New insights into the dissociation of mixed CH4/CO2 hydrates for CH4 production and CO2 storage

Pandey, Jyoti Shanker; Ouyang, Qian; Solms, Nicolas von

Published in:
Chemical Engineering Journal

Link to article, DOI:
10.1016/j.cej.2021.131915

Publication date:
2021

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Pandey, J. S., Ouyang, Q., & Solms, N. V. (2021). New insights into the dissociation of mixed CH4/CO2 hydrates for CH4 production and CO2 storage. Chemical Engineering Journal, 427, [131915]. https://doi.org/10.1016/j.cej.2021.131915

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
New insights into the dissociation of mixed CH4/CO2 hydrates for CH4 production and CO2 storage

Jyoti Shanker Pandey*, Qian Ouyang, Nicolas von Solms*

Center for Energy Resource Engineering (CERE), Department of Chemical Engineering, Technical University of Denmark, 2800 Kgs, Lyngby, Denmark

ARTICLE INFO

Keywords:
- Resistance measurement
- Enhanced CH4 recovery
- Production and storage optimization

ABSTRACT

Recent but limited studies have shown that multistep slow depressurization based on mixed CH4/CO2 hydrate dissociation can enhance CH4 recovery and increases CO2 storage after CO2 injection into CH4 hydrate [1,2]. For the first time, the resistivity variation and gas recovery and storage variation was investigated to study the change in hydrate saturation and production/storage yield. Lab-scale CH4 and CO2 rich mixed hydrates were synthesized to mimic the production and injection well scenario. The mixed hydrates were synthesized in sandstone with moderate to high water saturation using two different CH4/CO2 gas mixtures. Furthermore, mixed CH4/CO2 hydrates were dissociated three to six steps based on cyclic depressurization. Pressure, resistivity and gas chromatography data were collected. The presence of two thermodynamic stability zones provided an opportunity for additional CH4 recovery and CO2 storage during mixed hydrate dissociation. Gas and water migration between the injection and production well caused CO2 hydrate reformation, improvement in CO2 sweep area and movement of the CO2 hydrate front toward the production well. Multiple peaks in CH4 recovery and CO2 storage suggest major dissociation and reformation. Peak values were independent of mixed hydrate type. Peaks values of CH4 rich hydrates occurred at high pressure than peak values of CO2 rich hydrates. The slight change in resistance during depressurization below pure CH4 hydrate stability pressure confirms the loss of CH4 hydrate mass. This study discusses the correlation between the change in resistivity and type of guest molecule and its concentration and initial water saturation. The results of this study will be useful to explore the application of slow depressurization for the dissociation of CH4/CO2 mixed hydrates to improve CH4 recovery and CO2 storage.

1. Introduction

Gas hydrates are ice-like compounds of water and certain gases under high pressure and low temperature. The ice-like crystalline compounds are formed by hydrogen bonding and van der Walls forces [3,4]. Naturally occurring gas hydrate deposits contain large amounts of natural gas and are considered a potential gas supply source [5-7]. Attempts are being made to extract gas from these deposits, both in permafrost and in deep oceans. The depressurization based production method is the most discussed and tested [8]. There are many variations of depressurization to optimise gas recovery. These variations include constant rate decompression [9], cyclic decompression [10,11], and slow multistage decompression [12-16]. To overcome the challenges associated with depressurization, hybrid techniques combined with other production techniques have also been proposed, including hybrid with gas injection [17,18] or hybrid with thermal stimulation. The main purpose of the hybrid technique is to avoid geo-mechanical instability, increase heat input to prevent ice or secondary hydrate formation, and enhance CH4 recovery without excessive water or sand production.

Among hybrid techniques proposed, depressurization combined with CO2 injection is very promising due to the potential to store CO2 while producing CH4 from CH4 hydrate dissociation. CO2 rich gas injection into CH4 hydrate itself is a promising technique that offers CO2 storage and assists CH4 gas in hydrate reservoir [19-24]. Pilot tests [25,26] showed that the method leads to lower CH4 recovery and store less CO2 that did not justify the capital investment in CO2 transportation, infrastructure in remote locations etc. The main reason for lower yield is the mass transfer barrier created by CO2 hydrate film [27-29] formation at the injection well that reduces gas injectivity and CO2 sweep area. Gas molecules transport and CO2 concentration at CH4 hydrate surface also reduced due to decreased relative gas permeability caused by hydrate film formation. In laboratory-scale experiments, CO2 injection into CH4...
hydrate would lead to inlet plugging due to CO₂ hydrate formation, resulting in low CH₄/CO₂ hydrate saturation and heterogeneous hydrate distribution.

The depressurization based hybrid method could be a solution to solve this mass transport problem and improve CH₄ recovery and storage yield [18, 27, 28]. In a recent preliminary study, CO₂ gas was injected into depressurized methane hydrate [29], while in another study, depressurization was performed after CO₂ injection [30]. Rapid depressurization before CO₂ injection could be risky as it could trigger significant hydrate dissociation that could not be prevented by CO₂ injection later. Morphology study based on CO₂ injection into depressurized CH₄ hydrate shows the water production was probabilistic after pure CO₂ injection, and probability of water production and presence of hydrates depends on CO₂ concentration in injected gas, injection gas pressure and degree of depressurization [29]. In another study, depressurization was carried out before CO₂ injection and depressurization only contributed 10% in overall CH₄ recovery [31]. On the other hand, mixed CH₄/CO₂ hydrate, when depressurized using stepwise dissociation, showed multiple dissociations and reformation events between CH₄ and CO₂ stability pressure. This phenomenon was exciting as it led to free water consumption in creating CO₂ hydrate, and the risk of water production was reduced [1].

The efficiency of the hybrid depressurization combined with the CO₂ injection technique is dependent on two key factors. First, higher CO₂ injectivity caused a large CO₂ sweep area, and the second is the appropriate depressurization technique. Higher CO₂ injectivity can be improved if CO₂ hydrate film formation can be delayed. A hydrate inhibitor such as low dosage MeOH can improve CO₂ injectivity by delaying CO₂ hydrate film formation at an injection well. MeOH is known to be a thermodynamic hydrate inhibitor when used at concentrations above 30 wt%; however, when used at low or ultralow concentration, it behaves as a promoter [32, 33] or an anti-agglomerate additive [34]. Delayed CO₂ hydrate film formation would allow a larger gas–liquid contact area, and a higher sweep area can be achieved. In our recent studies, experimental studies showed a longer induction time during CH₄ hydrate formation in the presence of MeOH compared to water or other promoters [30]. The selection of appropriate depressurization techniques is also another critical variable. It has been shown that the slow depressurization method is more advantageous compared to direct rapid depressurization. Studies show that slow depressurization [12–14], including cyclic and stepwise, reduces water and sand production risk, maintains the reservoir temperature [33–35], and avoids ice and secondary hydrate production when applied on pure CH₄ hydrate. When cyclic depressurization was applied on CH₄ hydrate, the CH₄ recovery factor improved from 42% to 71% [11]. Moreover, the average production rate increased 17 fold compared to rapid dissociation [10].

In a recent study, we studied cyclic depressurization based on CH₄/CO₂ hydrate dissociation in bulk and unconsolidated sand, with and without additives [2]. It was observed that when cyclic depressurization was implemented between CH₄ and CO₂ hydrate stability pressures, improvement in CH₄ mole fraction and reduction in CO₂ mole fraction was observed. CH₄ recovery rates were higher for higher CH₄ hydrate saturation and T > 0°C.

At the field scale, CO₂ injection into CH₄ hydrate would initiate the CH₄/CO₂ mixed hydrate synthesis with low CH₄ recovery and CO₂ storage yield [29]. CO₂ injection into CH₄ hydrate introduces two gas hydrate stability boundaries (pure CH₄ hydrate and pure CO₂ hydrates) and many intermediate stability zones due to the different compositions of CH₄/CO₂ mixed hydrates. The presence of undissociated CH₄ hydrate and a CO₂-rich vapour phase presents an opportunity that could be further exploited, such that undissociated CH₄ hydrate melt and released water are mixed with the CO₂ vapour phase triggers CO₂ hydrate reforming. Therefore, further insight into the dissociation of CH₄/CO₂ mixed hydrates below the CH₄ hydrate stability is needed. In particular, this is needed to confirm CH₄ hydrate dissociation and CO₂–hydrate reforming from free pore water, which could improve CH₄ recovery and CO₂ storage without loss of hydrate saturation and sediment strength.

Resistivity variation can be used to study hydrate saturation and hydrate stability. Electrical resistivity logs in conjunction with other logs such as electromagnetic measured are typically used to identify and estimate gas hydrate concentration, distribution, and quantification [35–37, 41–43]. As hydrates are poor conductors of electricity compared to the formation water, hydrate formation would indicate an increase in
electrical resistance [38] due to the conversion of formation water into hydrate. Studies show that electrical resistivity is dependent on hydrate saturation, pore water salinity, and hydrate morphology [37,39]. Hydrate conductivity is lower than water [38]. Therefore electrical resistivity could be used to identify formation and dissociation and increase in hydrate saturation that suggests a change in physical properties of hydrate-bearing sediments [40–43]. Studies show that sediment stiffness and electrical resistivity follow a similar trend; therefore, increased electrical resistivity would increase hydrate strength and stiffness [44]. Another area of research is the optimization of gas recovery and storage. Optimization is essential to minimize the production time and increase the gas recovery rate. No such previous study is available yet.

