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Insights into multistep depressurization of CH$_4$/CO$_2$ mixed hydrates in unconsolidated sediments

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Abstract

Natural gas hydrates (NGH) are potential energy resource and distributed in unconsolidated marine sediments. CH$_4$–CO$_2$ swapping combined with depressurization is a promising method for simultaneously enhancing CH$_4$ recovery and CO$_2$ storage in NGH. This combined method was previously studied on CH$_4$/CO$_2$ mixed hydrates in consolidated sediments but no such studies are available for unconsolidated sediments. In this study, we investigated dissociation characteristics of CH$_4$/CO$_2$ hydrates in unconsolidated sediments using slow multistep depressurization. CH$_4$/CO$_2$ hydrates were formed in unconsolidated sandpack. The effects of CH$_4$/CO$_2$ molar ratio (CH$_4$-rich and CO$_2$-rich) in hydrate, residual water saturation (9.2% to 31.7%) and reservoir temperature (−3.3 °C to 2.2 °C) on production and storage efficiencies were mainly investigated, and the results were compared to those of bulk water and consolidated sediments in literatures. The results showed that CO$_2$ was preferably encaged in hydrate than CH$_4$ and this phenomenon was most apparent in unconsolidated sediments. CH$_4$-rich hydrates in unconsolidated sediments were recommended to be exploited by multistep depressurization. Higher residual water saturation was unbeneficial to CH$_4$ gas recovery, while a lower value was not conducive to CO$_2$ storage in hydrate. Temperature below or above freezing point mainly decided ice formation and affected CH$_4$ gas yield and CO$_2$ retention by mass transfer. CH$_4$ recovery was primarily dependent on degree of depressurization with higher CH$_4$ recovery percent at lower depletion pressure. The maximum increment of CH$_4$ concentration (6.5 mol%) and the highest CO$_2$ storage efficiency (88.2%) were achieved in CH$_4$-rich hydrates at optimum residual water saturation of 17.7% and temperature above 0 °C. In addition, sediments were the key factor controlling production and storage performances, and unconsolidated sediments provided a larger contact area among CO$_2$ gas, CH$_4$ hydrate and mobile water than consolidated sediments and bulk water. The results in this work could be useful for future NGH exploitation after CO$_2$ injection into CH$_4$ hydrates in unconsolidated sediments.

Keywords:
Natural gas hydrates
Unconsolidated sediments
Multistep depressurization
CH$_4$ recovery
CO$_2$ storage

1. Introduction

Natural gas hydrates (NGH) are ice-like crystalline compounds formed by light gases (CH$_4$, C$_2$H$_6$, CO$_2$ etc.) and water at specific high-pressure and low-temperature [1]. These conditions occur in marine sediments and permafrost regions. It is estimated that the reserve of organic carbon bounded in NGH (mainly CH$_4$) exceeds twice amount of that in coal, oil and gas resources [2–4]. One volume of hydrate can release 164 vol of CH$_4$ at standard temperature and pressure [5]. Majority of NGH reserve is found at depths over 300 m in marine, where accumulation conditions are loose unconsolidated sediments such as sand, silt and gray, whereas minority is distributed at 200–1700 m under continental permafrost, in which are consolidated sediments such as sandstone and shale [6,7]. Nevertheless, hydrates in porous media cement particles and thus maintain strength and stiffness of sediments [8].

Abundant reserve and high energy density of NGH trigger extensive investigation on exploitation methods in either laboratory or field test, including depressurization [9,10], thermal stimulation [11,12], inhibitor injection [13,14] and CH$_4$–CO$_2$ swapping [15,16]. Depressurization is regarded the most economical for its operation simplicity. The principle is reducing reservoir pressure to below hydrate equilibrium pressure through fluid extraction. NGH therefore become thermodynamically unstable and dissociate into water and gas.

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However, direct depressurization easily induces problems of hydrate reformation or ice formation due to insufficient heat supply. Hence, different depressurization strategies are proposed to ensure efficient gas production, such as constant-rate depressurization [17,18], cyclic depressurization [19,20] and stepwise depressurization [21–23]. Specifically, constant-rate depressurization controls specific reduction rate of reservoir pressure. Cyclic depressurization consists of pressure reduction with constant production pressure, closing of production well for a period, reopening of production well and repetition of these operations. Stepwise depressurization is based on direct depressurization that reduces reservoir pressure to target value in multiple steps with shut-in period. Hence, the minimum temperature in this scenario can be increased to weaken Joule-Thomson effect and avoid hydrate reformation [24]. The limitation of these depressurization methods is that hydrate dissociation weakens cementation of hydrates within sediments. This decreases strength and stiffness of sediments and triggers related geological hazards [25,26].

CH4–CO2 swapping is recognized for its advantage of simultaneous CH4 recovery and CO2 storage [27,28]. It is performed by injecting CO2 (gas, liquid emulsion) or CO2 mixed gas into NGH reservoir and swapping CH4 in hydrate. Exothermic swapping reaction occurs spontaneously because CO2 hydrates are more thermodynamically stable than CH4 hydrates. Note that swapping between CH4 and CO2 experiences no massive hydrate dissociation, which retains enough hydrates and stabilizes hydrate-bearing sediments [29,30]. Meanwhile, CH4–CO2 swapping consumes no energy and produces almost no water, which increases its competitiveness compared with other exploitation methods [27]. Nevertheless, low reduction rate of CH4–CO2 swapping due to mass transfer restrictions hinders it from commercial applications [31,32].

