

Article

Design and Optimization of Bottom-Hole Temperature–Pressure Combinations in Gas Production from Gas Hydrates via Carbon Dioxide Replacement Strategy

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Abstract

Carbon dioxide replacement represents a promising hydrate development strategy that effectively balances production efficiency and environmental considerations. However, its production efficiency is lower than that of the depressurization strategy. This limitation can be effectively alleviated by coupling carbon dioxide replacement with inhibitor injection. The design and optimization of the temperature–pressure operating window constrain its effective implementation. In the present work, the phase equilibrium conditions of carbon dioxide hydrate and methane hydrate were experimentally investigated. It was found that the experimental values obtained in this study are in excellent agreement with those calculated by the CSMHyd program. The average absolute relative deviations (AARD) for the experimental versus calculated results are 5.77% for methane hydrate and 2.66% for carbon dioxide hydrate. Then, the methodology for determining the recommended temperature–pressure combinations used in the carbon dioxide replacement strategy was proposed, and the size of region in which these combinations occur was quantified. The investigation results found that there are significant differences in the size of the recommended region for different sea areas, and inhibitor injection reduces the size of this recommended region. Injection of 3.0 wt% NaCl solution reduces the size of recommended region from 10.968 K·MPa to 8.366 K·MPa for pure methane hydrate, and a similar trend is also observed for natural gas hydrates. Based on the experimental results, the carbon sequestration potential of natural gas hydrate development using the carbon dioxide replacement strategy on core size was analyzed. The final simulation results show that 9.05 mol of carbon dioxide hydrate was obtained in the reaction vessel, which achieves effective CO₂ sequestration. The investigation in this work provides theoretical support for dual goals of carbon sequestration and efficient gas production from gas hydrates.

Keywords: natural gas hydrate; CO₂ sequestration; CO₂ replacement; inhibitor injection; temperature–pressure window

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1. Introduction

The global energy system is currently experiencing a rapid transition toward low-carbon and diversified development [1–3]. Natural gas, as a relatively clean transitional energy source, is expected to continue playing a significant role in the foreseeable future [4–6]. Natural gas resources are widely distributed and originate from various sources, such as shale gas and coal-bed methane. Natural gas hydrates are widely regarded as one of the most promising unconventional natural gas resources due to the enormous resource abundance and widespread distribution [7–9]. However, the formation and dissociation of gas hydrates are highly sensitive to temperature and pressure conditions. Consequently, hydrate exploitation fundamentally depends on deliberately disturbing the original thermodynamic equilibrium of the hydrate-bearing formation [10–12]. Following this principle, several major development strategies for natural gas hydrates have been proposed and extensively investigated, including depressurization, thermal stimulation, and inhibitor injection. Among them, the depressurization method, which induces hydrate dissociation by reducing the bottom-hole pressure, is currently the most mature and widely applied strategy in field-scale production trials or laboratory-scale studies [13,14]. Nevertheless, rapid hydrate dissociation induced by this strategy in the near-wellbore region can significantly weaken the sediment, thereby exacerbating wellbore instability or sediment stability [15–17]. The thermal stimulation approach enhances hydrate dissociation by injecting hot fluids or applying electrical heating to raise the formation temperature. However, its practical application is constrained by high energy requirements, inefficient heat transfer, and elevated operational costs. The injection of thermodynamic inhibitors (e.g., methanol and salts) is a strategy that induces hydrate dissociation by changing hydrate equilibrium conditions [18–20]. However, the effectiveness of this method is often constrained by the limited diffusion range of the inhibitors, and it may also exert adverse impacts on wellbore and sediment stability [21,22]. These single development strategies present evident shortcomings with respect to production efficiency, operational safety, and economic feasibility, and thus fail to meet the demands of sustainable, long-term, and large-scale hydrate development.