This study assumes that replacement has already occurred and the CH₄/CO₂ mixed hydrate system has been formed. Such systems will be present after injection of CO₂ into CH₄ hydrates as the distribution between injection and production well varies depending on CO₂ sweep efficiency. We have tried to find an answer to the following questions: (1) How do the different CH₄/CO₂ mixed hydrate systems behave during slow depressurization? (2) How does the occurrence of reformsations below the CH₄ hydrate stability pressure affect the resistivity? A change in resistivity would indicate a change in hydrate volume that affects the geo-mechanical stability of hydrate-bearing sediments [40–43]. Studies show that sediment stiffness and electrical resistivity follow a similar trend; therefore, increased electrical resistivity would increase hydrate strength and stiffness [44]. Another area of research is the optimization of gas recovery and storage. Optimization is essential to minimize the production time and increase the gas recovery rate. No such previous study is available yet.

This study assumes that replacement has already occurred and the CH₄/CO₂ mixed hydrate system has been formed. Such systems will be present after injection of CO₂ into CH₄ hydrates as the distribution between injection and production well varies depending on CO₂ sweep efficiency. We have tried to find an answer to the following questions: (1) How do the different CH₄/CO₂ mixed hydrate systems behave during slow depressurization? (2) How does the occurrence of reformations below the CH₄ hydrate stability pressure affect the resistivity? A change in resistivity would indicate a change in hydrate volume that affects the geo-mechanical stability of hydrate-bearing sediments [40–43]. Studies show that sediment stiffness and electrical resistivity follow a similar trend; therefore, increased electrical resistivity would increase hydrate strength and stiffness [44]. Another area of research is the optimization of gas recovery and storage. Optimization is essential to minimize the production time and increase the gas recovery rate. No such previous study is available yet.

This study assumes that replacement has already occurred and the CH₄/CO₂ mixed hydrate system has been formed. Such systems will be present after injection of CO₂ into CH₄ hydrates as the distribution between injection and production well varies depending on CO₂ sweep efficiency. We have tried to find an answer to the following questions: (1) How do the different CH₄/CO₂ mixed hydrate systems behave during slow depressurization? (2) How does the occurrence of reformations below the CH₄ hydrate stability pressure affect the resistivity? A change in resistivity would indicate a change in hydrate volume that affects the geo-mechanical stability of hydrate-bearing sediments [40–43]. Studies show that sediment stiffness and electrical resistivity follow a similar trend; therefore, increased electrical resistivity would increase hydrate strength and stiffness [44]. Another area of research is the optimization of gas recovery and storage. Optimization is essential to minimize the production time and increase the gas recovery rate. No such previous study is available yet.

This study assumes that replacement has already occurred and the CH₄/CO₂ mixed hydrate system has been formed. Such systems will be present after injection of CO₂ into CH₄ hydrates as the distribution between injection and production well varies depending on CO₂ sweep efficiency. We have tried to find an answer to the following questions: (1) How do the different CH₄/CO₂ mixed hydrate systems behave during slow depressurization? (2) How does the occurrence of reformations below the CH₄ hydrate stability pressure affect the resistivity? A change in resistivity would indicate a change in hydrate volume that affects the geo-mechanical stability of hydrate-bearing sediments [40–43]. Studies show that sediment stiffness and electrical resistivity follow a similar trend; therefore, increased electrical resistivity would increase hydrate strength and stiffness [44]. Another area of research is the optimization of gas recovery and storage. Optimization is essential to minimize the production time and increase the gas recovery rate. No such previous study is available yet.
injection well, while CH₄-rich hydrates are mostly concentrated closer to the production well. Therefore, in our study, we have investigated CO₂ rich and CH₄ rich mixed hydrate dissociation.

Five experiments were conducted to investigate hydrate saturation and optimal storage and recovery yield from CH₄/CO₂ mixed hydrate dissociation using the MCD technique. The methodology of the experiments is explained in Fig. 2. The core flow experiment was conducted assuming one injection well and one production well.

The results and discussion are divided into two sections. Section 3.1 deals with CH₄/CO₂ hydrate synthesis using two different gas mixtures, while section 3.2 focuses on mixed CH₄/CO₂ hydrate dissociation using Multi-step cyclic depressurization (MCD) in a porous medium. Resistivity, P-T and GC analysis data were collected.

In the first stage, mixed CH₄/CO₂ hydrates were synthesized using two different feed gasses (30% CO₂ and 70% CO₂) in sandstone with different initial water saturations. The main advantage of using a CH₄/CO₂ gas mixture to synthesise mixed CH₄/CO₂ hydrates is that we can produce different CH₄/CO₂ mixed hydrate types and improve the overall hydrate saturation and distribution along the core length. In the lab scale study, we did not inject pure CO₂ or use kinetic inhibitors/anti-agglomeration agents. We synthesized CH₄/CO₂ mixed hydrate directly from CH₄/CO₂ gas mixture and circumvented the problems with CO₂ injectivity.

To achieve a higher CH₄ and CO₂ molar number in the hydrate and a uniform distribution in the pore space between inlet and outlet, heating and cooling cycles between 1 and 25°C were applied. Using a CH₄/CO₂ gas mixture to achieve uniform hydrate distribution was better than CO₂ injection into CH₄ hydrates. It was a common observation that pressure differential between inlet and outlet was negligible before dissociation, confirming uniform distribution. Pressure and resistance variations were used to investigate whether water and gas migration occurred during the heating and cooling cycle, leading to dissociation and new formation of hydrates.

Hydrate formation was considered complete when pressure remained constant over time, and no differential improvement in hydrate saturation was observed. At this point, a GC sample was taken to examine the change in moles of CH₄ and CO₂ in the vapour phase, which in turn was used to calculate the moles of CH₄ and CO₂ stored in the hydrate (see Appendix A).

During the study, the resistivity variation was also measured. In each experiment, the resistivity was normalized twice. First, during CH₄/CO₂ hydrate synthesis, the resistivity value was normalized concerning the initial resistance value (before formation). The different experiments had different initial resistance values due to the different gas/water distribution caused by pressure, initial water saturation, temperature and confining pressure. Therefore, first normalization (NR1) allowed the comparison of the resistance variations between the different experiments.

The second resistance normalization (NR2) was performed in the MCD method. The resistance change was normalized with respect to the resistance value at the beginning of the MCD method. This was done to measure the increase/decrease in resistivity, which could provide information about the change in hydrate volume and overall hydrate saturation during the MCD method. To apply the MCD method, the outlet valve was opened and closed rapidly so that the pressure fell in the range of 2–6 bar. Before closing the valve, a gas sample was taken to record the mole fraction in the gas phase for the mass balance analysis. The shut-in took 10–20 h to allow gas-water mixing, phase change, and fluid redistribution. Previous studies on the slow, gradual depressurization technique have been limited to pure CH₄ hydrate dissociation. Three types of pressure history curves have been described in the literature when cyclic depressurization was performed on CH₄ hydrates.
pressure rise curve below CH₄ hydrate stability pressure and a later flatter curve. To the best of the author’s knowledge, the pressure response curves during CH₄/CO₂ mixed hydrate dissociation using the slow depressurization method have not been studied previously. Previous studies show that parameters such as shut-in period, pore water chemistry and degree of hydrate saturation also affected the pressure response curve [14] and are therefore studied in the current study.

The presence of CH₄ and CO₂ in the hydrate create two thermodynamic stability boundaries (Pure CH₄ hydrate and Pure CO₂ hydrate) within the CH₄/CO₂ mixed hydrate system. These zones’ boundaries depend on the reservoir properties, including pore size distribution, pore water chemistry, reservoir temperature, hydrate morphology, etc. The CH₄ hydrate stability pressure remains above the CO₂ hydrate stability pressure at the hydrate formation temperature (temperature below 280 K). Between the thermodynamic stability limits of CH₄ and CO₂ hydrate, there may be other temporary hydrate stability boundaries controlled by the composition of the CH₄/CO₂ mixed hydrates. Information on pure stability zones is required to design the slow depressurization scheme. It is advantageous to depressurize the mixed hydrate system so that the pressure is below the CH₄ hydrate phase but above the CO₂ pure hydrate phase. For simplicity, we used the CSMGem-based hydrate stability zones for the bulk-only phase; however, in a porous medium, the stability zones would be different.