To overcome the restrictions of individual depressurization and CH4–CO2 swapping, the combination of them was proposed [33–37]. Successful CH4 recovery and CO2 storage in the field test of Ignik Sikumi proved the partial feasibility of swapping combined with depressurization [38]. Technically, either depressurization or CH4–CO2 swapping can be performed firstly and the other followed. For lab-scale investigation on combination of first swapping and second depressurization, many researchers experimented the optimized conditions. Zhao et al. [33] performed fast one-step depressurization after swapping to melt parts of CH4 hydrates and enhance CO2 diffusion in tightly packed sand. About 10% of CH4 gas production was enhanced with pressure decreased from 31 bar to 16 bar during 3-h shut-in period. Yang et al. [34] conducted depressurization aided flue gas (14.6 mol% CO2/N2) injection in silica sand pack. Depletion was completed from 42 bar to just above CH4 hydrate dissociation pressure. CH4 mole fraction in vapor phase was elevated from 20 mol% to 50 mol% after flue gas injection and then from 50 mol% to 90 mol% by depletion, with total 70% of CO2 converted into hydrates. Chen et al. [36] adopted similar technique and found that when pressure reduced to just above CO2 hydrate stability pressure, breaking of CH4 hydrate cages and stabilizing of CO2 hydrate were achieved. Meng et al. [39] employed three-stage depressurization after CO2-enriched gas swapping from 85 bar to 33 bar, finding CH4 recovery percent could be improved from 41.5% to 74.4% while CO2 storage ratio reduced from 8.4% to 7.4%. Sun et al. [37] implemented three-time pressure oscillation (pressure depletion) after swapping at 17.4 bar for 30 min. The results of maximum CH4 recovery percent (32.66%) and CO2 storage efficiency (27.88%) nearly doubled than those without pressure oscillation.

In the situation of CH4–CO2 swapping followed by depressurization, the reverse strategy is depressurization followed by CO2 gas injection. Pandey et al. [40] adopted immediate pressure reduction to initiate hydrate cage breakage and create gas diffusion channels for swapping. Maximum CH4 recovery percent of 41% was obtained by an initial pressure reduction of 28 bar. Lee et al. [26], depressurized CH4 hydrate-bearing sediments initially and then injected CO2, finding that higher dissociation ratio (degree of depressurization) caused lower enhancement of CH4 recovery. Sun et al. [41] designed pre-depressurization before gas injection to improve diffusion of injected gas, and eventually enhanced CH4 recovery percent from 60% to 76% and CO2 storage ratio from 35% to 40%.

To sum up, although either swapping aided depressurization or depressurization aided swapping can boost both CH4 gas recovery and CO2 storage at varying degree, the possible concurrent optimization of CH4 production and CO2 retention is rarely concerned. The optimized ending depletion pressure deserves systematically examined regarding economy and safety of depressurization exploitation. In our recent study on micromodel visualization [42], CH4/CO2 hydrates were dissociated with depletion pressure below CH4 hydrate equilibrium pressure but above CO2 hydrate equilibrium pressure. The results indicated concurrent CH4 hydrate decomposition and CO2 hydrate recovery. Based on this, we extensively studied dissociation manners of CH4/CO2 hydrates by either pure CO2 injection into CH4 hydrate or directly using CH4/CO2 gas mixture. In one study [43], CH4/CO2 hydrates were synthesized using pure CO2 injection into CH4 hydrates in sandy media. The results affirmed additional CH4 recovery and CO2 retention after hydrate swapping. In the other study [44], CH4/CO2 hydrates formed by either CH4-rich gas or CO2-rich gas mixture in consolidated sand (sandstone). The resistivity results confirmed CO2 hydrate retention compensated CH4 hydrate loss. Another study demonstrated the effects of three critical parameters on production performances in sandstone [45]. In spite of these studies, dissociation characteristics of CH4/CO2 hydrate during slow depressurization in unconsolidated sediments are still unclear. The investigations above-mentioned interpreted the effects of pressure drop range, number of depletion stage, hydrate saturation and water saturation on production performances. However, optimization of CH4 recovery and CO2 storage through controlling these parameters in unconsolidated sediments at specific conditions needs further evaluation.

In this work, enhancements of CH4 production and CO2 storage were explored through multistep pressure depletions, i.e. multistep depressurization on CH4/CO2 hydrates in unconsolidated sand after CH4–CO2 swapping. It is assumed that CH4–CO2 swapping of NGH have proceeded and thus mixed hydrates have existed prior to multistep depressurization. The effects of CH4/CO2 hydrate composition (CH4-rich or CO2-rich), residual water saturation (Sm < 35%), and reservoir temperatures (Tt, above, equivalent and below 0 °C) were systematically examined. Optimized conditions were investigated, with the ending depletion pressure determined regarding maximized efficiencies of CH4 production and CO2 retention. The parameters described the efficiencies included CH4 mole fraction in produced gas (XCH4), CH4 recovery percent (RCH4) and CO2 storage ratio (SCO2). The results on enhanced exploitation characteristics of CH4/CO2 hydrates in unconsolidated sediments during multistep depressurization will be valuable for hydrate exploitation in continental hydrate reservoir.

2. Methodology

Two mixed gases (Air Liquide Corporation, Denmark) were used with one of them containing CH4 (70 mol%) and CO2 (30 mol%) and the other containing CH4 (30 mol%) and CO2 (70 mol%). Deionized (DI) water was produced (resistivity of 18.25 mΩ•cm−1) in the laboratory. Coarse sand (Dansand A/S Corporation, Denmark) was of unconsolidated type with grain size range of 0.90–1.60 mm.

A schematic of the apparatus for hydrate formation and exploitation via multistep depressurization is shown in Fig. 1. Detailed information on experimental apparatus, experimental procedures and relevant calculations are described in Appendix A.