In recent years, a combined development strategy integrating carbon dioxide replacement of methane hydrates with inhibitor injection has been proposed as an innovative technological route [23–25]. This strategy not only enhances gas production efficiency but also offers the potential for carbon dioxide storage. In this strategy, the core mechanism is governed by the difference in thermodynamic stability between carbon dioxide and methane hydrates. At given temperature and pressure conditions, carbon dioxide hydrates are thermodynamically stable compared to methane hydrates [26]. This difference enables carbon dioxide to selectively replace methane molecules within the hydrate structure without completely destroying the original hydrate skeleton. Meanwhile, methane can be released while the relative stability of the geological structure is maintained [3,16]. Simultaneously, the injection of inhibitors adjusts the chemical potential of pore fluids and consequently changes equilibrium conditions of gas hydrates. In this way, the kinetics of the replacement dissociation process can be effectively regulated or controlled. The synergistic effect of these two approaches helps alleviate the severe temperature and pressure disturbances induced by rapid hydrate dissociation during standalone depressurization or thermal stimulation [27,28]. In addition, it can, to some extent, suppress the secondary formation of hydrates and the resulting blockage of flow channels [29].

In recent years, increasing investigation efforts have been devoted to carbon dioxide replacement of gas hydrates and inhibitor-assisted hydrate development. However, these existing studies have mainly focused on replacement feasibility, reaction kinetics,

and qualitative or quantitative analyses of production behavior. To name a few, Liu et al., (2022) summarized the feasibility of the CO₂ replacement strategy, and proposed corresponding measures to improve replacement efficiency based on an analysis of the replacement mechanisms [30]. It was found that hydrate exploitation based on CO₂ replacement reaction is theoretically feasible. However, uncertainties persist regarding reservoir stability in field-scale production, mainly due to the unclear dissociation behavior of methane hydrates during replacement. Wang et al. (2021) summarized representative strategies for carbon dioxide displacement enhancement and conducted a comparative analysis of their EGR performance [31]. It was demonstrated that, relative to mixed-gas replacement, the combined CO₂ displacement and depressurization strategy provides a more effective means of enhancing methane recovery. Wu et al., (2025) conducted experimental investigations on carbon dioxide–methane hydrate replacement using a dual-well injection–production scheme to identify the optimal CO₂ injection configuration [32]. It was found that the displacement reaction rate attains its highest value at a CO₂ injection rate of 0.210 mL/min, after which it decreases progressively. These studies contribute significantly to the understanding of the fundamental theoretical basis of methane extraction through CO₂ displacement. Nevertheless, several limitations remain in the existing studies, which warrant further investigation and in-depth exploration. One of the most critical limitations lies in the design and regulation of suitable temperature and pressure windows for methane replacement via carbon dioxide hydrate formation. This is primarily due to the differences in phase equilibrium between CO₂ and CH₄ hydrates [33,34]. The prerequisite for effective replacement is the establishment of a thermodynamic window that guarantees CO₂ hydrate stability while promoting CH₄ hydrate dissociation [35]. From another perspective, most existing studies focus on a single CO₂ replacement strategy, without integrating it with other enhancement approaches. For example, its combination with injection-chemistry-based practical strategies remains largely unexplored. This is primarily due to the fact that injection of chemical agents, especially the use of hydrate inhibitors, can markedly modify the phase equilibrium characteristics of CO₂ hydrate, as well as and CH₄ hydrate [36,37]. Finally, existing investigations predominantly consider pure methane hydrate systems, while the dissociation gases in natural settings typically consist of complex multicomponent mixtures.

A systematic investigation of these three aspects will further facilitate the development of effective production strategies for natural gas hydrates and the optimization of corresponding engineering measures. Motivated by these considerations, the effects of inhibitors—primarily—on the phase equilibrium conditions of methane hydrates, carbon dioxide hydrates, and natural gas hydrates were experimentally investigated in this study. These results provide a theoretical foundation for the numerical simulation of subsequent CO₂ replacement reactions. Meanwhile, differences in the temperature and pressure windows resulting from multiple influencing factors were examined based on the experimental findings. Finally, the gas production performance of natural gas hydrates developed through the combined application of CO₂ replacement and inhibitor injection was systematically investigated using numerical simulations.

2. Experimental Section

In this study, the effects of inhibitors on the thermodynamic equilibrium conditions of various hydrate systems—primarily carbon dioxide hydrates, methane hydrates, and natural gas hydrates—were experimentally investigated. Therefore, this section presents a comprehensive description of the experimental system, materials, and method employed in this study.