There are many variations of the slow depressurization technique, e. g., cyclic, constant pressure, constant rate, etc. Most of these studies are limited to pure CH₄ hydrate dissociation. The application of slow depressurization on CH₄/CO₂ mixed hydrates is very new, and there are still many unknowns. There is no study comparing the best available option between different variants, and this should be the subject of further research. Our previous publication was based on cyclic depressurization, which involved a controlled pressure drop and an extended shutdown period (20 h) [2]. The cyclic pressure release was chosen to allow sufficient time for the reformation to be triggered. There are many unknowns, such as pressure drop, the number of pressure steps, and the total shut-in period. During the shut-in phase, there is continuous mixing of the liquid gas in the pore space. This mixing triggers CO₂-rich hydrate reforming below the CH₄ hydrate stability pressure.

During MCD, the system pressure moves through different stability pressure zones. When the system pressure is above the CH₄ hydrate stability boundary, only the free gas phase is produced, and all hydrate phases remain stable, including pure CH₄, pure CO₂ and mixed CH₄/CO₂ hydrate. Below the CH₄ hydrate stability pressure, pure CH₄ hydrate would dissociate into water and gas. The mixing of released gas and water in the pore space would trigger the formation of CH₄/CO₂ mixed hydrate and CO₂ hydrate [1,2]. Therefore, below the CH₄ hydrate stability zone, the produced gas phase would be rich in CH₄. As the pressure moves further away from the CH₄ hydrate stability boundary and approaches the CO₂-hydrate stability pressure, the unstable mixed hydrate would dissociate, and the CO₂ content in the mixed hydrate would increase.

3. Results and discussion

3.1. CH₄/CO₂ mixed hydrate synthesis

Artificial CH₄/CO₂ hydrates were formed in sandstone with pure water and two different gasses (Gas A, Gas B). Gas A with 30%CO₂ and gas B with 70% CO₂ resulted in different synthesized CH₄/CO₂ mixed hydrates (refer to Table 2 in Appendix A). Hydrate formation and dissociation affect hydrate-containing sediments’ physical properties, including porosity, permeability, tensile strength, stiffness, and resistivity. Fundamental properties such as initial water saturation, initial injection pressure, formation temperature, and CO₂ mole content in the CH₄/CO₂ gas mixture affect the moles of CH₄/CO₂ stored in the hydrates.

Gas A (30 mol% CO₂) was used to form CH₄/CO₂ hydrates in sandstone in Exp.1–3 (Table 2 in Appendix A). Swi varied between 46% and 69%, injection pressure varied P inj = 80–91 bar, and formation temperature varied T f = 1.0–2.1°C. Exp.1–3 underwent 3–4 heating and cooling cycles. During the last cooling, the temperature was gradually reduced from 5°C-6°C to 1-2°C to improve hydrate formation in the pore space. Fig. 4 shows the variation of pressure (inlet and outlet), T (inlet) and NR1 in Exp.1–3.

In general, it was observed that no pressure difference developed between inlet and outlet during hydrate formation. In Exp.3, where pressure difference was developed, there was no correlation between pressure difference (measured at inlet and outlet) and normalized resistance (refer to Fig. 3C). It can be said that the pressure variation was more of a localized phenomenon that may have affected the hydrate distribution in the core but not the resistivity variation. Due to the high water saturation, the hydrate morphology was considered to be pore-filling [47]. Using the methodology in Appendix B, the moles of CO₂ and CH₄ stored in the hydrates were calculated. It was found that the ratio of moles of CH₄/CO₂ stored in the hydrate varied between 1.8 and 2.0, indicating that CH₄/CO₂ hydrates are CH₄-rich and are referred to here as type A hydrates.

The NR1 variation in Exp.2 and Exp.3 was different. Exp.2 and Exp.3 had similar pressure drops at the end of the formation (39 bar in Exp.2 and 38 bar in Exp.3). However, in Exp.2, the CO₂ concentration stored in hydrates was higher due to the higher initial injection pressure (91 bar in Exp.2 and 79 bar in Exp.3, see Table A2 in Appendix A). A recent study showed that the conductivity of hydrate crystals depends on the guest molecules. The study shows that pure CO₂ hydrates have higher conductivity (lower resistivity) than pure CH₄ hydrates [48]. Therefore, in Exp.2, the CO₂ hydrate concentration increased during the subsequent cooling and heating cycles, resulting in a lower NR1 (NR1 was 1.1
In Exp.4–5, gas B (70 mol% CO$_2$) was used to form CH$_4$/CO$_2$ hydrates. S$_{wi}$ varied between 54% and 89%, injection pressure varied $P_{inj} = 54$–70 bar, and formation temperature varied $T_f = 0.8$–1.7 $^\circ$C. Fig. 4 shows the variation of pressure (inlet and outlet), $T$ (inlet) and NR1 in Exp.4–5. During the experiment, 2–3 heating and cooling cycles were performed. During the last cooling, the temperature was gradually reduced from 4.5$^\circ$C to 0.1$^\circ$C to promote hydrate formation in the pore space.

Due to the different initial operating pressure, S$_{wi}$ values and water distribution in the pore space, NR1 varied in Exp.4 and 5. The NR1 value was higher in Exp.4 than in Exp.5 due to the higher total moles and CO$_2$ moles in the hydrates in Exp.4 (see Table A2 in Appendix A). In Exp.4, NR1 value further decreased during the subsequent heating and cooling cycles, which could be attributed to the preferential formation of CO$_2$-rich hydrates over CH$_4$-rich hydrates. This could be due to the higher CO$_2$ solubility in the water phase and the more significant thermodynamic driving force (Higher injection pressure in Exp.4). The discussion of NR1 and its correlation with hydrate mass volume indicate that the resistivity of CH$_4$/CO$_2$ mixed hydrates may be influenced by the nature of the guest molecule and the total hydrate volume. Normalized resistance variation during hydrate formation showed that NR1 increased by 10–14% (in Type A) and 14–19% (in Type B) compared to the initial conditions. The increase in NR1 confirms the presence of hydrate due to the decrease in conductivity caused by the increase in hydrate volume and decrease in pore water volume. The increase in hydrate saturation suggests increased stiffness as resistivity and stiffness follow a similar trend during hydrate formation.

Fig. 5 summarises the main results, including the moles (total, CH$_4$, CO$_2$) in the hydrates and the resistivity (NR1) in Exp.1–5. For Exp.1–3, the total moles stored in the hydrates were higher than Exp.4–5 due to the higher initial injection pressure. The higher water saturation in Exp.4–5 provides a larger gas–liquid contact area, which accelerated

Fig. 6. shows the variation in $P$, $T$, NR2 and XCH$_4$/XCO$_2$ in Exp.1–3 (Type A). A) shows the variation of $P$, $T$, NR2 and XCH$_4$/XCO$_2$ in Exp.1, CH$_4$ stability pressure $P_{CH4} = 31.7$ bar, CO$_2$ stability pressure $P_{CO2} = 15.8$ bar at $T = 2.0$ $^\circ$C. CD stage is divided into seven pressure steps (step A to step G). Starting pressure $P_{start} = 37.3$ bar, and final pressure $P_{finish} = 22.1$ bar, B) shows the variation of $P$, $T$, NR2 and XCH$_4$/XCO$_2$ in Exp.2 CH$_4$ stability pressure $P_{CH4} = 30.8$ bar, CO$_2$ stability pressure $P_{CO2} = 15.2$ bar at $T = 1.7$ $^\circ$C. CD stage is divided into six pressure steps (step A to step F). Starting pressure $P_{start} = 52.5$ bar, and final pressure $P_{finish} = 21.2$ bar. C) shows the variation of $P$, $T$, NR2 and XCH$_4$/XCO$_2$ in Exp.3 CH$_4$ stability pressure $P_{CH4} = 28.4$ bar, CO$_2$ stability pressure $P_{CO2} = 10.3$ bar at $T = 0.9$ $^\circ$C. CD stage is divided into 5 pressure steps (step A to step E). Starting pressure $P_{start} = 41.1$ bar, and final pressure $P_{finish} = 19.4$ bar.
higher CO₂ mole stored than CH₄ mole when CO₂ rich gas (Gas B) was used. The average NR1 values for Exp.4–5 were higher than NR1 values in Exp.1–3. It can be said that NR1 variations correlate with S₈₉₄ values. A similar correlation was observed in our previous study [49]. The correlation between S₈₉₄ and NR1 also shows that the hydrate distribution is heterogeneous and non-uniform along the core length. The resistance variation in the CH₄/CO₂ mixed hydrate system depends on the CH₄ and CO₂ moles stored in the hydrates and the initial water saturation.

Type A and type B hydrates are also expected to differ in hydrate morphology. CH₄-rich type A hydrates are expected to be dominated by hydrate films encapsulating the gas phase, whereas CO₂-rich type B hydrates are formed in the liquid phase due to CO₂ solubility in the water phase. The correlation between NR1 and total hydrate volume is shown in Table A2 in Appendix A. It can be seen that for type A, an increase in hydrate mass volume correlates with a decrease in NR1, while for type B, an increase in hydrate mass volume correlates with an increase in NR1.