3. Results and discussions

3.1. CH4/CO2 hydrate formation

70 mol%CH4/CO2 and 30 mol%CH4/CO2 were injected to synthesize...
CH$_4$/CO$_2$ hydrates. Two reasons account for injection of these two mixed gases, rather than injecting CO$_2$ into CH$_4$ hydrates. One is that two largely different CH$_4$/CO$_2$ hydrates can be formed by injecting the target mixed gas. The other is that direct CO$_2$ injection into CH$_4$ hydrate induces CO$_2$ hydrate formation and causes blockage at the inlet. Data on hydrate formation is exhibited in Table S1 and Table S2 of Appendix B. The CH$_4$/CO$_2$ hydrates in Exp1-2, 4-9 were formed with 70 mol%CH$_4$/CO$_2$. It was identified that the range of CH$_4$/CO$_2$ mole ratio stored in hydrate (refer as RH(CH$_4$/CO$_2$) in this work) was 1.16–1.74. This denoted that the formed CH$_4$/CO$_2$ hydrates were CH4-rich and thereby defined as Type A hydrates. The CH$_4$/CO$_2$ hydrates in Exp3 were synthesized with 30 mol%CH$_4$/CO$_2$. The value of RH(CH$_4$/CO$_2$) in Exp3 was 0.25, which confirmed that more CO$_2$ than CH$_4$ entering into hydrate phase. The synthesized CH$_4$/CO$_2$ hydrates in Exp3 were CO$_2$-rich and referred as Type B hydrates. Furthermore, the CH$_4$/CO$_2$ hydrates formed by mixed gas were assumed to mimic those after CH$_4$–CO$_2$ swapping, whereas differences were noted between them. It is difficult to generate CH$_4$/CO$_2$ hydrates in the laboratory by injecting CO$_2$ into CH$_4$ hydrates because CO$_2$ hydrates form at the inlet and injection cannot continue. This technique for forming CH$_4$/CO$_2$ hydrates would be inherently probabilistic, the CH$_4$/CO$_2$ hydrates would not be evenly distributed in sediments, and we would have no control over the formation of CH$_4$- and CO$_2$-rich hydrates. Therefore, we used CH$_4$/CO$_2$ gas to generate CH$_4$/CO$_2$ hydrates while controlling the CH$_4$ and CO$_2$ molecules in the gas phase. This is a limitation of this work. Therefore, the CH$_4$/CO$_2$ hydrates in our study were assumed similar to the CH$_4$/CO$_2$ hydrates produced by CO$_2$ injection into CH$_4$ hydrates.

For CH$_4$/CO$_2$ hydrate synthesis and growth, water diffusion played a significant role and the hydrate films around water phase acted as diffusion barriers [31,46]. Three cycles of cooling and heating were thought to improve uniform CH$_4$/CO$_2$ hydrate distribution after synthesis [47,48], as shown in Fig. 2. For CH$_4$/CO$_2$ hydrates formed as a result of hydrate swapping, CO$_2$ gas diffusion dominated mass transfer through outer CO$_2$ hydrate films and inner hydrates [49,50]. Laboratory-scale experiments on CO$_2$ injection into CH$_4$ hydrates would trigger inlet blockage in that CO$_2$ hydrate formation and thus cause low CH$_4$/CO$_2$ hydrate saturation and heterogeneous hydrate distribution [44]. The consistence between the mixed hydrates formed by mixed gas and CH$_4$–CO$_2$ swapping, however, were that pure CH$_4$ hydrates, pure CO$_2$ hydrates and CH$_4$/CO$_2$ mixed hydrates coexisted in both scenarios.

Fig. 2 presents the profiles of pressure and temperature during CH$_4$/CO$_2$ hydrate formation with varying compositions. Three cycles of cooling and heating were employed to form mixed hydrates in each experiment. During the cooling process in Exp1, the induction time was about 45 min at each cooling cycle, as shown in Fig. 1 (a). Afterwards, sudden increase of temperature was seen as hydrate formation process started. Pressures decreased gradually due to CH$_4$/CO$_2$ gas consumption. Similar pressure drop was observed in Fig. 2 (b). The corresponding induction time was 30 min for Type B hydrates, which was shorter than that for Type A hydrates. This may be attributed to higher solubility of 30 mol%CH$_4$/CO$_2$ in water than 70 mol%CH$_4$/CO$_2$. It can be concluded that for Type B hydrates, and the driving force of CO$_2$ in 30 mol%CH$_4$/CO$_2$ gas for Type B hydrate formation is the largest at the condition of similar initial pressure and reservoir temperature [54–56]. Comparably, the range of RH(CH$_4$/CO$_2$) in Type A hydrate included that (1.63) in unconsolidated sand after CO$_2$ injection into CH$_4$ hydrates [43], indicating hydrate formation by CH$_4$/CO$_2$ gas can represent the scenario of CO$_2$ injection into CH$_4$ hydrates. One possible class of chemicals that could be used in pure CO$_2$ injection into CH$_4$ hydrate is anti-agglomeration compound/kinetic inhibitor that delays the formation of CO$_2$ hydrate films during CO$_2$ injection [51]. Low dosage of methanol (5 wt%) with dilute CO$_2$ (with N$_2$) injection was tested and found with promising results, and kinetic promoters (SDS and methionine) were tested to enhance CH$_4$–CO$_2$ swapping as well [43,51]. Therefore, CO$_2$ gas injection into CH$_4$ hydrates with these chemicals in unconsolidated sand can improve CO$_2$ hydrate formation at varying degrees [51], causing lower RH(CH$_4$/CO$_2$) of 0.01–0.17 in Type B hydrate than that of 0.25 (without chemicals) in this work. In addition, RH
(CH$_4$/CO$_2$) in this work were both lower than those of Type A hydrate (1.52–2.10) and Type B hydrate (0.21–0.40) in consolidated sandstone [44,45]. The reason for this was that unconsolidated sand can provide larger surface area between gas and water, causing more thermodynamically favorable CO$_2$ captured in hydrate [57]. Additionally, differences of RH(CH$_4$/CO$_2$) between unconsolidated sand and bulk water were related to gas compositions [52] and P-T conditions [53] besides the factor of porous media. Nevertheless, lower RH(CH$_4$/CO$_2$) in unconsolidated sediments implied that CO$_2$ was more preferably encaged in hydrate than CH$_4$.

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

After hydrate formation, multistep depressurization of 7–15 bar pressure drop and 4-h shut-in interval was employed to dissociate CH$_4$/CO$_2$ hydrates as fixed scheme concluded from previous study [45]. The effects of gas collection position (top or bottom), hydrate composition (Type A or Type B), residual water saturation ($S_{rw}$), and reservoir temperatures ($T_r$) were investigated to correlate them with CH$_4$ recovery and CO$_2$ storage. Information is summarized in Table 1. Hydrate equilibrium was calculated using CSMGem for bulk-only phase and differed in different porous media [58]. Note that hydrate equilibrium was regarded unchanged during slow depressurization because reservoir temperatures remained almost constant.

