13] and CH$_4$-CO$_2$ swapping [14,15]. The depressurization method reduces the reservoir pressure, thus drawing thermodynamic conditions out of the hydrate stability zone. This thermodynamic instability causes NGHs to decompose and produce CH$_4$ and water. However, endothermic dissociation of NGHs via rapid pressure drop can cause partial ice or hydrate reformation and then stop CH$_4$ production. Thermal stimulation is also a thermodynamic method that disrupts phase equilibrium conditions of NGHs. However, large heat loss makes it uneconomical, and more effective heating techniques need to be investigated. Inhibitor injection can moderate the equilibrium of NGHs and thus inducing hydrate dissociation. However, this exploitation method is restricted in

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application because of high cost and environmental pollution. Compared to other methods, CH₄-CO₂ swapping is an energy efficient and non-hazardous method, and can achieve a win-win situation of simultaneous CH₄ recovery and CO₂ sequestration [16,17]. The principle is that CO₂ can form hydrate under more moderate thermodynamic conditions, replacing CH₄ in existing hydrate cages by forming new CO₂ hydrates [18]. This kind of swapping process between CH₄ and CO₂ without violent destruction of the hydrate structure can stabilize the stratum that probably collapses during the NGH exploitation process through depressurization and thermal stimulation [19].

Among these exploitation methods, depressurization is demonstrated to be the most commercial method and has been used to develop NGHs in several field tests [20–23]. Rapid/direct depressurization technique tends to trigger the formation of ice or secondary hydrates, which blocks fluid flow channels and reduces gas production. To avoid these problematic issues, a slow depressurization technique with well-controlled pressure drop rate or gradient pressure drop was designed, achieving efficient and continuous gas production. Fig. 1 presents an overview of slow depressurization-based CH₄ production from CH₄ hydrate and CH₄/CO₂ mixed hydrate together with its technical concerns, which affect factors and efficiency parameters. As shown in Fig. 1, this technique can be mainly classified into constant-rate depressurization [24,25], cyclic depressurization [26,27] and stepwise depressurization [28–30]. These well-controlled slow depressurization may simultaneously reduce water production through gas/water migration and avoid stratum instability without sand production. The key parameters that affect gas production efficiencies include operating factors (depressurization pressure/temperature and shut-in period/frequency) and properties of the in situ reservoir (water/hydrate saturation and porous media) [31]. Another aspect that affects slow depressurization-based gas production is to combine it with other exploitation methods, such as depressurization combined with thermal stimulation/heating, with chemical inhibitor injection, and with CO₂ gas injection.

The single CH₄-CO₂ swapping method cannot meet the commercial NGH exploitation requirements due to the low CH₄ gas recovery efficiency [32]. The main reason for this low gas production is mass transfer caused by the formation of CO₂ hydrate films around CH₄ hydrates [33–35]. And the hydrate films also reduce gas molecules transport and CO₂ concentration around the surface of CH₄ hydrate by decreasing relative gas permeability. To overcome the drawbacks of CH₄-CO₂ swapping, the combination of swapping with the methods mentioned above have been studied [36–38], one of which is CH₄-CO₂ swapping combined with depressurization. This kind of combination method has been proven to be effective in the production testing of the Inik Sikumi field, where CO₂-rich gas injection and depressurization were performed accordingly, with a total of 24,410 STm³ CH₄ recovered from the hydrate-containing reservoir during a whole production period of 30 days [39]. The exploitation patterns of CH₄-CO₂ swapping combined with depressurization have also been reported in many experimental investigations. Zhao et al. revealed that CH₄-CO₂ swapping could be divided into two stages, and depressurization could induce partial melting of CH₄ hydrates and create pathways for CO₂ penetration in the second stage [36]. Chen et al. verified the feasibility of enhancing CH₄ recovery and CO₂ storage simultaneously with the assistance of depressurization operation. These two evaluation parameters of performance were integrated and indicated by the single parameter of CO₂ utilization efficiency. The results showed that both outlet and inlet pressures greatly affected CO₂ efficiency [40]. Yang et al. investigated flue gas injection into gas hydrate reservoir with further depressurization to generate CH₄-rich gas (up to 90 mol%) while storing CO₂ efficiently into hydrate (up to 80 mol%) [41,42]. In another study, Heydari and Peyvandi performed CH₄-CO₂ swapping followed by pressure reduction with the addition of rhamnolipid. The result of the CH₄ mole fraction was around 52 mol% in the gas phase, with the CH₄ recovery efficiency of 18.02% at the ending point [43]. These studies, however, paid less attention to the simultaneous maximization of CH₄ recovery and CO₂ storage. To do this, strategies can be decided from thermodynamic consideration. Goel [44] proved that the partial pressure of CH₄ increased with the decomposition of CH₄ hydrates, and a small amount of the decomposed CH₄ gas could reform hydrates when the partial pressure of CH₄ reached the phase equilibrium of the mixed CH₄/CO₂ hydrates. Nevertheless, the ideal operation pressure is that between the equilibrium of CH₄ hydrates and CO₂ hydrates to release as much as CH₄ while storing as much as CO₂ from the perspective of thermodynamic stability [45,46]. It is known that hydrate loss would increase pore pressure and weaken soil particles link, triggering instability of sediments. CH₄-CO₂ swapping can address this concern by storing CO₂ in the form of hydrates, and CO₂ hydrate-bearing sediments are stiffer than CH₄ hydrate-bearing sediments [47]. It is anticipated that further depressurization on

Fig. 1. Slow depressurization-based method for hydrate exploitation from CH₄ hydrate and CH₄/CO₂ mixed hydrate with its technical concerns, affecting factors, and efficiency parameters.
hydrates sample would cause a redistribution of CH$_4$/CO$_2$ in hydrate and change of hydrate volume accordingly. Thus, it is needed to quantify the volume change of CH$_4$/CO$_2$ hydrates to consider potential stiffness failure of hydrate-bearing sediments because too much hydrate loss may loosen cementation or skeleton of sediment [48]. From the perspective of electrical properties, NGHs are electric insulator and electrical resistance as one of the crucial electrical properties, can represent hydrate saturation in hydrate-bearing sediment system. It is proved that electrical resistance increased with hydrate formation and decreased with hydrate decomposition [49,50]. And it could be more reasonable to evaluate whether the stability of hydrate-bearing sediment was improved or not by electrical resistivity instead of hydrate volume change, because electrical resistivity was mainly affected by fluid saturation, types of guest molecules and total hydrate volume [51]. Although the study showed that pure CO$_2$ hydrates have lower resistance than pure CH$_4$ hydrates [52], the resistivity behavior of CH$_4$-rich and CO$_2$-rich mixed hydrates during depressurization is still not well understood.

In our preliminary investigation, depressurization combined with CH$_4$-CO$_2$ swapping was designed, i.e. replacing the residual CH$_4$ within the hydrate cage with CO$_2$ after the operation of pressure reduction [33]. However, water production and hydrate reformation problems occurred when employing this combination method to exploit NGHs, though CH$_4$ recovery efficiency was enhanced. In another experimental study, CH$_4$-CO$_2$ swapping combined with three-stage gradient depressurization was proposed to address the problem of mass transfer during CH$_4$-CO$_2$ swapping exploitation of NGHs [53]. According to the phase equilibrium difference between CH$_4$ hydrates and CO$_2$ hydrates, depressurization after CH$_4$-CO$_2$ swapping would enhance CH$_4$ production and CO$_2$ storage within a hydrate-bearing reservoir at the pressure below equilibrium conditions for CH$_4$ hydrates as well as above that for CO$_2$ hydrates. This assumption has been demonstrated by our recent studies, in which CH$_4$-CO$_2$ mixed hydrates dissociation induced by controlled multistep depressurization can increase both CH$_4$ recovery and CO$_2$ storage more efficiently [45,46,54]. However, different influencing factors on CH$_4$ recovery and CO$_2$ storage performance have not been comprehensively analyzed thus far. More importantly, unknowns on the optimization of both CH$_4$ recovery and CO$_2$ storage still exist.

This study extended investigation on CH$_4$-CO$_2$ swapping combined with depressurization by experimentally studying CH$_4$-CO$_2$ mixed hydrate dissociation through controlled multistep depressurization. Assumptions were preset that CH$_4$-CO$_2$ swapping for NGHs exploitation has already occurred and CH$_4$/CO$_2$ mixed hydrate have formed before multistep depressurization. Influencing factors such as hydrate composition, residual water saturation ($S_{rw}$) and shut-in period during multistep depressurization were explored. Characteristics of CH$_4$ mole fraction in gas phase ($X_{CH_4}$) were monitored, CH$_4$ recovery percent ($R_{CH_4}$) and CO$_2$ storage ratio ($S_{CO_2}$) during multistep depressurization were calculated in different operation conditions. Additionally, resistivity variation was studied to evaluate the effect of multistep depressurization on mixed hydrates saturation development.

2. Experimental methodology

2.1. Materials and apparatus

The mixed gas containing CH$_4$ (70 mol%) and CO$_2$ (30 mol%) and
the other mixed gas of CH₄ (30 mol%) and CO₂ (70 mol%) were purchased from Air Liquide (Denmark). The deionized water was produced in the laboratory. A schematic of the experimental apparatus of mixed hydrate formation and exploitation is presented in Fig. 2. The significant parts of the apparatus were the core holder with a maximum working pressure of 200 bar. The prepared sandstone sample was wrapped by a rubber sleeve (Fig. 3) and placed at center of the core holder, sealed by an inlet and outlet cap, respectively. The core holder had a temperature couple at the outlet and two differential pressure indicators. Two alligator clips measuring the electrical resistance were placed at the inlet and outlet, respectively. Our previous work can refer to more information on electrical resistance measurement [45, 55]. Gas cylinders injected different gases into sandstone samples through relief valves, control valves and supply lines. A high precision syringe pump (Teledyne ISCO) provided the sandstone sample with confining pressure by injecting deionized water to surround the rubber sleeve. A cooling bath controlled the system temperature by circulating antifreeze at the cooling jacket. Temperatures, pressures and electrical resistances were recorded by the data collector (Agilent 34972A, Agilent Tech.) at 10 s period. The gas samples were collected at the outlet of the core holder and analyzed by the in-line gas chromatograph (Micro-GC 490).