2.1. Experimental System

A schematic of the experimental system employed in this study is presented in Figure 1. As illustrated in Figure 1, the experimental setup consists of a high-pressure reactor, three gas cylinders, a temperature and pressure monitoring module, an inhibitor injection module, and a cold storage. Among these components, the high-pressure reactor is a key element of the experimental system. As illustrated in Figure 1, the high-pressure reactor is a cylindrical 316 stainless-steel structure with a radius of 15.0 cm and a height of 50.0 cm. The reactor is capable of withstanding both internal and external pressures up to 100 MPa. This pressure is substantially higher than the phase equilibrium pressures of the gases at the typical temperatures investigated in this study.

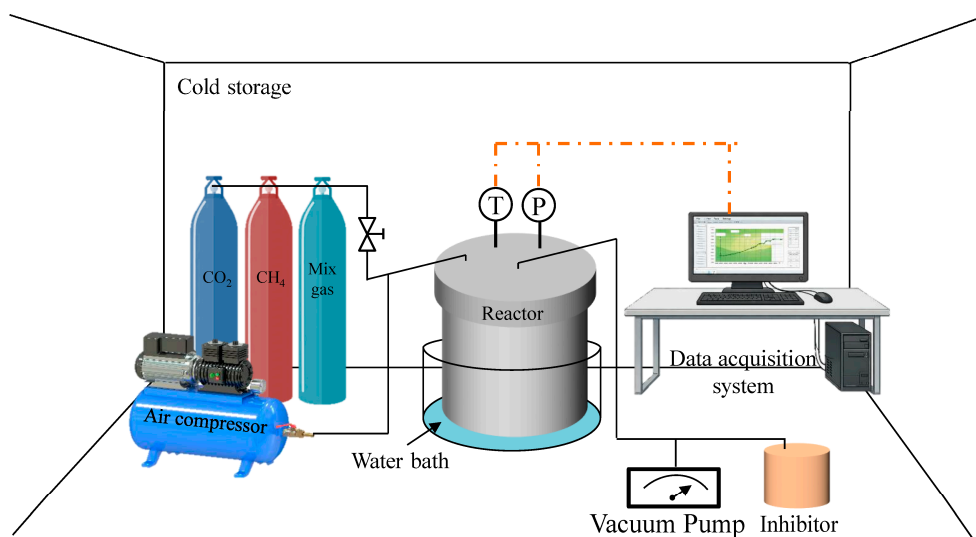


Figure 1. Schematic diagram of the experimental system.

Gas cylinders were employed to store three types of experimental gases, namely carbon dioxide, methane, and a mixed gas. Air compressors were used to regulate and maintain the pressure inside the high-pressure reactor. Due to the extremely high pressures required for the experiments, additional pump units shown in Figure 2 were employed. With the assistance of the air compressor and pump unit, the pressure within the high-pressure vessel was capable of being pressurized to 80 MPa. The reactor is equipped with four openings at its top, which serve for gas injection, inhibitor injection, and the measurement of temperature and pressure. Temperature and pressure are the key parameters measured in the experiment, and thus their accurate determination is of great importance. In the experiment, the pressure and temperature sensors provide high measurement accuracy, with uncertainties of ± 20 kPa and ± 0.1 °C, respectively.



Figure 2. Auxiliary pump unit (left), high-pressure vessel (middle) and gas cylinder (right).

Moreover, the data acquisition system is capable of collecting temperature and pressure at a maximum interval of 2 min. In this experiment, the data acquisition system was configured to collect measurements every 5 min. To ensure favorable conditions for hydrate formation, the experimental system was placed in a temperature-controlled cold storage. The cold storage has a refrigeration limit of $-20\text{ }^{\circ}\text{C}$, sufficient to replicate the temperature conditions of all potential hydrate-forming environments.

2.2. Experimental Materials

Besides pure methane and pure carbon dioxide, the experimental gases included mixed gases, which were designed according to the compositions of hydrate dissociation gases reported from different regions globally [38,39]. Table 1 lists the compositions of gases released during hydrate dissociation in several representative blocks worldwide. As shown in Table 1, methane constitutes the majority of hydrate dissociation gases, accompanied by varying proportions of ethane, carbon dioxide, and propane.