3.2.1. Effect of gas collection position

Fluid extraction can be conducted at either free gas zone or hydrate zone of reservoir in practical operation, [59–61]. In this work, pressure depletion was implemented from either upperpart with free gas or underpart with hydrates of the sandpack. As a result, two gas collection positions of top (Exp1) and bottom (Exp2), i.e. gas release from outlet control Valve 1 and Valve 2, were selected to investigate gas sample differences at similar experimental conditions. The gas composition difference may affect CH$_4$ recovery percent ($R_{CH_4}$) and CO$_2$ storage ratio ($S_{CO_2}$).

Fig. 4 shows characteristics of multistep depressurization on Type A
hydrate in Exp1 (gas sample collection from top). More information can be tracked in Table S4. CH₄ mole gas fraction (XCH₄) presented nearly no increase (0.5 mol%) throughout depletion. On the one hand, no hydrate reformation and dissociation occurred during shut-in period as no obvious pressure change. On the other hand, gas phase may refresh as hydrate phase varied, but chemical disequilibrium may induce gas exchange between gas phase and hydrate phase and thus offset the refreshed gas phase [62,63]. Nevertheless, gas samples at top with constant compositions cannot represent exploitation characteristics precisely. Additionally, larger pressure drops induced larger temperature drop at each depletion, indicating Joule-Thomson effect and forming ice when temperature decreased below freezing point. However, temperatures recovered to previous values in a few minutes. This interpreted that Joule-Thomson effect had unobvious effect on CH₄/CO₂ hydrates.

Similarly, multistep depressurization was performed on Type A hydrate in Exp2, as shown in Fig. 5. Gas collection point was at bottom. XCH₄ was 72.2 mol% initially and reached 74.0 mol% at the end of Stage E. Similar minor increase of XCH₄ with depletion was reported in sandstone study [44,45]. This increment of XCH₄ (ΔXCH₄ = 1.8 mol%) can be explained from the perspective of hydrate reformation. Due to depletion pressure above CH₄ hydrate stability pressure (PCH₄), both CH₄ hydrates and CO₂ hydrates tended to reform and thus hydrate formation competition existed. Note that pressure line crossed PCH₄ during Stage D. This pressure drop was mainly caused by CO₂-rich hydrate reformation, and the CO₂-rich hydrates did not decomposed until CO₂ hydrate stability pressure (PCO₂) in initial Stage F. During Stage E at which pressures were between PCH₄ and PCO₂, both CO₂-rich hydrate reformation (pressure drop) and CH₄-rich hydrate dissociation (pressure rebound) existed, whereas the former was stronger than the latter. This resulted in an overall small pressure drop throughout Stage E, which reflected just free gas removal and it is also reported in Phillips’s [22]. This phenomenon of concurrent CH₄ hydrate dissociation and CO₂ hydrate reformation was confirmed in our previous micromodel study [42].

Different from stable pressure drops during Stage A-E, pressure rebounds emerged during Stage F-G. These pressure rebounds were caused by massive CO₂-rich hydrate dissociation, leading to CO₂ mole fraction in gas phase (XCO₂) increase. Note that the rebounds in this work were smaller than those abrupt rebounds in stepwise depressurization on pure CH₄ hydrates in unconsolidated sand [22,64]. The differences can be explained by larger pressure drops and CH₄/CO₂ hydrates in this work. In addition, no pressure change was detected during Stage I because hydrate dissociation was almost completed and only free gas was released. This was corresponded with the depressurization behaviors in unconsolidated sediments [22]. In Table S4, the largest SCO₂ was 86.0% at the end of Stage F, which exhibited a dropping trend with pressure close to PCO₂. Note that both the highest CH₄ recovery and CO₂ storage were achieved between PCH₄ and PCO₂. After the pressure reduced below PCO₂, XCH₄ and SCO₂ presented decreasing trend. Hence, multistep depressurization should be ceased above PCO₂.

### 3.2.2. Effect of hydrate composition

Principally, hydrate compositions in reservoir change from CH₄-rich to CO₂-rich as more CH₄ produced and CO₂ stored during CH₄–CO₂ swapping. It is therefore essential to examine the effect of hydrate composition on CH₄ production and CO₂ retention during multistep depressurization. Thus, the exploitation characteristics of above-mentioned CH₄-rich hydrate (Type A) in Exp2 and the following CO₂-rich hydrate (Type B) in Exp3 were discussed.

**Table 1**

<table>
<thead>
<tr>
<th>Exp no.</th>
<th>Hydrate type</th>
<th>Sₘw/%</th>
<th>Sₘs/%</th>
<th>Total steps of depressurization</th>
<th>Collection point</th>
<th>T₀/°C</th>
<th>P₀/bar</th>
<th>PCH₄/bar</th>
<th>PCO₂/bar</th>
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<td>7.88</td>
<td>23.00</td>
<td>10</td>
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<td>0.6</td>
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<td>2</td>
<td>B</td>
<td>6.33</td>
<td>22.47</td>
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<td>Bottom</td>
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<td>28.40</td>
<td>13.80</td>
</tr>
<tr>
<td>4</td>
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<td>3.3</td>
<td>60.20</td>
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</table>
temperature recovery also indicated endothermic hydrate dissociation at initial shut-in period as it absorbed latent heat from ambient.

Based on hydrate composition study, ΔXCH₄ for Type A hydrate was 1.80 mol% at 20.68 bar, larger than that for Type B hydrate with 0.2 mol% at 14.16 bar. At selected pressures, however, RCH₄ and SCO₂ for Type A hydrate (82.1% and 85.3%) were both lower than those for Type B hydrate (85.9% and 87.6%). This was caused by higher ending pressure for Type A hydrate. Further depletion could be applied to improve RCH₄ and SCO₂ to 87.1% and 84.7%, while XCH₄ decrease to 66.40 mol% with pressure reduced just above PCO₂. Nevertheless, it was more efficient to perform multistep depressurization on Type A hydrate with the primary purpose of enhancing CH₄ recovery. The corresponding depletion pressure was suggested controlled right above PCO₂.