3.2. CH₄/CO₂ hydrate dissociation

Synthesized Type A and Type B hydrates were dissociated using Multi-step cyclic depressurization (MCD) to produce additional CH₄ stored in hydrate while storing CO₂ into hydrates. Typically, MCD included 5–7 steps, including rapid degassing followed by a 10–20 h long shut-in period sequence. (Please refer to Appendix B). Tables 3–5 shows the details of the mixed hydrate composition, the MCD scheme applied, and the gas yield and storage yield in Exp.1–5. Data processing concerning this section is supplied in Appendix C.

3.2.1. Cyclic depressurization of type A hydrates

Exp.1–3 typed A hydrates (rich in CH₄ hydrates) were dissociated by the MCD. (Refer to Tables 4 and 5 in Appendix B). Fig. 6 shows the variation of P, T, NR2 and XCO₂/CH₄ during the multistep cyclic depressurization based dissociation.

In Exp.1, MCD included 7 pressure drops and shut-in sequences steps (step A to step G). Of the 7 pressure drops, the pressure drop in the last 6 steps varied between 3 and 5 bar (step B to step G). The first pressure drop at the start of step A was 18 bar, which brought the system pressure into a zone between CH₄ and CO₂ stability pressure. During this rapid pressure drop, a pressure differential was created between the inlet and outlet. During the rapid degassing, the Joule-Thomson cooling may have resulted in ice and secondary hydrate formation at the outlet, which may have caused a pressure differential between the inlet and outlet. Later, due to the long shut-in period, sensible heat from the reservoir was sufficient to dissociate all accumulated hydrates and the pressure difference between inlet and outlet decreased. The pressure differential caused fluid movement in the pore space and additional gas-water mixing. No significant change in the CH₄ mole fraction was observed during step A. CH₄ mole fraction at the end of step A was 75.3%. Thereafter, degassing was not rapid between Step B and Step G, and a pressure drop of 2–4 bar on average was achieved before shut-in. During this time, there was no pressure difference between the inlet and outlet.

After degassing in each step, the pressure rebounced and remained stable between CH₄ and CO₂ hydrate stability line. At the end of step G, the CH₄ mole fraction was 70.1%, and the CO₂ mole fraction was 29.9%. No NR2 variation was recorded during Exp.1.

Fig. 6A show mole fraction variation during Exp.1. The CH₄ mole fraction varied from 70% to 77.6%, with a single peak at the end of Step C (at P = 24.0 bar). RCH₄ varied from 73% to 92.7%, with the first peak of 92.7% at the end of step B (at P = 24.1 bar) and the second peak of 79.2% at the end of step G. The peak CH₄ mole fraction and RCH₄ did not occur at the same pressure steps. It is possible that the gas mole fractions were dependent on the gas/water mixture and formation kinetics, while the recovery factors were related to the molar CH₄ concentration in the hydrates.

During the analysis, SCO₂ increases, reaching a single peak of 83.2% at the end of step D (at P = 22.4 bar). This indicates that the CO₂ concentration in the hydrates was highest at 22.4 bar and further pressure drops attenuated the driving force required for CO₂ hydrate reforming. The SCO₂ peak occurred after the peak in RCH₄, suggesting that CH₄ was involved in CO₂-rich hydrate formation after the peak in RCH₄ optimization. Most of the hydrate reforming was a CO₂-rich hydrate with a lower concentration of CH₄ hydrates.

The hydrate mass volume calculations show that the hydrate mass volume loss is most significant when the pressure is closer to the CH₄ hydrate stability pressure. When the pressure falls below the CH₄ hydrate stability pressure and is in the zone between CH₄ and CO₂ hydrate stability pressures, the loss of CH₄ hydrate volume is compensated by the formation of CO₂-rich hydrate volume. For example, the loss of hydrate volume was equal to ~1.159, which was highest at the end of step A (at P = 24.3 bar). ΔV began to decrease as the pressure dropped below 24.3 bar. At the end of step C, at P = 24 bar, the volume loss was reduced to ~0.694. Thus, while the pressure remained largely stable between step A and stepped C, dissociation and sequential shutdown led to rapid gas/water mixing, resulting in mixed hydrate reforming.

Fig. 6B and C shows the mole fraction variation in Exp.2–3 during the MCD method. Table 3 shows RCH₄, SCO₂ and the volume change in Exp.2–3. MCD was applied in 6 steps (step A to step F) in Exp.2 and pressure dropped from 52 bar to 21.2 bar, while in Exp.3, MCD was applied in 5 steps (step A to step E), and the pressure dropped from 41.1 bar to 19.4 bar. During step A, no drastic change in CH₄ mole fraction was observed (Exp.2–3) because the pressure was above the CH₄ hydrate stability pressure, and only free gas was removed. During step B (in Exp.2 and Exp.3), the pressure dropped below the CH₄ hydrate stability pressure at the beginning of step B. The total shut-in period was 20 h. At the end of step B, the CH₄ mole fraction increased from 72.1% to 78.1% (Exp.2), while it remained unchanged in Exp.3. In Exp.2, outlet pressure was quickly rebounded after degassing, and the pressure differential between inlet and outlet was minimized during the shut-in period. The NR2 value increased during the pressure rise, indicating either the formation of CH₄-rich mixed hydrates or an increase in gas saturation in the pore space.

In Exp.3, outlet pressure continued to drop after degassing, indicating rapid hydrate formation at the outlet. During the shut-in period, the pressure differential remained intact (see C in Fig. 6). The pressure curve at the outlet (Exp.3) indicates rapid reformation and dissociation along the core length, leading to an initial decrease in NR2 followed by an increasing trend. This suggests that CO₂-rich hydrate reformation causes a decrease in NR2. Rebound in pressure curve indicates the partial dissociation of CO₂-rich hydrate and subsequent increase in NR2. The difference in water saturation (In Exp.2 and 3) could have triggered the different responses during the shut-in period. Another factor could be the degree of degassing at the start of step B.

In Exp.2, XCH₄, RCH₄ and SCO₂ had two peaks. The CH₄ mole fraction varied from 72% to 78%, with the first peak XCH₄ = 78.1% at the end of step B (at P = 26.2 bar) and the second peak XCH₄ = 77.9% at the end of step D (at P = 22.0 bar). RCH₄ varied from 55% to 77.2%, with the first peak RCH₄ = 76.7% at the end of step C (at P = 21.9 bar) and the second peak RCH₄ = 77.2% at the end of step F. Another peak suggests increased CH₄ mole fractions in the vapour phase due to dissociation of CO₂-rich hydrates or dissociation of CH₄ hydrates that were screened by CO₂ hydrates [1]. Similarly, SCO₂ varied from 59% to 84.1%, with the first peak SCO₂ = 84.1% at the end of step D (at P = 22.0 bar) and the second peak SCO₂ = 84% at the end of step F (at P = 21.2 bar). The NR2 value decreased by 6%, and the value changed from 1 to 0.94 at the end of the experiment.

In Exp.3, the variation of CH₄ mole fraction and SCO₂ showed only one peak, while RCH₄ showed two peaks. For CH₄ mole fraction, peak XCH₄ = 78.3% was recorded at the end of step D (at P = 20.3 bar). For SCO₂, the peak SCO₂ = 82.9% was recorded at the end of step D (at P = 20.3 bar). For RCH₄, the first peak, RCH₄ = 74.3%, was recorded at the end of step B (at P = 21), and the second peak, RCH₄ = 75.2%, was
recorded at the end of step E (at P = 22.1 bar). NR2 continued to increase, and an overall improvement of 9% was recorded at the end of the experiment. Degassing at the lower pressure values did not cause any significant change in the CH$_4$ mole fraction. In general, after degassing, the pressure increased again within a few minutes and stabilized at a slightly lower pressure than the previous steps. After several steps (5–7), the pressure value stabilized in the 19–21 bar range.

The change in hydrate volume (ΔV) remained negative (in Exp.1–3), indicating the loss of hydrate mass volume during MCD-based dissociation of type A hydrates. The degree of loss in hydrate volume was different across the experiments. For example, the loss of hydrate volume was less in Exp.3 than in Exp.2, which may be due to the higher CO$_2$ mole fraction.

3.2.2. Cyclic depressurization of type B hydrates

Based on the assumptions and calculations described in Appendix B, parameters associated with type B hydrate dissociation is provided in Table 6 in Appendix B. Fig. 7 shows the variation of P, T, XCO$_2$/XCH$_4$, NR2 during Exp.4–5. Exp.4–5 contained type B hydrate (rich in CO$_2$), so the ratio of moles of CO$_2$/CH$_4$ stored in the hydrate varied between 2.3 and 2.6. $S_m$ before hydrate formation varied between 54% and 84%, resulting in a pore-filling hydrate morphology.