Table 1. Compositions of gases released during hydrate dissociation in several representative blocks worldwide [21–25].

Representative Blocks	Gas Compositions
Shenhu area, China	At 197.5 m: Methane 99.82% + Ethane 0.17% + CO ₂ 0.01%
	At 221.71 m: Methane 99.68% + Ethane 0.15% + CO ₂ 0.17%
Green Canyon 185, Gulf of Mexico, USA	Methane 71.69% + Ethane 13.09% + Propane 11.85%
KG Basin Site NGHP-01-10, India	CO ₂ 7.41% + Methane 92.59%
Lake Baikal, Russia	Methane 85.22% + Ethane 14.78%

The methane, carbon dioxide and mixed gas used in this study were supplied by Henan Keyi Gas Co., Ltd. (Zhengzhou, China) with a purity of 99.99%. In the experiment, eleven types of mixed gases were customized, and their compositions are shown in Table 1. KCl (purity 99%), purchased from China National Pharmaceutical Group (Beijing, China), was used as the hydrate inhibitor in the experiments.

2.3. Experimental Method

At present, three primary approaches are widely adopted to determine hydrate equilibrium conditions, namely the Isothermal Pressure-Search Method, the Isobaric Temperature-Search Method, and the Isochoric Method [40–42]. In this study, the phase equilibrium conditions of gas hydrates in various systems were determined using the Isochoric Method [43,44]. This method represents the most classical and extensively ap-

plied technique for laboratory determination of natural gas hydrate phase equilibrium conditions (i.e., P-T curves). The detailed experimental method is as follows:

- (1) **Experimental preparation and injection of inhibitor solution.** A system pressure of 2.0 MPa was achieved by introducing a controlled amount of methane or carbon dioxide into the experimental setup. Then, it is necessary to close all valves in the system and observe whether the value of the pressure sensor has changed. Stable sensor readings indicate that the experimental system is suitable for further experiments. Afterwards, the experimental system was evacuated to ensure the absence of interfering gases, and a prepared inhibitor solution with a specified mass fraction or pure water was injected into the reactor.
- (2) **Formation of gas hydrate.** Pure or mixed gas for hydrate formation is injected into the reactor, and then pressurized to the designed pressure via a pressurization system at room temperature (e.g., 15 °C). The temperature of the cold storage was ramped down at a low rate (e.g., 0.1–0.3 °C/h) to ensure continuous cooling of the reactor and its contents. Simultaneously, the evolutions of temperature and pressure were monitored and logged in real time. A sudden pressure decline on the P-T curve signifies the formation of hydrates. It should be emphasized that this stage is primarily designed to activate the hydrate system and does not serve to determine the final phase equilibrium state. Once the cold storage temperature is lowered to 2–4 K below the expected phase equilibrium temperature, it is maintained for a period of 2–6 h to ensure sufficient hydrate formation.
- (3) **Dissociation of gas hydrate.** After hydrate formation is complete, the temperature is increased at 0.1–0.3 K/h, with continuous monitoring of pressure and temperature. For each heating time increment, the system is held for several hours to allow equilibrium to be fully established. The heating process is continued until the pressure–temperature curve returns to a linear relationship. Throughout this process, continuous recording of temperature and pressure data remains necessary. The intersection of the pressure–temperature curves obtained in the above two processes represents the phase equilibrium condition of gas hydrates. Other phase equilibrium conditions can be determined by varying the initial P , T conditions and performing the aforementioned procedure again.

To provide a clearer illustration of the experimental procedure, the two panels in Figure 3 present the flowchart of the experimental process and the pressure–temperature curve of methane hydrate in pure water. From Figure 3, it can be seen that the geometry of P-T curves for hydrates of different gases varies greatly.