2.2. Core sample preparation

The preparation of the core sample included two parts: cleaning and saturating. The sandstone core was first washed with organic solvent (methanol and toluene) and then dried in an oven at 100 °C for 24 h. The dry weight of the sandstone core was subsequently recorded. For the core sample of low saturation, the dry sandstone core was immersed with ultrapure water in a beaker for 24 h. For the core sample of high saturation, the immersed sandstone core in a beaker was vacuumed simultaneously for 48 h, ensuring that the pores within the sandstone core were sufficiently degassed and thus saturated with water adequately. A prepared sandstone sample can be seen in Fig. 3. Core samples of different saturations using the preparation method above were obtained and summarized in Table 1.

2.3. Experimental procedure

2.3.1. Hydrate formation

The hydrate formation process in this study is consistent with our previous work [45]. The water-saturated core sample was wrapped tightly with a rubber sleeve and then packed into the core holder, with the inlet cap and the outlet cap pressing inwards. After connected the core holder with tubes and valves, the cooling bath was set to the desired temperature value. The core holder was flushed with target gas at 5 bar for 2 min to ensure the absence of air. Pressurization operation followed the following two steps: firstly, the desired confining pressure was achieved by water injection through ISCO pump; secondly, mixed gas was injected continually with the core pressure around 30 bar less than confining pressure. These two procedures were repeated for multiple injections until the confining pressure of 110 bar and core pressure of 70–90 bar were achieved. When the core pressure stabilized for 2 h at 22 °C, the temperature of the cooling bath was decreased to the experimental value. A noticeable pressure drop can be seen as the process of hydrate formation started. When the pressure of the core holder remained unchanged for 12 h, the hydrate formation process was determined to be completed. To improve water conversion into hydrate and liquid distribution, a temperature ramping (multiple cooling and heating cycles within the temperature range of 1 °C and 22 °C) was employed [56, 57]. Finally, if no pressure difference was seen between the inlet and outlet after temperature ramping operation, then the redistribution was regarded as completion totally inside the core sample due to adequate gas/liquid migration. Electrical resistance (R) between

Table 1
Information on injected mixed gas and prepared sandstone sample properties.

| Exp no. | Gas used | Core no. | Sandstone properties |
|---------|----------|----------|---------------------|
|         | Core weight/g | Diameter/cm | Length/cm | Density/g cm⁻³ | Porosity/% | Initial water saturation/% |
| 1       | 70%CH₄/CO₂ #4 | 71.74      | 2.55      | 7.20         | 2.60       | 24.96 | 81.9 |
| 2       | 30%CH₄/CO₂ #6 | 76.99      | 2.55      | 7.75         | 2.60       | 23.24 | 76.2 |
| 3       | 70%CH₄/CO₂ #5 | 79.31      | 2.55      | 7.75         | 2.60       | 22.93 | 82.2 |
| 4       | 70%CH₄/CO₂ #5 | 79.31      | 2.55      | 7.75         | 2.60       | 22.93 | 56.0 |
| 5       | 30%CH₄/CO₂ #7 | 81.93      | 2.55      | 7.75         | 2.60       | 20.38 | 88.6 |
| 6       | 30%CH₄/CO₂ #3 | 73.40      | 2.55      | 7.20         | 2.60       | 23.22 | 53.7 |
| 7       | 70%CH₄/CO₂ #3 | 73.40      | 2.55      | 7.20         | 2.60       | 23.22 | 54.2 |
| 8       | 70%CH₄/CO₂ #4 | 71.74      | 2.55      | 7.20         | 2.60       | 24.96 | 56.9 |

Fig. 4. Profiles of temperature (T), pressure (Pin & Pout) and NRI during CH₄/CO₂ mixed hydrate formation in: (a) Exp1; and (b) Exp2.
Fig. 5. A summary after mixed CH$_4$/CO$_2$ hydrate formation at different experiments: (a) total gas stored in hydrate, CH$_4$ in hydrate and CO$_2$ in hydrate, as well as NR$_1$; and (b) NR$_1$ to hydrate saturation.

the alligator clip 1 (inlet) and 2 (outlet), as well as pressure and temperature, were measured and recorded during the whole process. The R values were normalized during hydrate formation as the first normalization resistance (NR$_1$); a detailed description can be found in the Ref. [45].

### 3. Results and discussion

#### 3.1. Profile of CH$_4$/CO$_2$ mixed hydrate formation

A detailed description of CH$_4$/CO$_2$ mixed hydrate formation can be referred to our previous publication [45]. In this work, similar strategies were used to generate mixed CH$_4$/CO$_2$ hydrates. The profiles of temperature, outlet pressure (P$_{out}$), inlet pressure (P$_{in}$), and first normalized resistance (NR$_1$) in different experiments have a similar trend. Fig. 4 shows the profiles of CH$_4$/CO$_2$ mixed hydrate formation in Exp1 and Exp2, respectively. It should be noted that the hydrate morphology is pore filling for water saturation higher than 35% [58]. A summary of moles stored in hydrate (total, CH$_4$ and CO$_2$), the value of NR$_1$, and the valve of NR$_2$ to hydrate saturation after mixed CH$_4$/CO$_2$ hydrate formation were showed in Fig. 5 (a) and Fig. 5 (b). More detailed information can be tracked in Table S1 of Appendix A.

In Fig. 4, sudden pressures were observed in the initial stage of hydrate formation for each cooling cycle. This was the sign of massive hydrate formation consuming CH$_4$/CO$_2$ mixed gas. Comparably, the following gentle pressure drops and flat pressure lines were seen in the final stage of hydrate formation, which were caused by mass transfer barriers of hydrate films between water and gas molecules [33-35]. In Table S1 of Appendix A, the range of S$_{wi}$ was 53.75–88.62% and it seemed that lower initial water saturation (S$_{wi}$) induced a more significant total amount of gas stored in hydrate, i.e. higher hydrate saturation (S$_h$). Noted that water diffusion plays a dominant role during hydrate formation and growth, in which hydrate films formed around water

#### 2.3.2. Multistep depressurization

After CH$_4$/CO$_2$ mixed hydrate formation, the following R values were normalized as second normalization resistance (NR$_2$). The position of the thermocouple was placed at the outlet, which can monitor the temperature change at the production site when employing multistep depressurization. Pressure drop at each depressurization stage was controlled by opening and closing the outlet value quickly, with the gas samples simultaneously collected and analyzed through the in-line micro gas chromatographer. Change of gas composition and resistivity were determined to investigate the dissociation characteristics of CH$_4$/CO$_2$ mixed hydrates, i.e. R$_{CH_4}$, SCO$_2$, and percentage change of hydrate volume ($\Delta$ V) were calculated at the end of each depressurization according to mass balance. Percentage change of NR$_2$ before and after multistep depressurization ($\Delta$ NR$_2$) was calculated as well to analyze the variation of hydrate saturation during the multistep depressurization. The procedure of multistep depressurization proceeded with the pressure firstly decreased to CH$_4$ hydrate equilibrium pressure and then below it. This operation ceased until the value close to or under CO$_2$ hydrate equilibrium pressure. Noted that hydrate equilibrium was obtained from CSMGem for the bulk-only phase and it may differ in porous media. The hydrate equilibrium was assumed unchanged considering the reservoir temperature remained constant (small fluctuations in core temperature was ignored) during slow depressurization. Finally, the temperature was increased to 25 $^\circ$C to dissociate all the hydrates.

| Exp no. | Hydrate type | S$_{wi}$/% | S$_h$/% | Total steps of depressurization | Shut-in period/hour | Temperature/°C | P$_{CH_4}$/bar | P$_{CH_4}$/CO$_2$/bar | PCO$_2$/bar |
|---------|--------------|------------|--------|---------------------------------|---------------------|----------------|----------------|----------------------|-------------|
| 1       | A            | 77.3       | 4.68   | 13                              | 4                   | 0.7            | 27.84          | 23.61                | 8.39        |
| 2       | B            | 73.8       | 2.46   | 6                               | 4                   | 1.3            | 29.56          | 18.25                | 11.09       |
| 3       | A            | 78.9       | 3.29   | 8                               | 2                   | 0.2            | 26.23          | 22.01                | 6.04        |
| 4       | A            | 43.7       | 12.1   | 9                               | 2                   | 1.5            | 30.15          | 20.18                | 14.02       |
| 5       | B            | 86.6       | 2.39   | 9                               | 2                   | 0.3            | 26.75          | 14.84                | 12.85       |
| 6       | B            | 42.0       | 11.4   | 9                               | 2                   | 0.6            | 27.56          | 20.75                | 13.32       |
| 7       | A            | 43.7       | 10.6   | 14                              | 4                   | 0.7            | 27.84          | 21.24                | 13.19       |
| 8       | A            | 47.4       | 9.46   | 12                              | 8                   |                |                |                      |             |
phase acting as diffusion barrier [34, 59]. Comparably, CO$_2$ gas diffusion dominates the mass transfer during CH$_4$-CO$_2$ swapping on existing CH$_4$ hydrate [60, 61]. Nevertheless, mixed hydrates of pure CH$_4$, pure CO$_2$ and CH$_4$/CO$_2$ coexisted in both cases in which hydrates formed from either mixed gases or CH$_4$-CO$_2$ swapping, although heterogeneity and micro properties differed.