In Exp 4, MCD was applied in 3 steps (step A to step C). The CH$_4$ mole fraction (XCH$_4$) varied between 33.8% and 37%. XCH$_4$ had a single peak XCH$_4$ = 36.9% at the end of step A (at P = 15.1 bar). RCH$_4$ varied between 70% and 73.6%, with a peak of only 73.6% at the end of step C (at P = 14.3 bar). Similarly, SCO$_2$ varied between 77.8% and 78.4%, with two peaks at step A and C's end, respectively. The improvement of SCO$_2$ was marginal compared to the improvement of RCH$_4$. The variation of NR2 shows a loss of resistance, and the total value decreased from 1 to 0.97. This decrease in resistance could be due to either improvement in CO$_2$ hydrate concentration or decreased gas saturation.

Fig. 7A shows the response curve in Exp.4. The initial pressure before MCD was well below the CH$_4$ hydrate stability pressure of 30.8 bar. A degassing of 12 bar was performed before step A, which resulted in a pressure drop below the CO$_2$ hydrate pressure. In subsequent pressure drops, the pressure did not rebound and remained closer to the CO$_2$ hydrate stability pressure line. Due to the lower CH$_4$ stored in the hydrate, the CH$_4$ mole fraction increased slightly from 33.8% to 36.9%.

In contrast, the CO$_2$ mole fraction decreased from 66.25 to 65.4%. This suggests that dissociation closer to CO$_2$ stability pressure did not lead to any significant dissociation. The NR2 variation shows a loss of resistivity due to dissociation closer to CO$_2$ hydrate stability pressure. Extend of CO$_2$ hydrate formation was limited in this case; thus, loss of resistivity due to dissociation closer to CO$_2$ hydrate stability pressure. Due to the lower CH$_4$ was marginal compared to the improvement of RCH$_4$.

The pressure value stabilized in the 19–21 bar range. The degree of loss in hydrate volume was different across the experiments. For example, the loss of hydrate volume was less in Exp.3 than in Exp.2, which may be due to the higher CO$_2$ mole fraction.
Comparing NR2 variation with hydrate mass volume in Exp.4–5, it can be said that a higher increase in hydrate mass volume resulted from CO2 incorporation into the hydrate, leading to a decrease in NR2. In contrast, the minor increase in mass volume, but well distributed due to higher water saturation, caused an increase in NR2 in Exp.5.

Multiple peaks (XCH4) in the vapour phase indicate a primary dissociation and reforming event. Below pure CH4 hydrate stability, reforming involves the incorporation of CO2 gas molecules into the hydrate, increasing the CH4 mole fraction in the vapour phase. Another reason could be the dissociation of the CH4-rich mixed hydrate phase, increasing the CH4 mole fraction. Peaks in CH4 mole fraction closer to CH4 hydrate suggest reformation, while peaks in CH4 hydrate closer to CO2 hydrate indicate dissociation of CH4 hydrate (which was previously shielded by CO2 hydrate).

Fig. 8 summarizes the results collected in Exp.1–3 (Type A) and Exp.4–5 (Type B). From Exp.2–3 (Type A), it was found that peak RCH4 varied between 74% and 77% in the pressure range \( P = 20–23 \) bar. Peak SCO2 varied between 82% and 84% obtained in the pressure window of

\[
P_R > P_{CH4} \quad \text{Rapid depressurization} \quad P_R \geq P_{CH4} \quad \text{Concern associated with geo-mechanical stability} \quad P_R \leq P_{CH4} \quad \text{CH4 hydrate}
\]

\[
P_R > P_{CH4} \quad \text{Slow stepwise depressurization} \quad P_R \geq P_{CH4} \quad \text{Concern associated with geo-mechanical stability} \quad P_R \leq P_{CH4} \quad \text{CH4 hydrate}
\]

\[
P_R > P_{CH4} \quad \text{Slow stepwise depressurization} \quad P_R > P_{CH4} \quad \text{CO2/CH4 hydrate} \quad PCO2 < P_R < P_{CH4} \quad \text{CO2 hydrate}
\]

Fig. 8. Overview of parameter summary at the end of MCD method. Fig A-C) shows the RCH4, SCO2 and NR2 values in Exp.1–3 (Type A); Fig D-F) shows the RCH4, SCO2 and NR2 values in Exp.4–5 (Type B).

Fig. 9. Schematic diagram of the proposed production schematic showcasing CH4/CO2 hydrate phase transition during cyclic depressurization. (\( P_h = \) Hydrate reservoir pressure, \( P_{CH4} \) and \( P_{CO2} \) are stability pressure of CH4 and CO2 in reservoirs, KI/AA = kinetic inhibitor/anti agglomerate chemicals).
20 bar to 22 bar. In Exp.4–5 (Type B), peak RCH4 varied between 74% and 77% obtained in the pressure range P = 19–22 bar. The peak value of SCO2 varied between 83% and 84%, obtained in the pressure window of 20–21 bar. The peak values of RCH4 and SCO2 do not coincide but can occur within a specific pressure window. This pressure window was dependent on the type of hydrates. (20–23 bar for type A and 19–22 bar for type B). The peak values were not dependent on the type of mixed hydrates. The RCH4 and SCO2 values were near similar for type A and type B. It was frequently observed that the RCH4 value had two peaks. Multiple peaks in RCH4 confirmed primary dissociation but weaker reformation events. The second peak in RCH4 was closer to the CO2 hydrate stability pressure, suggesting that CH4 gas remains stable in hydrates, either in the form of CO2-rich mixed hydrates and/or protected by a CO2 hydrate layer.

3.3. Practical implications on field-scale trial

Fig. 9 shows the present status of research focused on depressurization based gas production from CH4 hydrates. Previous research studies on depressurization include rapid depressurization, which raises many concerns, including significant dissociation, ice formation, sand/water production, and well bore damage. The primary concern is geo-mechanical instability due to hydrate dissociation. Currently, no long-term field-scale observations could improve our understanding of what happens when pressure is below the thermodynamic stability pressure. To address this concern associated with rapid degassing, a new research is currently focused on implementing slow incremental degassing to optimize production and to address concerns associated with rapid degassing. Slow pressure reduction (degassing) prevents icing, maintains reservoir temperature, prevents rapid dissociation, and avoids downhole damage. As the methane saturation across the hydrate reservoir is heterogeneous, methane stability pressure varies due to the pore size distribution that causes uneven hydrate dissociation and gas production. Thus, even though slow depressurization (degassing) prevents any significant dissociation, concerns associated with geo-mechanical instability below CH4 stability pressure remains there.

In our proposed method, CO2 injection into the partially depressurized CH4 hydrate reservoir is suggested. The partial depressurization is achieved by a slow depressurization technique, which allows optimal CH4 production without destabilization of the in situ hydrates. CO2 injectivity into partially depressurized CH4 would be higher due to improved permeability and availability of migration pathways. To further improve CO2 injectivity and achieve a high sweep range, kinetic inhibitors or anti-agglomeration agents are required to avoid forming a mass transfer barrier (CO2 hydrate film) at the injection well [30,45].

A high CO2 injection volume (in partially depressurized CH4 and in the presence of kinetic inhibitors/anti-agglomeration agents) would ensure a high CO2 concentration in the vapour phase, high CO2 solubility in the residual pore water, and enhanced synthesis of CH4/CO2 mixed hydrates. The CO2 itself is stored in the form of pure CO2 hydrates. The next step in our proposed method is to dissociate CH4/CO2 mixed hydrates by slow depressurization (stepwise/cyclic) to enhance CH4 recovery further and store additional CO2.

The quantity and quality of mixed CH4/CO2 hydrate formation in the porous medium varies due to several factors. In the hydrate production scheme with injection and production well and the presence of good CO2 injectivity and a large sweep region, the hydrate distribution between injection and production well can be divided into three main zones. Type B (CO2 rich) mixed hydrate would be available closer to the injector well, while type A (CH4 rich) hydrate would be available further away from the injection well. Pure CH4 hydrate would be available closer to the production well. The interfaces between the different zones and CH4/CO2 mixed hydrate distribution depend on the total amount of CO2 injection, permeability and porosity of hydrate-bearing sediments, relative CO2 permeability, pore size distribution, initial water saturation, and reservoir temperature.

The differences in hydrate distribution indicate heterogeneity in the system. The presence of heterogeneity in the hydrate system due to CO2 injection would affect the gas production behaviour during depressurization. The gas production technique would also affect the production behaviour. Recent studies indicate that it is beneficial to use a slow stepwise or cyclic method of depressurization [2,16]. In the MCD method, the reservoir pressure initially moves towards the pure CH4 hydrate stability boundary. This would cause pure CH4 hydrate to dissociate at the production well first. The sensible reservoir heat recovers the temperature loss at the production well during the shut-in period, and unwanted hydrate/ice formed at the production well would dissociate. During the MCD technique (or other slow depressurization techniques), when the pressure value falls below the CH4 hydrate stability pressure, mixed hydrate dissociates according to their stability pressure decided by CO2 and CH4 gas concentration inside the hydrates. If the pressure drops further below the CH4 hydrate stability pressure, type A mixed hydrates would dissociate first as their stability pressure is reached. During the shut-in period, gas/water mixing may occur, and any temperature loss would be recovered. Mixed hydrates, when dissociate, releases water and gas. Fig. 10 shows the hydrate distribution after CO2 injection (Fig. 10 A) and during the MCD (Fig. 10B). The released gas, containing both CH4 and CO2, mixes with water and accelerates the formation of CO2-rich mixed hydrate. The likelihood of CO2-rich mixed hydrate formation would be higher because a higher partial pressure-based driving force is available for CO2 hydrate than...
CH₄ hydrates.