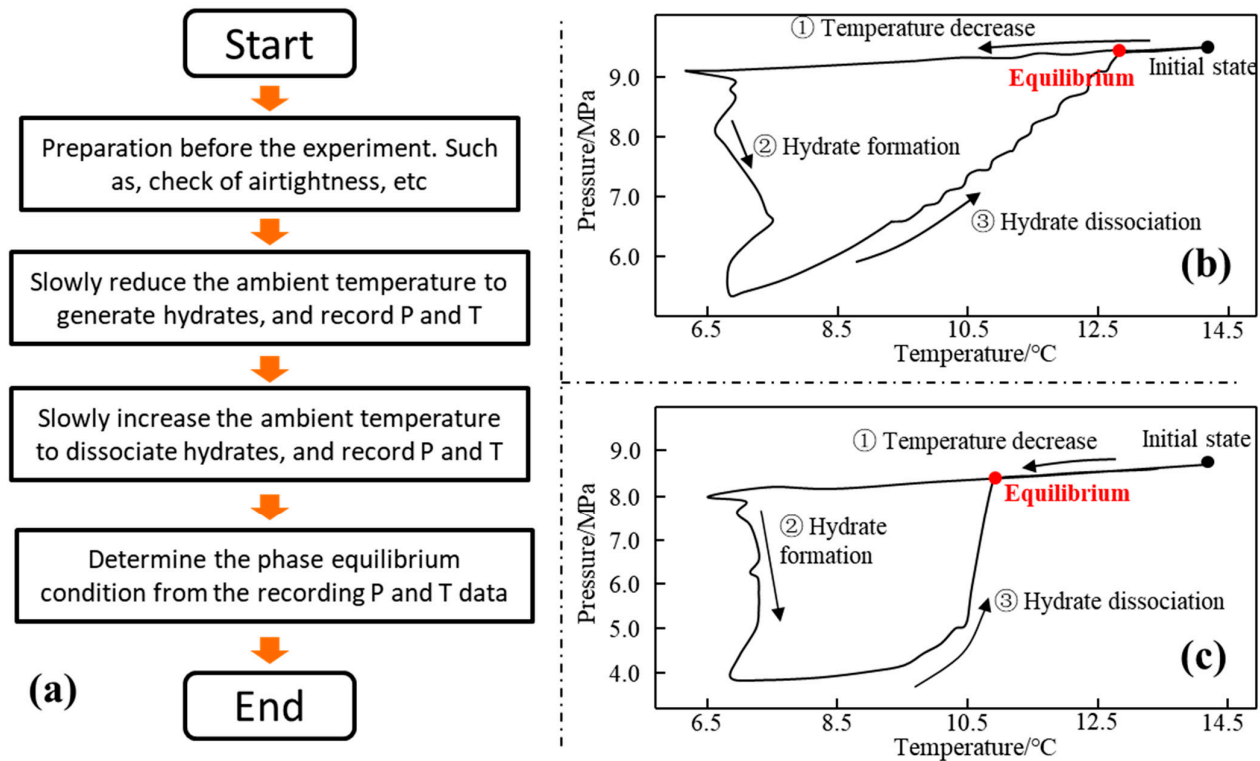


Figure 3. Experimental process and P-T curve. (a) Flowchart of experimental method; (b) P-T curve for methane hydrate in pure water; (c) P-T curve for CO₂ hydrate in pure water.

2.4. Comparison Between Experimental and Calculated Phase Equilibrium Data

To validate the applicability of the experimental methodology and the accuracy of the obtained results, the experimental phase equilibrium conditions were compared with those calculated by the CSMHyd program, as illustrated in Figure 4. As observed in Figure 4, both methane hydrate and CO₂ hydrate show excellent agreement between experimental and calculated values.