It can be seen from Fig. 5 (a) that the mole of CH$_4$ in hydrate phase was higher than that of CO$_2$ in Exp1, Exp3-4 and Exp7-8, i.e., the mole ratio of CH$_4$ to CO$_2$ in the hydrate phase (RH) was greater than 1 shown in Table S1. This showed that mixed hydrates are rich in CH$_4$ and therefore classified as Type A. Comparably, the mole of CH$_4$ in hydrate phase was less than that of CO$_2$ in Exp2 and Exp5-6, which indicated that the CO$_2$-rich hydrates formed and thus were referred as Type B. Noted the values of RH for Type A hydrates (1.51–2.10) and Type B hydrates (0.15–0.27) were consistent with those calculated from CSMGem in Table S1. Additionally, a range of NR$_2$ (1.07 to 1.50) was observed, indicating an increase of hydrate saturation during CH$_4$/CO$_2$ mixed hydrate formation. Generally, it can be speculated from Fig. 5 (b) that higher hydrate saturation triggered higher NR$_2$ regardless of hydrate type. Nevertheless, the different amounts of CH$_4$ and CO$_2$ moles stored in mixed hydrates and heterogeneous hydrate distribution contributed to the difference of NR$_2$ within a range of similar hydrate saturation.

### 3.2. CH$_4$/CO$_2$ mixed hydrate dissociation

After synthesis of CH$_4$/CO$_2$ mixed hydrates of two types, different depressurization strategies were introduced. The detailed information on well-controlled manners is listed in Table 2. Next, different parameters including hydrate compositions, residual water saturation (S$_{rw}$), and shut-in period, were investigated for their correlations with CH$_4$ recovery and CO$_2$ storage. Specifically, Type A and Type B hydrates were synthesized in Exp1 and Exp2, respectively, to examine the effect of hydrate compositions on production and storage parameters during multistep depressurization. The effect of higher and lower S$_{rw}$ was then studied in Exp3-6 to determine the value of S$_{rw}$ that benefited CH$_4$ recovery and CO$_2$ storage for Type A and Type B hydrates. Finally, shut-in durations of 2 h (Exp4), 4 h (Exp7) and 8 h (Exp8) were employed to find a relatively beneficial selection for multistep depressurization on CH$_4$/CO$_2$ mixed hydrates.

#### 3.2.1. Effect of hydrate composition

In realistic hydrate exploitation, CH$_4$/CO$_2$ mixed hydrates would exist at the CH$_4$ hydrate reservoir after CO$_2$ injection. In this case, kinetic inhibitors and anti-agglomerate chemicals are recommended to be added together with CO$_2$ injection to eliminate CO$_2$ plugging at the injection site. This could further improve CO$_2$ injectivity and allow a high CO$_2$ sweep range [37, 63]. The following CO$_2$ migration from the injection site depends on permeability of hydrate-bearing sediment and relative permeability of CO$_2$, resulting in CO$_2$-water interface and CO$_2$-hydrate interface moving forward. This further induces formation and growth of both pure CO$_2$ hydrate and CH$_4$/CO$_2$ mixed hydrate. The CO$_2$ concertation decreases as the distance increases from injection site, causing CO$_2$-rich hydrates to enrich nearby the injection well and CH$_4$-rich hydrates to stay closer to the production well. As more CH$_4$ is produced from production well, CO$_2$ migration is driven from injection well to production well. This may alter the previous CH$_4$-rich hydrate zone into CO$_2$-rich one because of water and gas redistribution. Therefore, we investigated and compared the dissociation characteristics of CH$_4$-rich (Exp1) and CO$_2$-rich (Exp2) mixed hydrates, respectively. Additionally, the mole ratio of CH$_4$ to CO$_2$ in hydrate was 2.10 in Exp1 and 0.15 in Exp2, and the residual water saturation in Exp1 (77.3%) and Exp2 (73.8%) were similar. The shut-in period was controlled at 4 h between multistep depressurization. More information can be referred in Table 2 above and Table S1 of Appendix A.

Fig. 6 presents the profiles of CH$_4$ and CO$_2$ mole fraction in collected gas samples (CHX$_4$ & XCO$_2$), pressure (P$_{in}$ & P$_{out}$), temperature (T) and NR$_2$ during the multistep depressurization on Type A hydrate in Exp1. It should be noted that P$_{out}$ refers to depressurization pressure because pressure release was conducted in the outlet. Table S2 of Appendix A lists the values of those evaluation indicators at the end of different stages. The shut-in period was set to 4 h with a total of 13 pressure drops (Stage A to Stage M). It can be seen that the first drop was 6 bar, which brought the pressure to equilibrium pressure of mixed CH$_4$/CO$_2$ hydrate (P$_{CH4/CO2}$) at 0.7 $^\circ$C. The following pressure drops were controlled at 3–4 bar (stage B to stage J) to explore the characteristics of multistep depressurization. The final pressure drops were made at 8 bar to approach the equilibrium pressure of CO$_2$ hydrate (P$_{CO2}$).

It was inspected that from Fig. 6 initial XCH$_4$ was 73.7 mol% before the multistep depressurization. This value decreased to 66.7 mol% at the end of Stage A without pressure rebound. Then XCH$_4$ increased as well as fluctuated around 70.0 mol% from Stage B and Stage D with pressure rebound. The increase of XCH$_4$ was attributed to the dissociation of CH$_4$-rich hydrate. It was noted that a pressure differential existed between outlet and inlet until stage G, in which a noticeable spike was detected on the outlet pressure curve. Pressure differential between outlet and inlet mainly redistributed gas and water in the pores. Subsequently, continuous pressure fluctuation was observed during Stage H and XCH$_4$ peaked at 78.6 mol% at the end of Stage H. This was caused by CH$_4$-rich hydrate dissociation and continuous fluid movement and gas-water mixing in the pore. It was noted that water production occurred at the end of Stage L with obvious pressure rebound, which were produced by a large amount of CO$_2$-rich hydrates dissociation. This should be avoided because CO$_2$ release would reduce CO$_2$ storage efficiency and massive CO$_2$-rich hydrate loss may trigger instability of hydrate-bearing sediment. According to the Table S2 of Appendix A, a continuous increase of RCH$_4$ was observed at Exp1 from 72.0% at Stage A to 79.7% at Stage M. This was caused by gradual CH$_4$ hydrate dissociation when depressurization pressure was reduced gradually. However, actual CH$_4$ recovery efficiency would be decreased because of obvious XCH$_4$ decrease in the later steps of depressurization. The problematic issues of water production and dramatic XCH$_4$ decrease were therefore co-considered to cease multistep depressurization at selected stage.

In terms of enhanced CO$_2$ storage in Type A hydrates, SC02 experienced an increase before the end of Stage H with the highest value of 84.0% and then decreased slightly until the end of multistep
Fig. 7. Profiles of XCH₄ & XCO₂, Pᵢn and Pₒu during the multistep depressurization on Type B hydrate in Exp2. Shut-in period = 4 h, T = 1.3 °C, Pₒu = 29.56 bar, P(CH₄/CO₂) = 18.25 bar with 35.2 mol% CH₄/CO₂ gas right before the first depressurization. Pₒ₂C₂ = 11.09 bar. Bᵢn refers that Stage B proceeded overnight.

During the multistep depressurization on Type B hydrate in Exp2, Supplementary data can be referred to the Table S2 in Appendix A. It can be seen from Fig. 7 that the number of pressure drops was 6 in total (Step A to Step F). When the depressurization was performed from 50.8 bar to 41.2 bar, it can be seen that XCH₄ increased from 35.2 mol% at the beginning to 37.0 mol% at the end of Stage A. Since the pressure (41.2 bar) during Stage A was still higher than Pₒ₂CH₄, the slight increase of XCH₄ above was induced by CO₂-rich hydrate reformation, which was supported by a minimal pressure drop during Stage A. Noted that significant hydrate reformation was shown as sharp pressure drop just before the end of Stage B. The amount of CH₄ and CO₂ forming hydrate were equivalent, and therefore, the XCH₄ at the end of Stage B (36.6 mol%) was nearly equal to that at the end of Stage A (37.0 mol%).

It was noticed from Fig. 7 that the pressure differential between outlet and inlet occurred throughout the multistep depressurization. At the beginning of Stage D, a sudden pressure drop induced dissociation of CO₂-rich hydrates to release water and gas. On the one hand, this caused a 1.2 mol% increase of XCO₂. On the other hand, mass transfer was alleviated because of partial hydrate dissociation. Water and gas redistributed from outlet to inlet with time, causing hydrate dissociation and reformation along with the core, showed as pressure fluctuation during Stage D. The value of XCH₄ decreased from 34.8 mol% to 31.6 mol% from Stage D to Stage F. This was caused by the fact that the existing CO₂-rich hydrates tend to be unstable when depressurization pressure was close and below P(CH₄/CO₂). As a result, partial CO₂-rich hydrates dissociated and released more CO₂ than CH₄ and decreased XCH₄. Nevertheless, as seen in Table S2, RCH₄ increased from initial 30.4% as more CH₄ recovered with multistep depressurization. The highest RCH₄ was 81.2% acquired at the end of Stage F.

As for CO₂ storage for Type B hydrate in Exp2, an increasing trend of SCO₂ was observed with stages, and the highest SCO₂ was 82.8% nearly at the end of Stage E. During the multistep depressurization, the depressurization pressure was above PCO₂, CO₂-rich gas tended to form hydrate. The process of multistep depressurization was suggested terminated at the end of Stage E because massive water production occurred at the end of Stage F. The positive ∆V in Exp2 of Type B hydrate in Table S2 indicated a gain of hydrate mass volume during multistep depressurization on CO₂-rich hydrates, i.e. the amount of CO₂ reformation was larger than total loss of CH₄ hydrates. A maximal of ∆V (109.57%) was observed in the suggested ceasing point. Additionally, NR₂ increased with multistep depressurization indicating hydrate saturation in sediment increased.