When CH₄-rich hydrate (both pure and type A) begins to dissociate at reservoir pressures below the CH₄ hydrate stability pressure, the CH₄ mole fraction in the production well will increase. Due to hydrate dissociation, hydrate saturation in the pore space would decrease, which would improve relative gas permeability and gas migration ability.

Additional CO₂ from the injection well side starts to move towards the production well, and gas and water mix happen closer to the production well during the shut-in period.

During the shut-in period, CO₂ saturated pore water may also transport in the pore space, which could trigger CO₂-rich hydrates at the gas-liquid interface. This would improve the CH₄ mole fraction in the residual vapour phase. CH₄ mole fraction is also affected by the CH₄ hydrate saturation remaining in the hydrate and the pressure difference between type A and type B hydrates. When the CO₂ hydrate reforming is triggered near the production well, the CO₂-rich type B hydrate front moves toward the production well and the type A hydrate would decrease. (see Fig. 10B). The advancement of the type B front toward the production well indicates that the CO₂ sweep area increases and additional CO₂ gas molecules may interact with the surface of the CH₄ hydrates, leading to CH₄ production by hydrate exchange. CO₂ reformation kinetics below CH₄ hydrate stability pressure is essential in optimizing CH₄ recovery below CH₄ hydrate stability pressure without destabilizing hydrate-bearing sediments.

In this study, no significant loss of resistivity was observed. The increase in resistivity value and improvement in hydrate mass volume at high water saturation is attributed to CO₂ rich hydrate reformation enhanced by uniformly dispersed CO₂ saturated liquid phase. This reduced the risk of water production or loss of hydrate mechanical strength. Further experiments on mechanical strength during cyclic depressurization are needed to compare the strength of CO₂-rich hydrate versus CH₄-rich hydrate.

Key factors that can trigger and control reforming include pore water chemistry, gas/water contact area, formation kinetics, gas/water migration, capillary forces, and pore water freshening. Although an extended shut-in period is beneficial because it provides sufficient time for reformation and hydrate redistribution and storage, valuable production time is lost. Therefore, it is necessary to minimize the shut-in period to optimize gas production while maintaining reservoir temperature, avoiding ice formation and hydrate strength, and allowing hydrate reformation [11]. Chemical compounds such as kinetic inhibitors/agglomeration inhibitors would affect the reforming kinetics at the gas/liquid interface and affect the shut-in period. The shut-in period may either prolong or shorten due to pore water chemistry alteration. Therefore, further studies on the slow depressurization of CH₄/CO₂ mixed hydrate in the presence of different chemicals are needed.

The speed and magnitude of the pressure drop control the driving force of hydrate dissociation. Large and rapid pressure drops could result in a significant temperature drop that may trigger ice formation during production, requiring a longer shutdown time. A study showed that smaller pressure drops improve the dissociation behaviour than more significant pressure drops for a pure CH₄ hydrate system [12]. Similar studies are required for the mixed CH₄/CO₂ hydrate system.

4. Conclusions

CO₂ injection into a CH₄ hydrate reservoir produces CH₄/CO₂ mixed hydrates with CO₂-rich mixed hydrates closer to the injection well and CH₄-rich mixed hydrates away from the injection wells. The presence of two distinct hydrate stability regions allowed us to produce CH₄ gas while storing additional CO₂ in hydrates using the Multistep cyclic depressurization relief (MCD) technique [2]. This study investigated the resistivity variation and CH₄ production/CO₂ storage behaviour for CH₄-rich and CO₂-rich mixed hydrates synthesized in the sandstone pores. The main conclusions are given below:

- The ratio of CH₄/CO₂ stored in hydrates depends on the CH₂/CO₂ composition in the feed gas. CH₄-rich feed gas produces a CH₄-rich mixed hydrate system, while CO₂-rich feed gas produces a CO₂-rich mixed hydrate system. The relative content of CH₄/CO₂ in the feed gas also controls the hydrate morphology. CH₄-rich hydrate morphology would be dominated by hydrate films encapsulating the gas phase and high residual water saturation, while CO₂-rich hydrate formation involves crystalization of gas-saturated water and low residual water saturation.
- In the synthesis of CH₄/CO₂ mixed hydrates, the resistance variation shows 10–14% improvement for CH₂-rich mixed hydrates and 14–19% for CO₂-rich hydrates. The resistance variation depends on the initial water saturation (S_wi), the type of guest molecule and its concentration, the total hydrate volume. The resistance variation correlated with the pressure variation but could not account for the heterogeneity of hydrate saturation over the core length.
- Dissociation of CH₄/CO₂ mixed hydrates shows that the peaks of the XCH₄ and RCH₄ variants do not coincide. Multiple peaks indicate primary dissociation and reformation events. Peaks in RCH₄ indicate significant dissociation and reformation during the shut-in period, while peaks in SCO₂ indicate significant reformation.
- Peaks in RCH₄ closer to CO₂ hydrate stability pressure suggest that CH₄ may remain stabilized in hydrate closed to CO₂ hydrate stability pressure, either in the form of CO₂ rich hydrate or self-preserved surrounded by CO₂ hydrate crystals.
- The results show that the peak values in RCH₄ and SCO₂ do not depend on the type of mixed hydrates. The peak values in RCH₄ and SCO₂ occur at a higher pressure for CH₄-rich hydrates than CO₂-rich hydrates.
- NR2 varied between −6% to ± 9% during 3–7 steps based on slow cyclic depressurization, confirming the presence of hydrate volume mass as pressure approached CO₂ hydrate stability pressure. Thus, the significant loss of CH₄ hydrate mass volume was compensated by CO₂ hydrate mass volume formation. Positive hydrate mass volume was formed during the CO₂-rich mixed hydrate dissociation, whereas hydrate mass volume decreased during the CH₄-rich mixed hydrate dissociation.

Funding

The Danish Council for Independent Research funds this research.

CRediT authorship contribution statement

Jyoti Shanker Pandey: Writing – original draft, Visualization, Writing – review & editing, Conceptualization, Methodology, Formal analysis, Supervision, Data curation. Qian Ouyang: Formal analysis, Investigation, Visualization. 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.
Appendix A. CH\textsubscript{4}/CO\textsubscript{2} hydrate synthesis information in Exp. 1–5

A.1 Core samples used in the study.

A.2 CH\textsubscript{4}/CO\textsubscript{2} hydrate synthesis in a porous medium

Appendix B. Dissociation data from MCD

B.1 Dissociation summary

B.2 Dissociation data during application of MCD on Exp. 1–5

Table 4
Details CH\textsubscript{4} recovery and CO\textsubscript{2} storage yield from Type A Hydrate (Exp. 1). The table includes information about RCH\textsubscript{4}, SCO\textsubscript{2} and NR2 values at the end of each step. (Peak values are bold and underline).

Table 3
Experimental details of mixed hydrates system in sandstone. T\textsubscript{SD} is the temperature during cyclic depressurization, P\textsubscript{CH\textsubscript{4}} = CH\textsubscript{4} hydrate stability pressure at T\textsubscript{SD}, P\textsubscript{CO\textsubscript{2}} = CO\textsubscript{2} hydrate stability pressure at T\textsubscript{SD}; nCO\textsubscript{2} and nCH\textsubscript{4} are the moles of CO\textsubscript{2} and CH\textsubscript{4} stored in the hydrates. P\textsubscript{start} = pressure before the first pressure drop, P\textsubscript{finish} = pressure at the end of the experiment.

Table 2
Shows the formation experiments that were performed, which included the first formation and followed by dissociation. Exp. 1–3 used 30% CO\textsubscript{2} to form CH\textsubscript{4}/CO\textsubscript{2} hydrate (Type A) while Exp. 4–5 used 70% CO\textsubscript{2} to form CH\textsubscript{4}/CO\textsubscript{2} hydrates (Type B). Swi = Initial water saturation, Pi, Ti are initial pressure and temperature.