Fig. 7 summarizes XCH₄, SCO₂ and RCH₄ with depletion pressure during multistep depressurization in Exp1-3. The depletion pressure with the highest XCH₄ was primarily marked as the ending point (Pend) of multistep depressurization, and suggested depletion range for efficient CH₄ recovery and CO₂ storage was between PCO₂ and Pend as suggested in Fig. 7. Compared Exp1 (top gas release) with Exp2 (bottom gas release), gas collection point had an effect on exploitation characteristics, i.e. nearly no ΔXCH₄ in Exp1 (0.5 mol%) whereas 1.8 mol% of ΔXCH₄ in Exp2. Furthermore, SCO₂ and RCH₄ were 86.7% and 82.6% at 19.60 bar in Exp1, competitive with 85.3% and 82.1% at 20.68 bar in Exp2, indicating RCH₄ and SCO₂ were almost same with the designed depletion. On the one hand, production well is preferably schemed at bottom reservoir in realistic hydrate exploitation, because depletion can trigger more CH₄ hydrate dissociation into gas and water. This also contributes to downward CO₂ retention in hydrate, which consumes more CO₂ from top free gas. On the other hand, gas sample composition from bottom can reflect in-situ hydrate composition. Hence, multistep depressurization was implemented at bottom of hydrate reservoir in the following experiments.

In regard with hydrate composition study, types of hydrate (Type A in Exp2 and Type B in Exp3) imposed a great influence on XCH₄, CH₄-rich gas recovery on Type A hydrate allowed an efficient CH₄ production with XCH₄ over 70 mol%. However, CH₄-lean gas production on Type B hydrate with XCH₄ under 35 mol% caused inefficiency of exploitation. Additionally, SCO₂ and RCH₄ in Exp2 were both over those in Exp3 at same depletion pressure, making Type A hydrate a preferable exploitation scheme. Therefore, it was advised to cease depletion before CH₄-rich hydrate reservoir turned into CO₂-rich one.

Fig. 8 summarizes the exploitation performances of multistep depressurization and CO₂ swapping combined with multistep depressurization for different hydrate compositions. More details are available in Table S7 and the data is compared with those in references. The gas production percentages (Gp) in pure CH₄ hydrate-bearing unconsolidated sand at Zhao’s [32] and Lv’s [65] were about 63% and 71% at 30 bar, lower than RCH₄ in Exp1-3 at 14-25 bar. This demonstrated that multistep depressurization with lower depletion pressure after swapping obtained a higher CH₄ yield. For CO₂ swapping combined with multistep depressurization, few steps of depletion, i.e. 3 stages at Sun’s [37] and 1 stages at Zhao’s [33], may be not the most suitable for efficient hydrate exploitation. In contrast, 8/5/4 steps of multistep depressurization in this work contributed to higher RCH₄ and SCO₂. The highest RCH₄ (85.9%) and SCO₂ (87.6%) were realized in CO₂-rich hydrates, however, CO₂-rich hydrates brought a much lower XCH₄ in produced gas and
significantly reduced economy. In summary, multistep depressurization was recommended for CH$_4$-rich hydrates with higher RH(CH$_4$/CO$_2$) and ceased before CH$_4$-rich hydrate reservoir became into CO$_2$-rich one.

3.2.3. Effect of residual water saturation

Porous media in hydrate reservoir is mainly filled with hydrate and water. The following water saturation before multistep depressurization is referred to residual water saturation (S$_{rw}$). It was known that S$_{rw}$ influenced hydrate reformation directly as forming molecules, and affected hydrate exploitation performance indirectly through mass transfer and heat transfer [24].

Fig. 9 illustrates the characteristics during multistep depressurization on Type A hydrate with S$_{rw}$ of 9.22%. XCH$_4$ was 72.9 mol% at the starting point and continually increased from Stage A to Stage G. Combined with minor pressure drops during shut-in intervals, CO$_2$-rich hydrate reformation was inferred above PCH$_4$. Note that XCH$_4$ reached the highest 74.3 mol% at 22.33 bar and gradually decreased afterwards. This was caused by CO$_2$-rich hydrate decomposition with pressure close to PCO$_2$, and further supported by minor pressure rebounds right after closing gas production. RCH$_4$ and SCO$_2$ were not at the peak values (79.8% and 83.7%) at the highest XCH$_4$, indicting a compromise regarding the ceasing point, as shown in bold in Table S5.

Fig. 10 shows XCH$_4$ & XCO$_2$, pressure and temperature during multistep depressurization on Type A hydrate in Exp4 (S$_{rw}$ = 9.22%). Gas collection point at bottom. PCH$_4$ = 28.12 bar and PCO$_2$ = 13.64 bar at $T_r$ = 0.8 $^\circ$C.

Fig. 11 presents multistep depressurization on hydrate reservoir with the highest S$_{rw}$ of 31.7%. Overall XCH$_4$ growth from Stage A to Stage G and slight pressure drops during shut-in intervals verified CO$_2$-rich hydrate reformation. More pressure drops due to hydrate reformation appeared during Stage F because of adequate water availability in higher S$_{rw}$, which was consistent with that in Exp5. The largest XCH$_4$ (74.9 mol%) appeared at 26.7 bar just below PCH$_4$. In Table S5, RCH$_4$ increased gradually throughout depressurization with the highest SCO$_2$.
Fig. 11. Variations of XCH$_4$ & XCO$_2$, pressure and temperature during multistep depressurization on Type A hydrate in Exp6 (S$_{rw}$ = 31.71%). Gas collection point at bottom. PCH$_4$ = 28.12 bar and PCO$_2$ = 13.80 bar at T$_r$ = 0.9 °C. No bottom temperature recorded in Exp5.

Fig. 10. Variations of XCH$_4$ & XCO$_2$, pressure and temperature during multistep depressurization on Type A hydrate in Exp5 (S$_{rw}$ = 17.81%). Gas collection point at bottom. PCH$_4$ = 28.40 bar and PCO$_2$ = 13.80 bar at T$_r$ = 0.9 °C. No bottom temperature recorded in Exp5.

(88.2%) at pressure close to PCO$_2$. Pressure rebounds were attributed to massive CO$_2$-rich hydrate decomposition. Similar sudden temperature drop, temperature recovery and inverse increase were detected because of Joule-Thomson effect, heat absorption and ice formation, respectively.