According to the Table S2, the highest XCH₄ for Type A hydrate (78.6 mol% at 18.48 bar) was more than twice larger than those any value of XCH₄ for Type B hydrate, although RCH₄ at 18.48 bar for Type A hydrate (74.8%) was a lower than that for Type B hydrate (79.4%). This is important because CH₄-rich mixed gas can be applied after purification through an economical separation method, while CO₂-rich one was costly to be used [64,65]. In terms of CO₂ storage, the highest SCO₂ for Type A hydrate (84.0%) was slightly more than that for Type B hydrate (82.8%). It seemed that the Type A hydrate-bearing reservoir was dominated by CH₄ recovery while Type B by CO₂ storage through multistep depressurization according to the negative ∆V in Exp1 and positive ∆V in Exp2, respectively. However, ∆NR₂ values were both positive in Exp1 and Exp2, showing that sediment was stabilized with multistep depressurization operation. This can be understood that water gas transportation and distribution in the pore mainly affect the resistivity of hydrate-bearing sediment [51], although hydrate volume increased in Exp2 was mainly created with mass transfer barrier, which was supported by a minimal pressure drop during Stage A. Hence, resistivity is lower than CH₄ hydrate [52]. The results of negative ∆V in Exp1 and positive ∆V in Exp2 while both have increased NR₂ also indicated resistance was not directly correlated with mass volume but distribution that connected with fluid flow and water saturation. Therefore, the results above collectively indicated that it is better to perform multistep depressurization at the CH₄-rich hydrate zone to acquire and utilize CH₄ gas. This means the operation of multistep depressurization should cease before CH₄-rich hydrate changes into CO₂-rich one.

3.2.2. Effect of residual water saturation

Two types of hydrate deposits can be formed in porous media with different initial water saturation (Sᵢw), i.e. excess gas (Sᵢw > 50%) and excess water (Sᵢw > 50%). And excess water deposit may hinder gas production from depressurized hydrate reservoir [9]. It is noted that sandstones of high water saturation (>35%) generate hydrate morphology of pore-filling [58]. Therefore, Exp3-6 of excess water deposits (Sᵢw = 53.75-88.62%) were created with mass transfer barrier among pore-water/gas and pore-filling hydrates with CH₄ recovery and CO₂ storage. During gas production from hydrate reservoir with higher water saturation, multistate exits in the porous media and residual water saturation (Sᵢw) may be the dominant factor affecting heat transfer and mass transfer [66], and thus deciding CH₄ recovery and CO₂ storage by multistep depressurization. Therefore, the effect of different Sᵢw on multistep depressurization of CH₄/CO₂ mixed hydrate was investigated by performing experiments on Type A (Exp3 & Exp4) and Type B hydrate (Exp5 & Exp6), respectively. The mole ratio of CH₄ to
CO₂ in hydrate was 1.51 in Exp3 and 1.76 in Exp4, 0.21 in Exp5 and 0.27 in Exp6. The shut-in period was designed 2 h between multistep depressurization for Exp3-6, as described in Table 2 and Table S1 of Appendix A. This may be attributed to extreme inhomogeneity along the sandstone sediment. Table S3 in the Appendix A illustrates the data of XCH₄ in Stage H, resulting in both decreases in RCH₄ and SCO₂. It was noted that water was continuously produced from Stage E to Stage H proving massive hydrates continuously dissociated, suggesting depressurization should be stopped before the end of Stage E. It can be seen from Table S3 that ΔV in Exp3 was negative, and its value decreased with time. This indicated that the amount of CH₄ recovered was greater than that of CO₂ stored over time. A negative range of ΔNR₂ (−2.6% to 9.9%) was also observed during multistep depressurization, confirming hydrate loss in hydrate-bearing sediment.

3.2.2.1. Type A mixed hydrate. In Exp3 of Type A hydrate sample, the higher S_out of 82.2% triggered higher S_NH of 78.9% and lower S_H of 3.29% after hydrate formation. Fig. 8 shows the profiles of Type A mixed hydrate dissociation during multistep depressurization of 8 steps in Exp3. When performing multistep depressurization above P_C3 in Type A hydrate during Stage A and Stage B, no drastic change of XCH₄ was detected (only from 76.9 mol% to 77.9 mol%). This was caused by slight CH₄-rich hydrate dissociation, as shown a pressure rebound appeared just after shut-in operation. A noticeable pressure drop occurred across the P_C3 line and the XCH₄ decreased from 77.9% to 75.8% during Stage C, indicating massive reformation of CH₄-rich hydrates. Subsequently, a pressure differential occurred between outlet and inlet, and XCH₄ was nearly unchanged during Stage D, showing nearly no gas composition change at the outlet. Water production was observed during gas collection at the end of Stage E, which can be predicted based on the pressure rise during Stage E as a result of massive hydrate dissociation. It was interesting to observe both dissociation and reformation of mixed hydrate with pressure increasing and decreasing during Stage G, while only hydrate dissociation dominated during Stage H with pressure rising.

When multistep depressurization was conducted between P_C3 and P_CO₂, most CH₄-rich hydrates dissociated and contributed to RCH₄ recovery and CO₂-rich hydrate formed to enhance CO₂ storage. Practically, depressurization should controlled before Stage E in which water production started. To explore the highest values of RCH₄ and SCO₂ with the depressurization reduced close to P_CO₂, further multistep depressurization was introduced after water production at the end of Stage E. It should be noted that pressure differences existed again during Stage G. This may be attributed to extreme inhomogeneity along the sandstone sample. Table S3 in the Appendix A illustrates the data of XCH₄, RCH₄, SCO₂, ΔV, and ΔNR₂ in Exp3. It can be seen that RCH₄ increased to peak values of 87.6% and SCO₂ increased to 86.2% at the end of Stage G. However, CO₂-rich hydrates occurred to dissociate significantly with depressurization pressure decreasing close to P_CO₂ at the end of Stage G, which was indicated as an obvious increase in pressure and a decrease in XCH₄ in Stage H, and then decreased gradually as a result of CO₂-rich hydrate dissociation caused by depressurization pressure performed below P_CO₂. The phenomenon of water production appeared at the end of Stage G, which was the indicator of unwanted massive dissociation of hydrates and herby multistep depressurization needed to be terminated. In Table S3 of Appendix A, the negative value of ΔV showed that the amount of CO₂ hydrate storage was less than that of the recovery of CH₄ hydrate during the whole depressurization. It was interesting ANR₂ that was initially positive at Stage A-D, indicating that multistep depressurization on lower S_NH hydrate sample improved gas water distribution at these stages. Subsequently, ANR₂ was negative since stage E, and the sediment became less stable with loss of hydrate saturation than before employing multistep depressurization. Nevertheless, the suggested ceasing point was selected at the end of Stage G with a relative lower ANR₂ of −1.2%.

It was inspected that Exp3 of higher S_NH was not suitable for...
Although lower RCH in Exp4 was much more reserved and gas water distribution was improved in Exp4 of application of multistep depressurization in such hydrate reservoir. This was caused by a slow water–gas distribution process along the core. More information can be found in the Table S4 in Appendix A. Initially, the pressure was brought below PCO2 by performing 6 steps of depressurization at the outlet. It was observed that the inlet pressure was first above Pout and then plummeted below the corresponding Pout. This was caused by a slow water–gas distribution process along the length of sandstone. It was interesting that XCH4 peaked at 38.3 mol% at stage C, where the Pout was equal to the Pout. It seemed that there was a blockage between the outlet and the inlet after stage E, since the pressure differential came and existed within the rest time. At the early stage of Stage G, two obvious pressure drops were inspected, indicating that CO2-rich gas reformed hydrates as the pressure below PCO2. This was supported by the indicators of SCO2, which reached the highest values of 88.7% at the end of Stage G. The value of XCH4 decreased significantly with more steps of depressurization at the pressure close to PCO2. Nevertheless, it was observed that water production occurred at the end of Stage G and thus ceasing point was selected accordingly.

Collectively, multistep depressurization was highly proposed to improve CH4 recovery from the CH4-rich hydrate reservoir of lower Srw and most of the CO2 can be stored safely within the pressure window. Indicating that both scenarios were potential selections for CO2 storage.

3.2.2.2. Type B mixed hydrate. The effect of different Srw on dissociation manners of multistep depressurization was also investigated in Type B hydrates. Exp5 was conducted in Type B hydrate sample of higher Srw = 86.6% in Exp5. Shut-in period = 2 h, T = 0.3 °C, PCH4 = 30.15 bar, P(CH4/CO2) = 14.84 bar with 39.8 mol% CH4/CO2 gas just before the first depressurization, and PCO2 = 12.85 bar. Gout refers that Stage G proceeded overnight.

Multistep depressurization because more hydrates dissociated and involved high risk of water production. Comparably, the drop in NR2 was lower in Exp4 than Exp3, denoting that hydrate saturation was much more reserved and gas water distribution was improved in Exp4 of lower Srw. Fig. 10 presented the correlation between RCH4 and SCO2 with depressurization pressure (Pout) in Exp3 and Exp4. A depressurization pressure window was proposed for the controlled pressure release operation. Specifically, the upper pressure window (Pupper) was equal to PCH4 and the lower pressure window (Plower) was the ceasing pressure where water started to produce. When the depressurization pressure was reduced below Pupper, even though a higher RCH of 79.0% was obtained in Exp3 at Plower of 17.6 bar, much larger negative value of ΔNR2 indicated huge loss of hydrate saturation in Exp3. This limited the application of multistep depressurization in such hydrate reservoir. Although lower RCH of 75.2% was achieved in Exp4 at Plower of 22.5 bar, less loss of hydrate mass and lower drop in ΔNR2 allowed more effective depressurization than Exp3. The highest CO2 storage ratio values were nearly the same in Exp3 (82.9%) and Exp4 (82.6%) at Plower, indicating that both scenarios were potential selections for CO2 storage.

Collectively, multistep depressurization was highly proposed to improve CH4 recovery from the CH4-rich hydrate reservoir of lower Srw and most of the CO2 can be stored safely within the pressure window. Indicating that both scenarios were potential selections for CO2 storage.

Collectively, multistep depressurization was highly proposed to improve CH4 recovery from the CH4-rich hydrate reservoir of lower Srw and most of the CO2 can be stored safely within the pressure window. Indicating that both scenarios were potential selections for CO2 storage.
6–10 bar. The 2-hour shut-in period was used to perform the stepwise operations. Fig. 12 listed the detailed description of gas composition, pressure, temperature and NR2 during multistep depressurization, and more data can be tracked in Table S4 of Appendix A.