Table 1
Shows experimental parameters for sandstone cores and feeds gas composition used for CH\textsubscript{4}/CO\textsubscript{2} hydrate synthesis. Swi = Initial liquid saturation. Table 1. The injected gas and prepared sandstone sample properties before the experiment.
Table 5

Provides details of CH₄ recovery and CO₂ storage yield from Type A Hydrate (Exp.2–3). The table includes information about RCH₄, SCO₂ and NR2 values at the end of each step.

| Exp.2(Sat. = 46%) PCH₄ = 30.8 bar, PCO₂ = 15.2 bar | Exp.3(Sat. = 69%) PCH₄ = 28.4 bar, PCO₂ = 10.3 bar |
|---------------------------------------------------|---------------------------------------------------|
| Stage P (bar) | ΔV (ml) | P (bar) | ΔV (ml) | Stage | ΔV (ml) | Stage | ΔV (ml) |
|--------------|---------|---------|---------|--------|---------|--------|---------|
| Yₚₑₜ        |         |         |         |        |         |        |         |
| 52.5        | 73.9    | 26.1    | 60.9    | 49.8   | 1.00    | 41.1   | 73.4    | 26.6    | 54.3   | 54.0   | 1.00    |
| 41.4        | 72.1    | 27.9    | 55.0    | 59.4   | 0.99    | -0.63  | 32.8    | 73.6    | 26.4    | 57.9   | 64.8   | 1.02   | -0.45 |
| 26.2        | 78.1    | 21.9    | 71.0    | 81.0   | 0.98    | -0.79  | 21.0    | 73.4    | 26.6    | 74.3   | 78.2   | 1.04   | -0.43 |
| C 21.9       | 76.0    | 24.0    | 76.7    | 82.8   | 0.98    | -0.88  | 20.6    | 77.1    | 22.9    | 73.5   | 81.6   | 1.06   | -0.43 |
| D 22.0       | 77.9    | 22.1    | 76.0    | 84.1   | 0.97    | -0.86  | 20.3    | 78.3    | 21.7    | 73.6   | 82.9   | 1.07   | -0.45 |
| E 22.1       | 77.6    | 22.4    | 76.0    | 83.9   | 0.95    | -0.86  | 19.4    | 76.8    | 23.2    | 75.2   | 82.5   | 1.09   | -0.34 |
| F 21.2       | 76.9    | 23.1    | 77.2    | 84.0   | 0.94    | -0.88  | 18.5    | 75.6    | 24.2    | 74.4   | 81.1   | 1.04   | -0.39 |

Table 6

Details associated with CH₄/CO₂ mole fractions, RH CH₄/SCO₂, NR2 and ΔV during Type B hydrate dissociation (Exp.4–5).

| Exp.4(Sat. = 58%) PCH₄ = 30.8 bar, PCO₂ = 15.2 bar | Exp.5(Sat. = 84%) PCH₄ = 37.8 bar, PCO₂ = 14.6 bar |
|---------------------------------------------------|---------------------------------------------------|
| Stage P (bar) | ΔV (ml) | P (bar) | ΔV (ml) | Stage | ΔV (ml) | Stage | ΔV (ml) |
|--------------|---------|---------|---------|--------|---------|--------|---------|
| Yₚₑₜ        |         |         |         |        |         |        |         |
| 23.0        | 33.8    | 66.2    | 44.1    | 63.0   | 1.00    | 37.8   | 29.3    | 70.7    | 47.3   | 51.1   | 1.00    |
| A 15.1      | 36.9    | 63.1    | 70.0    | 78.0   | 0.98    | 0.34   | 35.7    | 28.9    | 71.1    | 56.8   | 54.4   | 1.01   | 0.11 |
| B 14.7      | 34.6    | 65.4    | 72.6    | 77.8   | 0.98    | 0.33   | 14.6    | 35.2    | 64.8    | 81.5   | 85.4   | 1.01   | 0.18 |
| C 14.3      | 34.4    | 65.6    | 73.6    | 78.4   | 0.97    | 0.33   | 15.2    | 45.7    | 54.3    | 75.3   | 87.4   | 1.01   | 0.21 |
| D 15.2      | 41.0    | 58.9    | 77.6    | 86.7   | 1.01    | 0.19   | 14.6    | 42.9    | 57.1    | 77.7   | 87.3   | 1.00   | 0.20 |
| E 14.6      | 43.3    | 56.7    | 77.5    | 87.4   | 1.01   | 0.20   |        |         |         |        |        |        |        |

Appendix C

C.1 Artificial CH₄/CO₂ Hydrate

Initial moles of gas (n(CH₄), n(CO₂)) injected into the core flooding setup is given by

\[ n_{CH_4} = \frac{Y_{CH_4} P_i V_i}{z_i RT_i} \]  
\[ n_{CO_2} = \frac{Y_{CO_2} P_i V_i}{z_i RT_i} \]  

(1) \hspace{1cm} (2)

Where Pᵢ is the initial operating pressure recorded after gas mixture was injected, Vᵢ is the available gas volume inside the core, Tᵢ is the recorded experimental temperature at inlet corresponding to Pᵢ, R is the universal gas constant, and zᵢ is the compressibility factor at the given pressure and temperature, calculated from the Benedict–Webb–Rubin–Starling equation of state and corresponding mole fraction of each gas component respectively. Y(CH₄), Y(CO₂) are the gas mole fractions of CH₄ and CO₂ in the injected gas.

For constant volume processes, assuming, hydrate formation inside the core holder is batch process with constant gas volume, number of moles of each gas (n(CH₄), n(CO₂)) in vapor phase after mixed CH₄/CO₂ hydrate formed is determined by

\[ n_{CH_4} = \frac{Y_{CH_4} P_f V_i}{z_f RT_f} \]  
\[ n_{CO_2} = \frac{Y_{CO_2} P_f V_i}{z_f RT_f} \]  

(3) \hspace{1cm} (4)

Pᵢ is the stabilized pressure recorded at the end of the cooling cycle with the stabilized Tᵢ for hydrate formation, and zᵢ is the compressibility factor for Pᵢ and Tᵢ conditions and corresponding mole fraction of each gas component respectively. Thus, the moles number of CH₄ trapped in the solid hydrate crystal after hydrate formation Δn(CH₄,H) is given by

\[ Δn_{CH_4,H} = n_{CH_4,f} - n_{CH_4,i} \]  
\[ Δn_{CO_2,H} = n_{CO_2,f} - n_{CO_2,i} \]  

(5) \hspace{1cm} (6)

C.2. Experimental data processing during the multistep cyclic depressurization

To calculate the CH₄ recovery and CO₂ storage during MCD, simplified mass balance equations were used. Basic assumption during mass balance are following.
because the ratio of the cage to molecular diameter is optimized [34,35]. The results (see Table 7) show that the CH
and CO
J.S. Pandey et al.

> S

D.1 Calculation of moles of CH
Appendix D

Key assumption included,

1- \( \Delta n_{CH_4, step} \) is the number of moles of CH
remaining in the hydrate at the end of the cyclic depressurization. During multistep cyclic depressurization, when the pressure in the system was below the CH
hydrate stability pressure, it can be assumed that all moles of CH
are left stored in the hydrates \( \Delta n_{CH_4, step} = 0 \).

2- For simplicity, it was assumed that all gas escaping during MCD is rich in CH
as CH
hydrate dissociates and CO
2 go into hydrate during CO
hydrates reformation. Total CO
moles escaped during venting are negligible \( \Delta n_{CO_2, Re} = 0 \).

Before multistep cyclic depressurization technique implementation, moles of CH
and CO
in the vapor phase \( n_{CH_4, f}, n_{CO_2, f} \) and hydrate phase \( \Delta n_{CH_4, h}, \Delta n_{CO_2, h} \) were known. During the controlled multistep cyclic depressurization stage, the pressure at the outlet was rapidly dropped to \( P_{step, 2} \) and thereafter valve was shunted. After approximately 10–12 h of shut-in period, pressure changed to \( P_{step, 3} \) inside the core holder due to multi phase flow on account of dissociation and/or reformation. Change in CH
or CO
mole fraction in the cell indicating a change in molar concentration of CH
and CO
in vapor phase due to dissociation and reformation within CH
/CO
hydrate system. Assuming that this was last step no further pressure drops were applied. At this point, GC analysis was performed to know the mole fractions of CH
and CO
in gas phase. The number of moles at this stage was given by

\[
\begin{align*}
\Delta n_{CH_4, h} & = \frac{Y_{CH_4, step} P_{step, 2} V_1}{z_{CH_4, step} R T_{step, 2}} \\
\Delta n_{CO_2, h} & = \frac{Y_{CO_2, step} P_{step, 2} V_1}{z_{CO_2, step} R T_{step, 2}}
\end{align*}
\]

Where \( Y_{CH_4, step} \), \( Y_{CO_2, step} \) are the molar composition of the gas for pressure \( P_{step, 2} \) collected and determined by gas chromatography. Total CH
recovery \( R_{CH_4} \) during multistep cyclic depressurization technique from mixed hydrate can be given by

\[
R_{CH_4} (\%) = \frac{\Delta n_{CH_4, Re}}{\Delta n_{CH_4, h} + n_{CH_4, f}} \times 100
\]

\( \Delta n_{CH_4, Re} \) is the total CH
molecules released during the venting. It can be calculated based on the mass balance equation discussed previously. Total CO
storage \( S_{CO_2} \) during multistep cyclic depressurization technique is given by

\[
S_{CO_2} (\%) = \frac{\Delta n_{CO_2, step}}{\Delta n_{CO_2, h} + n_{CO_2, f}} \times 100
\]