Fig. 12 Summarizes the effect of S$_{sw}$ on characteristics during multistep depressurization. XCH$_4$ was the primary indicator for optimized depletion conditions. The largest ΔXCH$_4$ (6.5 mol%) was realized in Exp5 (S$_{rw}$ = 17.8%) compared with 4.2 mol% (S$_{sw}$ = 31.7%) in Exp6 and 1.4 mol% (S$_{rw}$ = 9.2%) in Exp4. On the one hand, S$_{rw}$ of high level was insufficient to enhance CH$_4$ recovery because of much water hindering CH$_4$ gas from escaping hydrate. According to Yang’s [66], residual water is supersaturated with CH$_4$/CO$_2$ gas, which metastably dissolved in water or formed nanometer size bubbles. When pressures were between PCH$_4$ and PCO$_2$, CH$_4$-rich hydrates initially dissociated at gas-hydrate interface and then released CH$_4$-rich gas. However, the residual water and dissociated water tended to envelope hydrates and thus inhibited further CH$_4$-rich hydrate dissociation due to diffusion limitation [66]. Therefore, S$_{rw}$ of high level was unbeneﬁcial to CH$_4$ production. This was consistent with the observation of higher water saturation in unconsolidated sand hindering CH$_4$ gas yield by depressurization [67]. S$_{sw}$ of low level, however, decreased water availability for CO$_2$ retention. Residual water tended to form thin water layers between hydrate and sand [66]. When CO$_2$-rich gas in water reached boundary of supersaturation, CO$_2$-rich hydrate nucleated and grew along these water layers at pressures between PCH$_4$ and PCO$_2$. In addition, CO$_2$-rich gas may be immobilized by surrounding hydrates with no supply of liquid water to promote CO$_2$-rich hydrate growth [42].

In summary, lower efficiency of CH$_4$ recovery was obtained in S$_{sw}$ of high level for much water immersing CH$_4$-rich hydrates; lower efficiency of CO$_2$ retention was achieved in S$_{rw}$ of low level for less water availability. Therefore, an optimum S$_{sw}$ existed in this work (17.8%) within the range investigated for multistep depressurization on Type A hydrate in unconsolidated sediments. An optimum value of water saturation at which hydrate dissociation presented the most efﬁcient dissociation patterns was reported [68].

Fig. 13 summarizes Gp, RCH$_4$ and SCO$_2$ regarding depressurization and multistep depressurization on CH$_4$ hydrates, and CO$_2$ swapping combined with multistep depressurization for different S$_{rw}$. More details are available in Table S7. It can be identiﬁed from Wan’s [69] that higher Gp was obtained with lower S$_{rw}$ at same pressure of 21 bar. Basically, there were two types of hydrate reservoir, “gas saturated” and “water saturated”, and Gp at “gas saturated” was higher [70]. In addition, Gp was mainly correlated with ending depletion pressure at same S$_{rw}$ according to Phillips’s [22] and Guo’s [23]. For CO$_2$ swapping combined with multistep depressurization, RCH$_4$ (78.8-80.8%) in Exp4-6 was inferior to Gp (82-100%) in references [22,23,69,70]. Additionally, N$_2$ addition in CO$_2$ gas injection would negatively affect CO$_2$ storage efﬁciency [34]. Nevertheless, an optimized S$_{sw}$ (17.8%) existed in this work at which both efﬁciencies of CH$_4$ recovery and CO$_2$ storage reached the highest values of 80.8% and 88.2%.

3.2.4. Effect of reservoir temperature

The primary driving force for hydrate decomposition/reformation after CH$_4$-CO$_2$ swapping is mainly dependent on pressure and temperature [71-73]. In practical hydrate exploitation, freezing point could be confronted in permafrost. At depressurization schemes with similar pressures, the effect of reservoir temperature (T$_r$) on CH$_4$ recovery and CO$_2$ storage efﬁciencies was studied at three temperatures, below (T$_r$ = −3.3 °C), equal to (T$_r$ = 0.2 °C) and above freezing points (T$_r$ = 2.2 °C). Note that T$_r$ is the average bottom temperature variation of time throughout multistep depressurization.

Fig. 14 illustrates the proﬁles of dissociation characteristics during multistep depressurization at T$_r$ = −3.3 °C. No change of XCH$_4$ and no pressure drops were detected during shut-in intervals from the beginning to Stage D. This demonstrated no evidence of improved CH$_4$ recovery and CO$_2$ storage at T$_r$ below freezing point, which was caused by mass transfer restrictions under ice formation within pore. This hindered water and gas transportation for CH$_4$ hydrate decomposition and CO$_2$ hydrate reformation, which was consistent with the radial extension behaviors of hydrate decomposition driven by ambient heat transfer [74]. Afterwards, XCH$_4$ decreased gradually from Stage E with pressure drops during shut-in period, indicating hydrate dissociation at pressure close to and below PCO$_2$. Note that CO$_2$_rich gas in water reached maximum (89.5%) at the end of Stage E and then decreased constantly below PCO$_2$ while RCH$_4$4 continuously increased, as exhibited in Table S6. Therefore, the suggested ending point of depletion was at 17.58 bar of ending Stage D.

Fig. 15 illustrates the effect of freezing point temperature (T$_r$ = 0.2 °C) on CH$_4$ recovery and CO$_2$ storage during multistep depressurization. XCH$_4$ reached the highest value (76.8 mol%) when pressure reduced below PCH$_4$. The largest SCO$_2$ was 88.2% in Table S6 before
pressure decreased below PCO$_2$. Further depletion with pressure approaching PCO$_2$ depressed XCH$_4$ because of CO$_2$-rich hydrates dissociation, as indicated by pressure rebounds during Stage G-J. Joule-Thomson effect at the bottom was caused by fast gas release during early depletion. However, it seemed that the heat consumption by gas expansion during fast gas release can be compensated by exothermic ice formation from dissociated water at sub-zero. This caused no more fast temperature drops after Stage G. Nevertheless, the ending point for depletion was marked at the end of Stage E with the highest XCH$_4$.

Fig. 16 presents the effect of temperature above freezing point (T$_r$ = 2.2 °C) on multistep depressurization. XCH$_4$ from initial 72.8 mol% to 74.9 mol% was attributed to CH$_4$-rich hydrate dissociation during Stage A-C, shown as immediate pressure rebounds after depletion. XCH$_4$ then decreased as CO$_2$-rich hydrate decomposed, supported by small and continual pressure rebounds during Stage D-H. In Table S6, the largest SCO$_2$ was 83.8% at the end of Stage D, after which it started to decrease as pressure reduced to PCO$_2$. RCH$_4$ at temperature above freezing point also present same increasing trend as those at other temperatures. The ending point for depletion was suggested at the end of Stage C with the highest XCH$_4$.