In Fig. 12, the initial XCH4 was 39.8 mol% before stage A. Subsequently, the depressurization pressures in Stage A and Stage B was decreased close to PCH4 and thus the XCH4 values were elevated to 42.0 mol% and 43.7 mol%. A significant pressure drop was observed during stage C, and XCH4 was reduced to 38.5 mol%. This was caused by CH4-rich hydrate reformation within stage C. The operating pressure fluctuated around PCO2 during Stage D and Stage E, having a marginal effect on the stability of CO2-rich hydrates without obvious change of XCH4. However, following depressurization was carried out during Stage F-I below PCO2, causing CO2-rich hydrates to dissociate and reduced XCH4. It was noticed that water appeared at the end of Stage H and therefore depressurization should be closed before it. Exp6 also witnessed a positive ΔV during whole stages, indicating that more CO2 was stored than CH4 hydrate was recovered. ΔNR2 was observed to be increasing with steps after Stage C, indicating an increase of hydrate saturation in terms of multistep depressurization on Type B hydrate of lower SWw.

It was concluded from Table S4 that both ΔV were positive and ΔNR2 increased with small fluctuations in Exp5 and Exp6, implying that Type B hydrate reservoirs of both higher SWw and lower SWw can be potential selection for multistep depressurization with slow manners. Fig. 13 showed the correlation between RCH4 and SCO2 with Pout in Exp5 of higher SWw = 86.6% and Exp6 of lower SWw = 42.0%. Regarding the depressurization pressure window of Pupper and Plower, it can be seen that the highest SCO2 was 88.7% for Exp5 of higher SWw at Plower of 15.97 bar, with a relative higher RCH4 of 87.4%. The corresponding ΔV was 108.27% and ΔNR2 was −1.9% at Plower, which indicated hydrate saturation gain during multistep depressurization. Comparably, Plower in Exp6 was 13.10 bar which was just above PCO2, with the relative higher RCH4 of 81.9% and SCO2 of 88.3%. ΔNR2 was only −0.8% and ΔV was 54.65% at this Plower denoted increased hydrate saturation after multistep depressurization. As a result, Type B hydrate reservoirs of either higher SWw or lower SWw is able to achieve high efficiency of enhanced CH4 recovery and CO2 storage via multistep depressurization. According to the Table S4 in Appendix A, it may increase the economic competitiveness in Exp6 of low SWw hydrate reservoir considering its higher XCH4 of 39.8 mol% than 32.2 mol% in Exp5 of higher SWw. Therefore, multistep depressurization was highly proposed for Type B hydrate of lower SWw. And the multistep depressurization was suggested to be conducted within the pressure window to efficiently enhanced CH4 recovery and CO2 storage.

Fig. 13. The correlation between RCH4 and SCO2 with Pout in Exp5 of higher SWw = 86.6% and Exp6 of lower SWw = 42.0%. SCO2 and RCH4 were calculated using equations described in Appendix B.2.

Fig. 14. Comparison of RCH4 and SCO2 in CO2 swapping combined with depressurization from references and this work at different residual water saturation [53,67]. More details can be referred to Table S6 in Appendix A.

Fig. 15. Profiles of XCH4 & XCO2, P in & P out, T and NR2 during the multistep depressurization on Type A hydrate in Exp7 of lower SWw = 43.7%. Shut-in period = 4 h, T = 0.6°C, PCH4 = 27.56 bar, PCO2(CO2) = 20.75 bar with 72.9 mol% CH4/CO2 gas right before the first depressurization, and PCO2 = 13.32 bar. D3mm refers that Stage D proceeded overnight.
3.2.3. Effect of shut-in period

Extension of shut-in period can allow enough time for water and gas migration, which is dependent on capillary forces. This migration of water and gas helps to avoid the blockage of fluid flow channels and thus transfer from reservoir to hydrate dissociation front and thus preventing gas storage evaluation, SCO2 was observed with a maximum value of 79.5 mol%, accompanied by the highest SCO2 of 84.9% at the end of Stage F. Therefore, the operation time of 48 h was marked at the end of Stage F with the maximum XCH4 and SCO2. The explanation for the above phenomenon was that massive CH4-rich hydrates dissociated CH4 together with many CO2-rich hydrates formed at the pressure below P(CH4/CO2). The following values of XCH4 and SCO2 declined with the next depressurization steps. RCH4, however, still grew to the highest value of 90.3% throughout continuous hydrate exploitation until the end of multistep depressurization. It was noted that water production started coming at the end of Stage H and multistep production should be ceased. The negative value of ΔV was the indicator of CH4 hydrate recovery over-numbered CO2 hydrate storage. Additionally, the negative value of ΔNR2 showed that overall hydrate saturation was decreased correspondingly. This may be because too much CH4 was recovered while CO2 was not stored equivalently with a longer shut-in period of 8 h.

Table 3 summarizes the depressurization schemes and exploitation performances in experiments with shut-in period of 2 h, 4 h and 8 h at the targeted ceasing point, P(out) is the depressurization pressure, XCH4 is the mole fraction of CH4 in gas phase, RCH4 is the CH4 recovery percent, and SCO2 is the CO2 storage ratio. ΔV is the percentage change of hydrate volume and ΔNR2 is the percentage change of normalized resistance.

![Fig. 16](image-url) Profiles of XCH4 & XCO2, Pin & Pout, T and NR2 during the multistep depressurization on Type A hydrate in Exp8 of lower S(w) = 47.4%. Shut-in period = 8 h, T = 0.7 °C, P(CH4) = 27.84 bar, P(CH4/CO2) = 21.24 bar with 75.1 mol% CH4/CO2 gas right before the first depressurization, and PCO2 = 13.19 bar.

| Exp | Shut-in period (h) | P(out) (bar) | Total production time (h) | XCH4 (%) | RCH4 (%) | SCO2 (%) | ΔV (%) | ΔNR2 (%) |
|-----|--------------------|--------------|--------------------------|---------|---------|---------|-------|---------|
| 4   | 2                  | 20.90        | 14                       | 78.6    | 76.6    | 85.1    | -65.71| -1.2    |
| 7   | 4                  | 20.74        | 24                       | 81.3    | 72.6    | 85.3    | -63.86| 10.2    |
| 8   | 8                  | 20.22        | 48                       | 79.5    | 75.0    | 84.9    | -73.91| -6.7    |
76.6%, 72.6%, and 75.0%. It is expected to see that the highest XCH4 came with the highest SCO2 (85.1%, 85.3% and 84.9 % for 2 h, 4 h and 8 h), which were nearly the same and indicated that most CO2 could form hydrates and remained stable during multistep depressurization at the pressure close to P(CH4/CO2). This meant that the most suitable depressurization schemes achieved simultaneous the highest efficiency of CH4 recovery and CO2 storage at the targeted ceasing pressure, with the total production time were 10 h, 24 h and 48 h for Exp4, Exp7 and Exp8, respectively. The Δ values for these three were almost same (~65.71%, –63.86% and –73.91% for 2 h, 4 h and 8 h), indicating a total loss of hydrate volume. However, the value of ΔNR2 was 10.2% for 4 h, which was higher than the negative values for 2 h (~1.2%) and 8 h (~6.7%). This means that hydrate-bearing sediment was improved through efficient gas water movement and distribution within core samples after multistep depressurization with 4-hour shut-in period. Fig. 17 shows the comparison of RCH4 and SCO2 in combination studies of CO2 swapping with depressurization from references and Section 3.2.3 in this work. It can be inspected from Sun’s work [31] that higher numbers of pressure drops with shorter shut-in period was more beneficial for CH4 production and CO2 retention. The SCO2 in Yang’s [41] was lower than those in Pandey’s [45], which was resulted from CH4/CO2/N2 mixed hydrate in Yang’s and CH4/CO2 mixed hydrates in Pandey’s. This indicated that multistep depressurization was suggested to be performed after CO2 injection in CH4 hydrates for higher efficiency of CO2 storage. It seemed that reducing shut-in period can improve CH4 recovery and CO2 storage slightly in terms of 24-hour and 12-hour cases in Pandey’s. Nevertheless, the RCH4 can be further enhanced from 71.0% to 73.8% to 75.0–79.4%, and SCO2 from 81.0% to 82.9% to 82.8–85.1%, respectively through reducing shut-in period from 12 h to 24 h to 2–8 h. This indicated that sufficient water and gas migration can be completed within a much shorter shut-in period (2–8 h) for efficient CH4 recovery and CO2 storage. But too long shut-in period (12–24 h) without depressurization may cause less efficiency on CH4-rich hydrate decomposition and CO2-rich hydrate reformation than those with shorter ones (2–8 h).

### 3.3. Comparison of efficiency and practical implication

Fig. 18 summarizes the changes of XCH4, SCO2, and RCH4 with Pout during multistep depressurization at Exp1-8. The assumptions and equations used to calculate SCO2 and RCH4 were described in the Appendix B. Noted that the lowest Pout was the point at which the multistep depressurization should be ceased as discussed above. As seen in Fig. 18 (a–c), the maximum values of XCH4 for Type A hydrate were 74–82 mol %, while those for Type B hydrate were 37–44 mol%. The maximum value of XCH4 (81.3 mol%) was observed in Exp7, accompanied by the peak SCO2 at the end Pout of 20.74 bar. No obvious differences in peak SCO2 values were observed between Type A hydrate (84–87%) and Type B hydrate (83–89%) in Fig. 18 (d–f), indicating that majority of CO2 in all scenarios can be stored as hydrate in sediment by multistep depressurization. And SCO2 can be enhanced generally with the reduced depressurization pressure at the conditions that CO2-rich hydrates can form thermodynamically. According to Fig. 18 (g–i), the maximum value of RCH4 seemed to depend mainly on Pout. When Pout was decreased close to 10 bar, the maximum value of RCH4 can be greater than 80% in Exp2, 3, 5–6. Compared to Exp1, 4, 7–8, when Pout was reduced to about 20 bar, the maximum value of RCH4 was less than 80%. This was following the fact that more CH4 can be recovered with the increase of depressurization step and the decrease of depressurization pressure.