\( \Delta n_{CO_2, step} \) is the total CO
molecules stored in the hydrate. It can be calculated based on the mass balance equation discussed previously. Total volume of hydrate mass was calculated using net moles produced or stored in each step. Positive \( \Delta V \) indicate gain in hydrate mass volume and negative \( \Delta V \) indicates loss in hydrate mass volume with respect to starting condition.

\[
\Delta V = \Delta VCO_2 (Stored) - \Delta VCH_4 (Produced)
\]

Appendix D

D.1 Calculation of moles of CH
and CO
stored in hydrates

Table 7 shows the ratio (mole of CH
/mole of CO
) in the experimental studies. Previous studies show that in the synthesis of CH
/CO
mixed hydrates, CO
goes into large cages \( 5^{12} 6^{2} \), and CH
molecules go into small cages \( 5^{12} \) because the ratio of the cage to molecular diameter is optimized [34,35]. The results (see Table 7) show that the CH
cage occupancy in large and small cages depends on the CH
concentration in the feed gas. Based on CSMGem calculation, in Exp. 1–3, the CH
hydrate cage occupancy in the large cage
Table 7

Provides the details of cage occupancy and total moles stored in hydrates for the CH4/CO2 gas mixture. R(CH4/CO2) is the ratio of CH4/CO2 moles stored in hydrates.

| Exp.1 | Exp.2 | Exp.3 | Exp.4 | Exp.5 |
|-------|-------|-------|-------|-------|
| CH4 at small cage | 1.359 | 1.313 | 1.447 | 0.874 | 1.201 |
| CH4 at large cage | 2.851 | 2.645 | 3.509 | 1.174 | 2.198 |
| CO2 at small cage | 0.208 | 0.232 | 0.133 | 0.530 | 0.292 |
| CO2 at large cage | 2.872 | 3.073 | 2.185 | 4.576 | 3.516 |
| R(CH4/CO2 (H-mol)) | 1.36 | 1.19 | 2.14 | 0.40 | 0.89 |

was higher than that in the small cage when 70% CH4 gas was used in the feed gas. When the CO2 mole fraction was 70%, CH4 cage occupancy was higher in the small cages than in the large cages. Exp. 1–3 (type A) the ratio was above 1, while in Exp. 4–5 (type B), the ratio was less than 1.

References

[1] J.S. Pandey, O. Strand, N. von Solms, G. Erland, S. Almenningen, Direct visualization of ch 4 /co 2 hydrate phase transitions in sandstone pores, Cryst. Growth Des. 21 (2021) 2793–2806.

[2] J.S. Pandey, C. Karantonidis, Q. Ouyang, N. von Solms, N. of cyclic depressurization-driven enhanced ch 4 recovery after ch 4 / co 2 hydrate, J. Phys. Chem. Lett. 35 (11) (2021) 9521–9537.

[3] E.D. Sloan, C.A. Koh, C.A. Koh, E. Sloan Jr., C. Koh, C. Koh, E.D. Sloan Jr., C. A. Koh, C.A. Koh, E.D. Sloan, C.A. Koh, C.A. Koh, Clash Hydrates of Natural Gases, 3rd ed., CRC Press, Boca Raton, FL, USA, 2007.

[4] C.A. Koh, E.D. Sloan, A.K. Sum, D.T. Wu, Fundamentals and applications of gas hydrates, Annu. Rev. Chem. Biomol. Eng. 2 (2011) 237–257.

[5] T. Collett, J.J. Bahl, R. Baker, R. Boswell, D. Divins, T.S. Collett, R.E. Lewis, W.J. Winters, M.W. Lee, K.K. Rose, R.M. Boswell, Apparatus therefore. U.S. Patent 5,261,490, 1993, pp. 1–13.

[6] T. Ebinuma, Method for dumping and disposing of carbon dioxide gas and methane hydrate. U.S. Patent 6,261,490, 1999, pp. 1–16.

[7] K. Ohgaki, K. Takeshiro, H. Takahashi, T. Matsubara, S. Nakano, Methane exploitation by carbon dioxide from gas hydrates. Phase equilibria for CO2/CH4 mixed hydrate system, J. Chem. Eng. Japan 29 (1996) 478–483.

[8] H.J. Lee, J.D. Lee, P. Linga, P. Englezos, Y.S.Y. Kim Do, M.S. Lee, Y.S.Y. Kim, Do Gas hydrate formation process for pre-combustion capture of carbon dioxide, Energy 35 (2010) 2729–2733.

[9] F.M. Orr Jr., CO2 capture and storage: are we ready? Energy Environ. Sci. 2 (2009) 449–460.

[10] H.S. Salem, G.V. Chilingarian, Determination of specific surface area and mean pore size of gas hydrate samples, J. Chem. Eng. Data 60 (2015) 319–329.

[11] H.K. Abay, T.M. Svartaas, Effect of ultralow concentration of methanol on methane hydrate dissociation in coarse-grained sediments by slow, stepwise depressurization test in mallik, northwest territories, Canada, Energy Fuels 30 (2016) 6210–6219.

[12] T. Collett, J.J. Bahl, R. Baker, R. Boswell, D. Divins, T.S. Collett, R.E. Lewis, W.J. Winters, M.W. Lee, K.K. Rose, R.M. Boswell, Apparatus therefore. U.S. Patent 5,261,490, 1993, pp. 1–13.

[13] T. Collett, J.J. Bahl, R. Baker, R. Boswell, D. Divins, T.S. Collett, R.E. Lewis, W.J. Winters, M.W. Lee, K.K. Rose, R.M. Boswell, Apparatus therefore. U.S. Patent 5,261,490, 1993, pp. 1–13.

[14] T. Collett, J.J. Bahl, R. Baker, R. Boswell, D. Divins, T.S. Collett, R.E. Lewis, W.J. Winters, M.W. Lee, K.K. Rose, R.M. Boswell, Apparatus therefore. U.S. Patent 5,261,490, 1993, pp. 1–13.

[15] T. Collett, J.J. Bahl, R. Baker, R. Boswell, D. Divins, T.S. Collett, R.E. Lewis, W.J. Winters, M.W. Lee, K.K. Rose, R.M. Boswell, Apparatus therefore. U.S. Patent 5,261,490, 1993, pp. 1–13.
[41] X. Zhou, S. Fan, D. Liang, D. Wang, N. Huang, Use of electrical resistance to detect the formation and decomposition of methane hydrate, J. Nat. Gas Chem. 16 (2007) 399–403.

[42] K.A. Birkedal, G. Ersland, L. Petter, Ø. Hauge, A. Graue, K. Hester, J. Stevens, J. Howard, Electrical resistivity measurements of ch4 hydrate-bearing Sandstone During Formation (2011).

[43] S. Li, X. Xia, J. Xuan, Y. Liu, Q. Li, Resistivity in formation and decomposition of natural gas hydrate in porous medium, Chin. J. Chem. Eng. 18 (2010) 39–42.

[44] J.W. Jung, J. Carlos Santamaria, 4-CO$_2$ replacement in hydrate-bearing sediments: a pore-scale study, Geochem. Geophys. Geosys. 11 (12) (2010) n/a-n/a.

[45] Prashant Jadhawar, Jinhyang Yang, Antonin Chapoy, Bahman Tohidi, Subsurface carbon dioxide sequestration and storage in methane hydrate reservoirs combined with clean methane energy recovery, Energy Fuels 35 (2) (2021) 1567–1579.

[46] T.X. Le, S. Rodt, D. Hautemayou, P. Aimedieu, M. Bornert, B. Chabot, A.M. Tang, Kinetics of methane hydrate formation and dissociation in sand sediment, Geomech. Energy Environ. 23 (2020) 100103.

[47] A. Kumar, B. Maini, P.R. Bishnoi, M. Clarke, O. Zatsepina, S. Srinivasan, Experimental determination of permeability in the presence of hydrates and its effect on the dissociation characteristics of gas hydrates in porous media, J. Pet. Sci. Eng. 70 (2010) 114–122.

[48] Stern, L.A.; Constable, S.; Lu, R.; Du Frane, W.L.; Roberts, J.M. Electrical conductivity of pure CO2 hydrate and CH4 hydrate: Role of the guest molecule 2021.

[49] Jyoti Shanker Pandey, Saad Khan, Adam Paul Karcz, Nicolas von Solms, Chemically modified hydrate swapping and hydrate stability during multistage CO2-N2 injection schemes, Fuel 299 (2021) 120711, https://doi.org/10.1016/j.fuel.2021.120711.

[50] K. Yamamoto, T. Kanno, X.X. Wang, M. Tamaki, T. Fujii, S.S. Chee, X.W. Wang, V. Pimenov, V. Shako, Thermal responses of a gas hydrate-bearing sediment to a depressurization operation, RSC Adv. 7 (2017) 5554–5577.

[51] Yongkoo Seol, Evgeniy Myshakina, Experimental and numerical observations of hydrate reformation during depressurization in a core-scale reactor, Energy Fuels 25 (3) (2011) 1099–1110.