Fig. 17 compares the effect of reservoir temperatures below (T$_r$ = 3.3 °C), equal to (T$_r$ = 0.2 °C) and above (T$_r$ = 2.2 °C) freezing point on production performances. The suggested ending point was marked with P$_{end}$ above-mentioned. It seems from Fig. 17(a) that T$_r$ = 2.2 °C in Exp9 was beneficial to CH$_4$ production regarding the largest $\Delta$ XCH$_4$ (1.9 mol%), compared with 0.3 mol% in Exp7 and 1.0 mol% in Exp8. This was achieved regarding a higher P$_{end}$ (27.03 bar) in Exp9 than those in Exp7 (17.58 bar) and Exp8 (22.41 bar). It means less demanding depletion for optimized CH$_4$ recovery in higher reservoir temperature. For CO$_2$ storage, it can be detected from Fig. 17(b) that T$_r$ = 3.3 °C was conducive to CO$_2$ storage regarding the largest SCO$_2$ (88.2%) at P$_{end}$. Nevertheless, RCH$_4$ with pressure depletion in Fig. 17(c) were nearly same at three temperatures, which were more dependent on depletion pressure.

The results in Fig. 17(b) revealed that temperature played an important role in deciding CO$_2$ storage efficiency. The largest SCO$_2$ at reservoir temperature below freezing point may be the consequence of enhanced residual water and solid (ice)-gas (CO$_2$) reaction [75]. CO$_2$ stored as hydrates in this work included CH$_4$–CO$_2$ swapping and direct CO$_2$-rich hydrate formation. CO$_2$ storage efficiency was negatively affected by ice layer outside CH$_4$ hydrates, but this may be compensated by CO$_2$ hydrate film formation directly from ice. Nevertheless, additional thermal stimulation inducing higher temperature after multistep depressurization on CH$_4$/CO$_2$ hydrates was confirmed unfavorable to
CO₂ storage.

The driving force of CH₄ hydrate dissociation was primarily dependent on pressure and temperature. On the one hand, CH₄ recovery was relied on pressure drop by depressurization and same range of depletion caused almost same RCH₄ regardless of temperatures, as shown in Fig. 17(c). On the other hand, ice formation below freezing point resulted in high resistance of heat transfer. It caused inefficiency of endothermic hydrate dissociation. Water and gas migration was inhibited at the presence of ice and this unfavorable mass transfer depressed CH₄ hydrate dissociation. This can be inspected from the aforementioned pressure curve after depletion. No flat pressure curve was observed at Tₑ = −3.3 °C after pressure release in Fig. 14 because ice blockage prevented gas release from hydrate. And it took about 2 h of shut-in duration for appearance of flat pressure curve at Tₑ = 0.2 °C in Fig. 15, while only 1 h at Tₑ = 2.2 °C in Fig. 16. It was implied that combination of thermal stimulation with multistep depressurization on CH₄/CO₂ hydrates might efficiently promote CH₄ recovery.

Fig. 15 illustrates the comparison of RCH₄ and SCO₂ regarding swapping exploitation and CO₂ swapping combined with multistep depressurization for different temperatures versus freezing point. For CH₄–CO₂ hydrate swapping, Zhao et al. [76] found that T > 0 °C brought the highest RCH₄, and RCH₄ reduced as temperature decreased below 0 °C. Xie et al. [77] concluded that higher RCH₄ at T > 0 °C and lower value at T < 0 °C, however, faster decomposition rate of CH₄ hydrates and more defects in ice layer occurred at T < 0 °C. Zhang et al. [78] identified that freezing point had much more influence on RCH₄ than SCO₂. They explained the ineffectiveness of CH₄ recovery at T < 0 °C was related to mass transfer. In this study, RCH₄ and SCO₂ were higher than those at hydrate swapping in references. On the other hand, additional CH₄ recovery and CO₂ storage was accomplished by depletion after CO₂ injection into CH₄ hydrates. On the other hand, freezing point had an inverse effect on RCH₄. The explanation was that final RCH₄ was dominated by depletion pressure more than freezing point. The actual RCH₄ & SCO₂ were (84.9% & 88.2%) at T < 0 °C, (85.7% & 88.2%) at T = 0 °C, and (88.4% & 83.1%) at T > 0 °C within same depletion pressure of 16–17 bar, i.e. RCH₄ was higher while SCO₂ was lower at T > 0 °C.

3.3. Comparison of efficiency and analysis of sediments

From one perspective of economy, higher XCH₄ in produced gas can reduce separation fee and more CO₂ storage can save cost for carbon capture and storage (CCS) techniques [79,80]. Thus, one economic characteristic can be determined based on Δ XCH₄ with the corresponding SCO₂. From the other perspective of economy, more CH₄ production can create profit and higher depletion pressure can reduce cost of depressurization. Thus, RCH₄ combined with depletion pressure is the other primary indicator. Fig. 19 exhibits the comprehensive analysis of SCO₂ to Δ XCH₄ and RCH₄ to depletion pressure in Exp1-9. For Δ XCH₄ and SCO₂ in Fig. 19 (a), Exp5 and Exp6 were recognized with Δ XCH₄ over 4.0 mol% and SCO₂ over 83.0%. In Fig. 19 (b), the corresponding depletion pressures were 19.9 bar (Exp5) and 26.7 bar (Exp6). These two pressures were located between PCH₄ and PCO₂. Additionally, RCH₄ was more related to depletion pressure, i.e. lower depletion pressure caused higher RCH₄, which was consistent with the finding in Ref. [23]. Nevertheless, multistep depressurization should be stopped when pressure reduced below PCH₄ and above PCO₂, and precise ceasing point (Pₑn) needs more investigation regarding specific hydrate reservoir conditions such as hydrate composition, fluid saturation and distribution.