When hydrates dissociate by depressurization in a porous medium, continuous mixing occurs between the liquid and gaseous phases due to capillary forces, differences in relative permeability, and mobilization of pore water. In a mixed hydrate system with two different hydrates (CH4 and CO2 hydrate of different composition), the CH4 hydrate can remain stable outside its stability zone because it is surrounded by a more stable CO2 hydrate layer. Therefore, the pressure response and production behaviors are influenced by the mass transfer barrier of the CO2 hydrate as well as the presence of two stability zones, resulting in the likelihood of hydrate reformation. This gives the mixed hydrate system additional stability compared to a pure CH4 hydrate system [46].

Generally, four types of dissociation and reformation characteristics during multistep depressurization mainly affecting CH4 recovery and CO2 storage can be recognized in this work, as summarized in Fig. 19. When the depressurization pressures were reduced below P(CH4/CO2) and above P(CH4/CO2), obvious wanted CH4-rich hydrate dissociation and CO2-rich hydrate reformation can be observed according to the profiles of pressure rebound and sharp decrease. Gas concentration changes regarding XCH4 and XCO2 also supported the explanation above. A similar phenomenon of pressure rebound was reported in the schemes of slow stepwise depressurization [30] and intermittent depressurization [68], which significantly contributed to the CH4 production. In addition, the pressure rebounded to just above P(CH4/CO2) at CH2-rich hydrate dissociation, indicating that further depressurization may improve CH4 recovery continuously. Noted that the gas compositions were collected and acquired at the end of each multistep depressurization while this dynamic hydrate dissociation-reformation, as well as water-gas distribution, may occur at any time during the shut-in period. In contrast, when the depressurization pressures were operated below P(CH4/CO2) or above P(CH4/CO2), unwanted CO2-rich hydrate dissociation or CH4-rich hydrate reformation were detected based on variations of pressure and CH4/CO2 fraction. The reforming CH4-rich hydrates were not problematic because they can be recovered with the depressurization pressure reduced below P(CH4/CO2). However, the dissociating CO2-rich hydrates should be avoided to decrease the efficiency of CH4 recovery and CO2 storage. These four types of pressure and gas composition characteristics can be employed to verify the occurrence of hydrate reformation and dissociation, thus enhancing CH4 production and CO2 retention via depressurizing stepdown pressure between P(CH4/CO2) and P(CH4/CO2).

In a more realistic production field, CH4 recovery and CO2 storage should be considered comprehensively because the former is related to the direct profit of CH4 product, and the latter can save undirected costs by CO2 sequestration. These two indicators, therefore, are being maximized. Additionally, the production time for the multistep depressurization is critical concerning the costly operation cost on the platform. Meanwhile, the stability of hydrate-bearing sediment needs to be maintained through increased hydrate saturation or improved gas water distribution. Fig. 20 is the combined analysis of SCO2 to increase of CH4 concentration (ΔXCH4), Pout to P(CH4/CO2), and production time to ANR2 at the optimized conditions in this work. From the perspective of higher
enhancement of CH$_4$ recovery and CO$_2$ storage, it can be speculated that Exp1, Exp4, Exp7, and Exp8 should be highlighted with the positive values of $\Delta X_{CH_4}$ (>0 mol%) and SCO$_2$ (>84.0%) simultaneously shown in Fig. 20(a). These positive $\Delta X_{CH_4}$ and higher SCO$_2$ values were obtained by performing multistep depressurization until $P_{out}$ was close to or just below the equilibrium pressure of mixed CH$_4$/CO$_2$ hydrates, shown in Fig. 20(b). Among these best four experiments, Exp7 emerged as the highest value $\Delta N_{R_{CH_4}}$ (10.2%) with a shorter production time (24 h: 4-h shut-in $\times$ 6 stages) in total, as indicated in Fig. 20(c). It should be noted that Exp1 was also marked as its $\Delta N_{R_{CO_2}}$ was of positive value (2.3%), however, the production time (32 h: 4-h shut-in $\times$ 8 stages) was relatively longer. Therefore, the 4-hour shut-in period may be the best option to enhance CH$_4$ recovery and CO$_2$ storage simultaneously during multistep depressurization in the CH$_4$-rich hydrate reservoir.

The scheme of an injection well and a production well to explore NGHs by swapping CH$_4$-CO$_2$ in the reservoir is highly recommended in the realistic production trial. Specifically, CO$_2$ is delivered to the reservoir from the injection well, while CH$_4$-rich gas is collected from the production well by depressurization. Herein, CH$_4$-rich hydrates around the production well tend to become CO$_2$-rich by dissociating and reformation hydrates with the risk of water production. Furthermore, further depressurization in the production well may yield lean CH$_4$ gas effluent, which needs to be costly to acquire a CH$_4$ gas product. Our work is concerned with the above issues and determines the patterns of different multistep depressurization. A suitable operation strategy of a 4-hour shut-in period with a production pressure close to $P_{(CH_4/CO_2)}$ is
Fig. 19. Four types of dissociation and reformation characteristics during multistep depressurization.

Fig. 20. Comprehensive comparisons at the optimized conditions of: (a) $X_{\text{CO}_2}$ to $\Delta X_{\text{CH}_4}$, (b) $P_{\text{out}}$ to $P_{(\text{CH}_4/\text{CO}_2)}$, and (c) production time to $\Delta NR_2$. $\Delta X_{\text{CH}_4}$ and $\Delta NR_2$ were calculated using equations described in Appendix B.2.
Table S1
Formation data at different experiments. P$_i$ and T$_i$ are initial pressure and temperature before hydrate formation. S$_{iw}$ is initial water saturation. P$_f$ and T$_f$ are final pressure and temperature after hydrate formation. ΔP is the pressure drop during hydrate formation. S$_{rw}$ and S$_f$ refer to residual water saturation and hydrate saturation after hydrate formation. V$_h$ is hydrate volume after hydrate formation. nCH$_4$(H), nCO$_2$(H), nCH$_4$(G) and nCO$_2$(G) are the mole of CH$_4$ and CO$_2$ in hydrate phase and gas phase, respectively. RH(CH$_4$/CO$_2$) refers to the mole ratio of CH$_4$ to CO$_2$ in hydrate phase. RH(CH$_4$/CO$_2$)$_{3D}$ refers to the RH(CH$_4$/CO$_2$) calculated from CSMGem software [62]. NR$_i$ is the first normalized resistance after mixed hydrate formation. Type A hydrate is CH$_4$-rich and Type B hydrate is CO$_2$-rich.

| Exp1 | Exp2 | Exp3 | Exp4 | Exp5 | Exp6 | Exp7 | Exp8 |
|------|------|------|------|------|------|------|------|
| P$_i$/bar | 75.90 | 68.45 | 82.10 | 89.90 | 89.34 | 73.30 | 80.80 | 83.40 |
| T$_i$/°C | 21.06 | 22.10 | 24.00 | 21.88 | 21.90 | 23.00 | 22.00 | 21.81 |
| S$_{iw}$_% | 81.93 | 76.20 | 82.20 | 55.97 | 88.62 | 53.75 | 54.22 | 56.87 |
| P$_f$/bar | 29.70 | 50.83 | 47.20 | 41.90 | 65.50 | 39.00 | 39.30 | 44.20 |
| T$_f$/°C | 0.85 | 1.40 | 0.40 | 0.80 | 1.26 | 0.47 | 0.47 | 0.80 |
| ΔP/bar | 46.20 | 17.62 | 34.90 | 48.00 | 23.84 | 34.30 | 41.50 | 39.20 |
| S$_{rw}$_% | 77.3 | 73.8 | 78.9 | 43.7 | 86.6 | 42.0 | 43.7 | 47.4 |
| S$_f$_% | 6.68 | 2.46 | 3.29 | 12.3 | 2.00 | 11.8 | 10.6 | 9.46 |
| V$_h$/cm$^3$ | 0.43 | 0.23 | 0.30 | 1.12 | 0.16 | 1.01 | 0.90 | 0.87 |
| nCH$_4$(H)/×10$^{-3}$mol | 2.69 | 0.27 | 1.66 | 6.58 | 0.26 | 1.96 | 5.61 | 5.16 |
| nCO$_2$(H)/×10$^{-3}$mol | 1.28 | 1.82 | 1.10 | 3.75 | 1.24 | 7.34 | 2.72 | 2.86 |
| nCH$_4$(G)/×10$^{-3}$mol | 4.45 | 2.67 | 4.67 | 13.12 | 1.79 | 5.32 | 11.24 | 11.85 |
| nCO$_2$(G)/×10$^{-3}$mol | 1.28 | 1.82 | 1.10 | 3.75 | 1.24 | 7.34 | 2.72 | 2.86 |
| RH(CH$_4$/CO$_2$) | 2.10 | 0.15 | 1.51 | 1.76 | 0.21 | 0.27 | 2.06 | 1.80 |
| RH(CH$_4$/CO$_2$)$_{3D}$ | 2.96 | 0.52 | 2.78 | 1.40 | 0.75 | 0.28 | 1.41 | 1.44 |
| NR$_i$ | 1.20 | 1.17 | 1.16 | 1.43 | 1.07 | 1.48 | 1.50 | 1.26 |
| Hydrate type | A | A | A | B | B | B | B | A |

Proposed for the original CH$_4$ hydrate reservoir. After the CH$_4$-rich hydrate reservoir is transformed into CO$_2$-rich by depressurization exploitation, multistep depressurization on CO$_2$-rich hydrates should be proposed to avoid the economic point of view due to the lean effluent of CH$_4$. Related to the initial water saturation, hydrate saturation appears to be less critical than operation modes and hydrate compositions, depending on the production performance. Furthermore, water production can be avoided from the economic point of view due to the lean effluent of CH$_4$-rich hydrates, and therefore, multistep depressurization must cease before the pressure decreases close to P$_{CO2}$. Depressurization was suggested reduced in steps and controlled at a certain pressure window to achieve wanted CH$_4$ recovery and CO$_2$ storage efficiency, water gas distribution in hydrate-bearing sediment during multistep depressurization. The suggested ceasing stage was marked with bold.