Fig. 20 summarizes RCH₄ and SCO₂ in hydrate swapping and CO₂ swapping with multistep depressurization. The comparisons were studied regarding bulk water and different sediments. The two cases for comparison were the optimized scenarios (Exp5 and Exp6) in this work. More relevant information can be found in Table S7. As shown in Fig. 20, RCH₄ and SCO₂ in bulk water (15.7–19.9% and 17.2–26.4%) [81] were lower than those (36.7–56.4% and 32–42%) in coarse sand [82]. Among hydrate swapping, RCH₄ and SCO₂ in unconsolidated coarse sand were the highest compared with those in fine marine sand (unconsolidated fine sand) [71] and mudstone (consolidated sand) [83]. For CO₂ swapping combined with multistep depressurization, RCH₄ and SCO₂ in this works were (79.8% & 83.7%) and (80.8% & 88.2%) in unconsolidated sand, slightly higher than those in references of consolidated sandstone [44,45].

From the view of mass transfer, increased contact area of CO₂ gas and CH₄ hydrates with porous media enhanced CO₂ storage and CH₄ production in comparison with bulk water. Furthermore, unconsolidated fine sand and consolidated mudstone/sandstone generally had much smaller grain size and pore size than coarse sand, which reduced permeability significantly and thus caused much inefficient contact among CO₂ gas, CH₄ hydrate and residual water. Pressure difference between outlet and inlet occurred and remained for a long time during hydrate exploitation within consolidated sediments [44,45], while no pressure difference was observed in unconsolidated sediments because
gas release at bottom hydrate phase always triggered pressure drop at top gas phase immediately. This indicated a much better pore connectivity within unconsolidated sediments despite of hydrate formation. Additionally, pressure rebounds at lower pressures close to PCO$_2$ were seen in unconsolidated sediments, compared with pressure rebounds at higher depletion pressures just under PCH$_4$ in consolidated sediments [44, 45]. This could be attributed to the effect of porous media on mixed hydrate equilibrium. Capillarity in small pore under mesoporous conditions (2–50 nm) had severe inhibited effect on hydrate formation [84, 85]. Although the particle size (0.9–1.6 mm) in this work was beyond mesoporous conditions, pore size of consolidated sediments was smaller than that of unconsolidated sediments. Thus, the interaction of pore-water with sediment particles involving van der Waals forces and capillary forces was stronger in unconsolidated sediments [86–88]. At the conditions of same reservoir temperature and similar CH$_4$/CO$_2$ gas compositions, lower hydrate equilibrium pressures because of the enhanced interaction were expected for hydrate dissociation in unconsolidated sediments. This explained that pressure rebounds appeared at lower depletion pressure in unconsolidated sediments compared to those in consolidated sediments.

Immobile water and clay in fine sand and mudstone would limit gas diffusion and had negative effect on CH$_4$ gas production and CO$_2$ hydrate retention [89–91]. Wetting effect of unconsolidated sand, by enlarging effective surface-to-volume ratio of hydrate in sediment, can also increase permeability in real systems [92]. This effect, however, was weak in consolidated sand and absent in bulk water. Another comparison was related with well pattern, i.e. it was more like a “huff

Fig. 17. Summary of characteristics during multistep depressurization at Exp7 (T$_r$ = –3.3 °C), Exp8 (T$_r$ = 0.2 °C), and Exp9 (T$_r$ = 2.2 °C): (a) XCH$_4$ with pressure depletion; (b) S0$_2$ with pressure depletion and, (c) RCH$_4$ with pressure depletion. Three vertical dash lines refer to three PCH$_4$ at Exp7-9 and P$_{end}$ is the suggested ending point.

Fig. 18. Comparison of RCH$_4$ and S0$_2$ of swapping exploitation and CO$_2$ swapping combined with multistep depressurization on hydrates for different temperatures [76–78]. More detailed information is in Table S7 of Appendix B.

Fig. 19. Comprehensive comparison of: (a) S0$_2$ to ΔXCH$_4$; and, (b) RCH$_4$ to depletion pressure.
and puff with a vertical well in this work compared with one injection well (inlet) and one production well (outlet) in consolidated sediment. More detailed information is in Table S7 of Appendix B.

Fig. 20. Comparison of RCH4 and SCO2 in CH4-CO2 swapping and CO2 swapping combined with multistep depressurization regarding different sediments in this work and references [44,45,71,81–83]. More detailed information is in Table S7 of Appendix B.

4. Conclusions

In this study, well-controlled multistep depressurization has been intensively investigated for enhanced CH4 recovery and CO2 storage. The effects of gas release point (top or bottom), hydrate composition (CH4-rich or CO2-rich), residual water saturation (9.2% to 31.7%), reservoir temperature (−3.3 °C to 2.2 °C) and sediments on CH4 yield and CO2 retention were experimentally studied. The conclusions are summarized:

- The ratio of CH4/CO2 in hydrate indicated CO2 preferable occupancy in hydrate than CH4 and this preference was most obvious in unconsolidated sediments.
- The increment of CH4 mole gas fraction was higher at bottom exploitation due to more underpart CH4-rich hydrate dissociation and more CO2 retention in hydrate.
- Enhanced exploitation of multistep depressurization on mixed hydrates should cease before CH4-rich hydrate reservoir turned into CO2-rich one.
- Residual water saturation existed an optimum value within range tested in this study. Below this optimum value, there was no apparent CO2-rich reformation for lacking adequate water. Above this optimum value, CH4-rich hydrate dissociation was hindered for mass transfer barriers.
- Reservoir temperature below freezing point was unbeneﬁcial to CH4 production due to ice formation hindering CH4-rich hydrate dissociation. However, this low temperature may favor CO2 storage because of residual water improvement and ice to CO2-rich hydrate formation.
- The highest CH4 mole gas fraction of 79.1 mol%, with CH4 recovery percent of 80.8% and CO2 storage ratio of 88.2%, was obtained at depresure point of 19.9 bar after six-stage multistep depressurization on CH4-rich hydrate reservoir.
- Sediments were the critical factor affecting efficiencies of CH4 production and CO2 storage. Gas diffusion in pore, contact between CO2 gas and CH4 hydrates, and CO2 forming hydrate with water were improved more effectively within unconsolidated sediments.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References