Table S2
Pressure, XCH$_4$, RCH$_4$, SCO$_2$, ΔV and ΔNR$_i$ at different stages of multistep depressurization in Exp1-2. XCH$_4$ is the mole fraction of CH$_4$ in gas phase. RCH$_4$ is the CH$_4$ recovery percent. SCO$_2$ is the CO$_2$ storage ratio. ΔV is the percentage change of hydrate volume and ΔNR$_i$ is the percentage change of normalized resistance. The suggested ceasing stage was marked with bold.

| Exp 1 Type A (Srw∼77.3%) | Exp 2 Type B (Srw∼73.8%) |
|---------------------------|---------------------------|
| Stage | Pout | XCH$_4$ | RCH$_4$ | SCO$_2$ | V  | ΔV  | ΔNR$_i$ | Stage | Pout | XCH$_4$ | RCH$_4$ | SCO$_2$ | V  | ΔV  | ΔNR$_i$ |
|      | bar  | %     | %     | %     | %  | %   | %     |      | bar  | %     | %     | %     | %  | %   | %     |
| A    | 23.60 | 66.7 | 72.0 | 67.7 | −59.77 | 0.1 | 50.83 | 35.2 |
| B    | 21.16 | 70.0 | 74.0 | 74.0 | −59.53 | 0.1 | 50.92 | 36.6 |
| C    | 20.98 | 69.3 | 74.4 | 73.6 | −60.23 | 0.8 | 51.80 | 36.1 |
| D    | 20.59 | 70.8 | 74.4 | 75.4 | −59.53 | 1.6 | 52.60 | 36.1 |
| E    | 20.39 | 73.9 | 73.6 | 78.3 | −57.21 | 2.8 | 53.40 | 33.8 |
| F    | 19.92 | 67.8 | 76.3 | 73.7 | −62.56 | 3.2 | 54.20 | 31.6 |
| G    | 20.20 | 78.4 | 72.4 | 82.3 | −53.95 | 2.5 | 55.00 | 31.6 |
| H    | 18.48 | 78.6 | 74.8 | 84.0 | −56.28 | 2.3 | 55.80 | 31.6 |
| I    | 18.54 | 77.6 | 75.1 | 83.2 | −56.98 | 4.0 | 56.60 | 31.6 |
| J    | 18.43 | 76.9 | 75.5 | 82.8 | −57.67 | 4.4 | 57.40 | 31.6 |
| K    | 18.16 | 76.4 | 75.6 | 82.4 | −57.91 | 5.1 | 58.20 | 31.6 |
| L    | 18.20 | 73.9 | 76.6 | 80.8 | −60.00 | 5.6 | 59.00 | 31.6 |
| M    | 16.88 | 69.5 | 79.7 | 79.2 | −64.42 | 5.5 | 60.80 | 31.6 |

4. Conclusion
The multistep depressurization on CH$_4$/CO$_2$ hydrates was intensively investigated to enhance CH$_4$ recovery and CO$_2$ storage. The effects of three critical parameters: hydrate compositions (Type A and Type B hydrate), residual water saturation (S$_{lw}$), and shut-in period (2 h, 4 h and 8 h) were studied to evaluate the gas compositions, CH$_4$ recovery and CO$_2$ storage efficiency, water gas distribution in hydrate-bearing sediment during multistep depressurization. The conclusions are summarized below.

- To maximize CH$_4$ recovery and CO$_2$ storage with higher CH$_4$ molar fraction in the gas phase (XCH$_4$) and CO$_2$ storage ratio (SCO$_2$), it was highly recommended to perform multistep depressurization on Type A hydrates (CH$_4$/CO$_2$ ratio of 1.76–2.06) of low S$_{lw}$ (43.7–47.4%).
- Depressurization was suggested reduced in steps and controlled at a certain pressure window to achieve wanted CH$_4$-rich hydrate dissociation and CO$_2$-rich hydrate reformation without water production. The final ceasing pressure was found close to the equilibrium pressure of CH$_4$/CO$_2$ mixed hydrates concerning the initial gaseous CH$_4$/CO$_2$ composition.
- With combined consideration of efficiency and production time, the highest XCH$_4$ reached 81.3 mol% and the corresponding SCO$_2$ was 85.3% through 6-step depressurization with 4-hour shut-in period,
Table S3
Pressure, XCH₄, RCH₄, SCO₂, ΔV and ΔNR₂ at different stages of multistep depressurization in Exp3-4. XCH₄ is the mole fraction of CH₄ in gas phase. RCH₄ is the CH₄ recovery percent. SCO₂ is the CO₂ storage ratio. ΔV is the percentage change of hydrate volume and ΔNR₂ is the percentage change of normalized resistance. The suggested ceasing stage was marked with bold.

| Stage | Pout | XCH₄ | RCH₄ | SCO₂ | ΔV | ΔNR₂ |
|-------|------|------|------|------|----|------|
|       | bar  | mol  | mol% | mol% | %  | %    |
| Before| 41.00| 77.7 | 66.8 | 77.7 | 55.44 | 1.5 |
| A     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| B     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| C     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| D     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| E     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| F     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| G     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| H     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| I     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| J     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| K     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| L     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| M     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| N     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |

Table S4
Pressure, XCH₄, RCH₄, SCO₂, ΔV and ΔNR₂ at different stages of multistep depressurization in Exp5-6. XCH₄ is the mole fraction of CH₄ in gas phase. RCH₄ is the CH₄ recovery percent. SCO₂ is the CO₂ storage ratio. ΔV is the percentage change of hydrate volume and ΔNR₂ is the percentage change of normalized resistance. The suggested ceasing stage was marked with bold.

| Stage | Pout | XCH₄ | RCH₄ | SCO₂ | ΔV | ΔNR₂ |
|-------|------|------|------|------|----|------|
|       | bar  | mol% | mol% | mol% | %  | %    |
| Before| 41.00| 77.7 | 66.8 | 77.7 | 55.44 | 1.5 |
| A     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| B     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| C     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| D     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| E     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| F     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| G     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| H     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| I     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| J     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| K     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| L     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| M     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| N     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |

Table S5
Pressure, XCH₄, RCH₄, SCO₂, ΔV and ΔNR₂ at different stages of multistep depressurization in Exp7-8. XCH₄ is the mole fraction of CH₄ in gas phase. RCH₄ is the CH₄ recovery percent. SCO₂ is the CO₂ storage ratio. ΔV is the percentage change of hydrate volume and ΔNR₂ is the percentage change of normalized resistance. The suggested ceasing stage was marked with bold.

| Stage | Pout | XCH₄ | RCH₄ | SCO₂ | ΔV | ΔNR₂ |
|-------|------|------|------|------|----|------|
|       | bar  | mol% | mol% | mol% | %  | %    |
| Before| 41.00| 77.7 | 66.8 | 77.7 | 55.44 | 1.5 |
| A     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| B     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| C     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| D     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| E     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| F     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| G     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| H     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| I     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| J     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| K     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| L     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| M     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |
| N     | 41.50| 77.6 | 66.8 | 77.7 | 55.44 | 1.5 |

and the depressurization pressure was reduced to 20.74 bar on Type A hydrates of 43.7% S₄w.

- The positive values of normalized resistance percent change (ΔNR₂) after multistep depressurization was correlated with S₄w and shut-in period. A suitable shut-in period of 4 h was most beneficial to both enhanced production performances and improved gas water distribution.

CRediT authorship contribution statement

**Qian Ouyang:** Writing – original draft, Investigation, Formal analysis, Validation, Visualization, Data curation. **Jyoti Shanker Pandey:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Nicolas von Solms:** Supervision, Project administration, Funding acquisition.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

See Tables S1–S6.

Appendix B. Calculation of experimental data

B.1. Hydrate formation

The moles of mixed hydrates \( n_{\text{CH}_4,H, \text{CO}_2,H} \) formed at core holder can be given using Eqs. (1) and (2):

\[
n_{\text{CH}_4,H} = n_{\text{CH}_4,i} - n_{\text{CH}_4,f}
\]

\[
n_{\text{CO}_2,H} = n_{\text{CO}_2,i} - n_{\text{CO}_2,f}
\]

where \( n_{\text{CH}_4,i}, n_{\text{CO}_2,i} \) and \( n_{\text{CH}_4,f}, n_{\text{CO}_2,f} \) are the moles of CH\(_4\) and CO\(_2\) in the gas phase at the starting point before and ending point after hydrate formation; they can be determined using the following Eqs. (3)–(8):

\[
n_{\text{CH}_4,i} = n_{\text{mix},i} \times X_{\text{CH}_4,i}
\]

\[
n_{\text{CO}_2,i} = n_{\text{mix},i} \times X_{\text{CO}_2,i}
\]

where \( X_{\text{CH}_4,i} \) and \( X_{\text{CO}_2,i} \) are the gas mole fraction of CH\(_4\) and CO\(_2\) initially. \( n_{\text{mix},i} \) is the mole amount of mixed gas in the sandstone, which can be calculated:

\[
n_{\text{mix},i} = \frac{P_i V_i}{Z_i R T_i}
\]

where \( P_i \) is the initial pressure at core after mixed gas injection and \( V_i \) is the gas volume inside the core. \( Z_i \) is the compressibility factor of mixed gas at a given temperature and pressure, calculated from Benedict–Webb–Rubin–Starling equation of state. \( R \) is the universal gas constant and \( T_i \) is the initial temperature at the outlet of the core holder.

Table S6
Summary of depressurization schemes in the literatures for comparison in this work. RCH\(_4\) is the CH\(_4\) recovery percent. SCO\(_2\) is the CO\(_2\) storage ratio. XCH\(_4\) is the mole fraction of CH\(_4\) in gas phase.

| Reference          | Water saturation (%) | Pressure drop (bar) | Shut-in period (hours) | Production performances |
|--------------------|----------------------|---------------------|------------------------|-------------------------|
| Sun et al. [67]    | 23.7                 | 37-20               | none                   | RCH\(_4\) = 76%, CO\(_2\) = 40% |
| Shi et al. [53]    | 19.2                 | 145-102-64          | ~100                   | RCH\(_4\) = 17.1%, CO\(_2\) = 41.7% |
| Sun et al. [31]    | 38.8                 | 29.2-17.4           | 50                     | RCH\(_4\) = 30.3%, CO\(_2\) = 16.0% |
| Yang et al. [41]   | 11.5                 | 42-39-35-31-28-25   | 24                     | XCH\(_4\) = 85mol%, CO\(_2\) = 28.8% |
| Pandey et al. [45] | 44.7                 | 37.3-24-24-24-24-24| 24                     | RCH\(_4\) = 73.8%, CO\(_2\) = 82.4% |

Saturation of depressurization schemes in the literatures for comparison in this work. RCH\(_4\) is the CH\(_4\) recovery percent. SCO\(_2\) is the CO\(_2\) storage ratio. XCH\(_4\) is the mole fraction of CH\(_4\) in gas phase.

Reference Water saturation (%)
Pressure drop (bar)
Shut-in period (hours)
Production performances

Sun et al. [67] 23.7 37-20 none RCH\(_4\) = 76%, CO\(_2\) = 40%
Shi et al. [53] 19.2 145-102-64 ~100 RCH\(_4\) = 17.1%, CO\(_2\) = 41.7%
Sun et al. [31] 38.8 29.2-17.4 50 RCH\(_4\) = 30.3%, CO\(_2\) = 16.0%
Yang et al. [41] 11.5 42-39-35-31-28-25 24 XCH\(_4\) = 85mol%, CO\(_2\) = 28.8%
Pandey et al. [45] 44.7 37.3-24-24-24-24-24 24 RCH\(_4\) = 73.8%, CO\(_2\) = 82.4%
Considering CH4/CO2 mixed hydrates occurs inside the core with a constant gas volume, moles of CH4 \( (n_{\text{CH}_4,f}) \) and CO2 \( (n_{\text{CO}_2,f}) \) in the gas phase after hydrate formation are calculated:

\[
\begin{align*}
n_{\text{CH}_4,f} &= n_{\text{mix},f} \times \chi_{\text{CH}_4,f} \\
n_{\text{CO}_2,f} &= n_{\text{mix},f} \times \chi_{\text{CO}_2,f} \\
n_{\text{mix},f} &= \frac{P_v V \chi}{Z_i R T_i} \tag{8}
\end{align*}
\]

where \( \chi_{\text{CH}_4,f} \) and \( \chi_{\text{CO}_2,f} \) are the mole fraction of CH4 and CO2 gas components after hydrate formation. \( n_{\text{mix},f} \) refers to the mole amount of residual mixed gas within the core, calculated from the same gas equation of state using Eq. (8).

In terms of the hydrate composition at the end of hydrate formation, the mole amount of CH4 in the hydrate phase \( (\Delta n_{\text{CH}_4,h}) \) and that of CO2 \( (\Delta n_{\text{CO}_2,h}) \) is given by Eqs. (9) and (10):

\[
\begin{align*}
\Delta n_{\text{CH}_4,h} &= n_{\text{CH}_4,f} - n_{\text{CH}_4,v} \\
\Delta n_{\text{CO}_2,h} &= n_{\text{CO}_2,f} - n_{\text{CO}_2,v} \tag{9, 10}
\end{align*}
\]

### B.2. Hydrate dissociation

Three indicators are employed to evaluate the performance of mixed hydrate dissociation, i.e. CH4 recovery percentage \( R_{\text{CH}_4}(\%) \), CO2 storage ratio \( S_{\text{CO}_2}(\%) \), hydrate volume percent change \( \Delta V(\%) \), and normalized resistance percent change \( \Delta N_{\text{R}}(\%) \). The total CH4 recovery percentage is calculated using the following equations based on different stages of mixed hydrate stability:

\[
R_{\text{CH}_4} = \frac{n_{\text{CH}_4,v}}{n_{\text{CH}_4,h} + n_{\text{CH}_4,f}} \times 100\% \tag{11}
\]

\[
n_{\text{CH}_4,v} \text{ is the total CH4 mole released during multistep depressurization, which can be obtained based on the mass balance and assumption calculation below:}
\]

\[
\begin{align*}
n_{\text{CH}_4,v} &= (\Delta n_{\text{CH}_4,h} + n_{\text{CH}_4,f}) - (\Delta n_{\text{CH}_4,v} + n_{\text{CH}_4,v1}) \tag{12}
\end{align*}
\]

where \( (\Delta n_{\text{CH}_4,h} + n_{\text{CH}_4,f}) \) is the total mole of CH4 at the beginning of multistep depressurization. \( n_{\text{CH}_4,h} \) and \( n_{\text{CH}_4,v1} \) are the mole amount of CH4 remaining in the hydrate and gas phases at the end of multistep depressurization, respectively. When the dissociation pressure is below the CH4 hydrate equilibrium pressure, it can be assumed that all CH4 are recovered, and no CH4 are left in the hydrate phase \( (\Delta n_{\text{CH}_4,v} = 0) \) in terms of the CH4 released during multistep depressurization. And \( n_{\text{CH}_4,v1} \) can be obtained by:

\[
n_{\text{CH}_4,v1} = y_{\text{CH}_4,v1} P_v V \frac{Z_i}{R T_i} \tag{13}
\]

where \( y_{\text{CH}_4,v1} \) is the mole fraction of CH4 in the gas phase after the multistep depressurization.

The corresponding total CO2 storage ratio \( S_{\text{CO}_2}(\%) \) can be given:

\[
S_{\text{CO}_2} = \frac{n_{\text{CO}_2,v}}{n_{\text{CO}_2,h} + n_{\text{CO}_2,f}} \times 100\% \tag{14}
\]

\[
n_{\text{CO}_2,v} \text{ is the total CO2 mole stored in hydrate during cyclic depressurization, which can also be obtained based on the mass balance calculation:}
\]

\[
\begin{align*}
n_{\text{CO}_2,v} &= (\Delta n_{\text{CO}_2,h} + n_{\text{CO}_2,f}) - (\Delta n_{\text{CO}_2,v} + n_{\text{CO}_2,v1}) \tag{15}
\end{align*}
\]

where \( (\Delta n_{\text{CO}_2,h} + n_{\text{CO}_2,f}) \) is the total mole of CO2 at the beginning of multistep depressurization. \( n_{\text{CO}_2,v} \) is the mole amount of CO2 recovered together with CH4-rich gas. When the dissociation pressure is above the CO2 hydrate equilibrium pressure, CO2 gas is enriched in the hydrate phase as CO2 hydrate reformation. It can be assumed that the recovered amount of CO2, together with CH4-rich gas released from CH4 hydrate dissociation, can be ignorable \( \Delta n_{\text{CO}_2,v} = 0 \). \( n_{\text{CO}_2,v1} \) is the mole amount of CO2 in gas phase at the end of multistep depressurization given by:

\[
n_{\text{CO}_2,v1} = y_{\text{CO}_2,v1} P_v V \frac{Z_i}{R T_i} \tag{16}
\]

where \( y_{\text{CO}_2,v1} \) is the mole fraction of CO2 in the gas phase after the multistep depressurization.

The hydrate volume percent change \( \Delta V \) is introduced to investigate the percentage change of mixed hydrate mass, with a positive value of \( \Delta V \) indicating hydrate mass increase and negative one means hydrate mass decrease.

\[
\Delta V = \left( \frac{\Delta V_{\text{CO}_2(0)} - \Delta V_{\text{CH}_4(0)}}{V_H} \right) \times 100\% \tag{17}
\]

where \( V_H \) is the hydrate volume before multistep depressurization, \( \Delta V_{\text{CO}_2(0)} \) and \( \Delta V_{\text{CH}_4(0)} \) refer to the volumes of CO2 stored, and CH4 released,
respectively and given by Equation (18-20):

\[
V_H = \frac{\Delta n_{\text{CO}_2} M_{\text{N}}}{\rho_{\text{CO}_2 H}} + \frac{\Delta n_{\text{H}_2} M_{\text{N}}}{\rho_{\text{H}_2 H}} \tag{18}
\]

\[
\Delta V_{\text{CO}_2(0)} = \frac{n_{\text{CO}_2,0} M_{\text{N}}}{\rho_{\text{CO}_2 H}} \tag{19}
\]

\[
\Delta V_{\text{H}_2(0)} = \frac{n_{\text{H}_2,0} M_{\text{N}}}{\rho_{\text{H}_2 H}} \tag{20}
\]

where \(M_n\) is the molar mass of water (18 g/mol), and \(N\) is the hydrate number (6.00). And \(\rho_{\text{CO}_2 H}\) (0.9 g/cm³) and \(\rho_{\text{H}_2 H}\) (1.1 g/cm³) are the density of \(\text{CO}_2\) hydrate and \(\text{H}_2\) hydrate [1].

The increase of \(\text{CH}_4\) concentration (\(\Delta X_{\text{CH}_4}\)) is calculated as followed:

\[
\Delta X_{\text{CH}_4} = X_{\text{CH}_4\text{lower}} - X_{\text{CH}_4f} \tag{21}
\]

where \(X_{\text{CH}_4\text{lower}}\) is the mole fraction of \(\text{CH}_4\) in the gas phase at the suggested ceasing point, \(X_{\text{CH}_4f}\) is the mole fraction of \(\text{CH}_4\) in the gas phase before multistep depressurization.

The normalized resistance percent change \(\Delta N_{\text{R}}\) is defined as followed:

\[
\Delta N_{\text{R}} = \frac{\text{NR}_{2f} - \text{NR}_{2j}}{\text{NR}_{2j}} \times 100 \tag{22}
\]

where \(\text{NR}_{2j}\) is the value of normalized resistance at the end of each stage and \(\text{NR}_{2f}\) is the corresponding value before multistep depressurization.

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