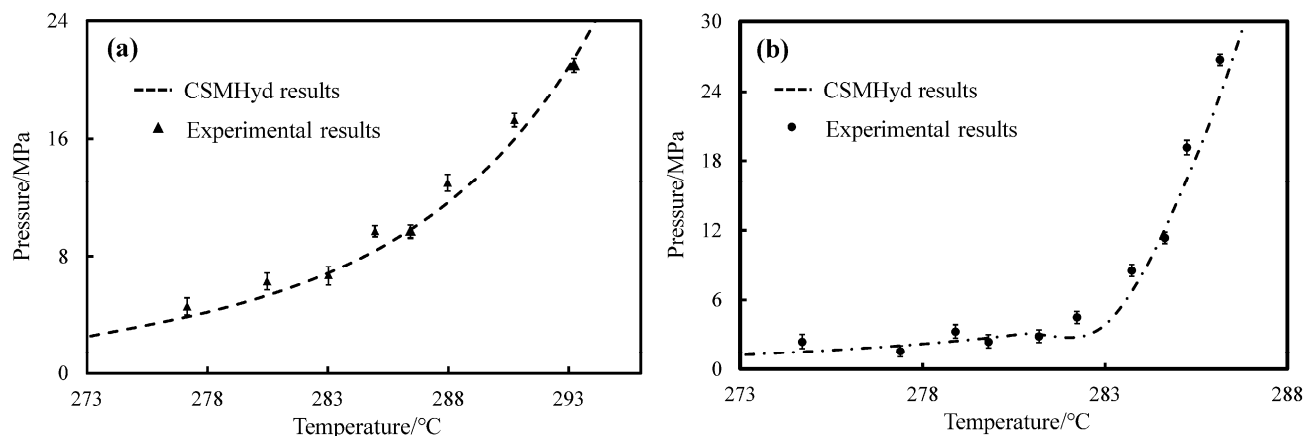


Figure 4. Comparison between experimental results and CSMHyd program calculation results. (a) methane hydrate; (b) CO₂ hydrate.

To quantitatively evaluate the deviation, the Average Absolute Relative Deviation (AARD) and Root Mean Square Error (RMSE) were calculated using the following equations:

$$AARD = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_{exo,i} - P_{cal,i}}{P_{exo,i}} \right| \times 100\% \quad (1)$$

where $P_{exp,i}$ and $P_{cal,i}$ represent the experimental and calculated equilibrium pressures, respectively, and N is the number of experimental data points.

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (P_{exo,i} - P_{cal,i})^2} \quad (2)$$

The deviation was quantitatively evaluated using the Average Absolute Relative Deviation (AARD) and Root Mean Square Error (RMSE) based on equilibrium pressure. The detailed calculation results are summarized in Table 2. As shown in Table 2, the AARD values are 5.77% for methane hydrate and 2.66% for carbon dioxide hydrate, with RMSE values of 0.45 MPa and 0.40 MPa, respectively. These deviation levels are acceptable when considering the wide pressure range studied and the experimental pressure uncertainty of ± 0.02 MPa. The results confirm that the experimental system and method employed in this study are reliable for determining the phase equilibrium conditions of gas hydrates.

Table 2. Deviation between experimental and CSMHyd calculated equilibrium pressures.

Representative Blocks	Evaluation Results	
Methane hydrate	AARD(%)	5.77
	RMSE(MPa)	0.45
Carbon dioxide hydrate	AARD(%)	2.66
	RMSE(MPa)	0.40

3. Experimental Results and Discussion

3.1. Determination of the Recommended Temperature-Pressure Combinations

As can be seen in Figure 4, the phase equilibrium conditions of CO₂ hydrate differ significantly from those of methane hydrate at identical temperatures. The differences in phase equilibrium behavior offer a theoretical foundation for the replacement of methane in natural gas hydrates with carbon dioxide. Within the low-temperature range, the phase equilibrium pressure of methane hydrate is generally higher than those of carbon dioxide hydrate [45,46]. By contrast, in the high-temperature range, methane hydrate exhibits a significantly lower phase equilibrium pressure than carbon dioxide hydrate. The variation in phase equilibrium behavior between the two hydrates at different temperature ranges also poses significant challenges for the determination of optimal operating temperatures and pressures [47–49]. For this reason, it is necessary to design and optimize the temperature and pressure conditions for the effective implementation of development operations.

In theory, the temperature and pressure conditions for development operations should satisfy the following criteria: carbon dioxide hydrate remains stable, while methane hydrate is unstable [50,51]. Based on the criterion, Figure 5 illustrates the method for determining the temperature and pressure window during the replacement of methane in methane hydrates with carbon dioxide. In Figure 5, two curves partition the entire temperature–pressure space into four areas, labeled I, II, III, and IV, respectively. Among them, the yellow-shaded region (i.e., area II) is the recommended temperature and pressure range for development design. When the bottom-hole temperature and pressure fall within this range, natural gas hydrates gradually dissociate, while carbon dioxide hydrates are formed accordingly, thereby completing the replacement process. In the remaining regions, either methane hydrate dissociation does not occur, carbon dioxide hydrate formation does not occur, or neither process takes place. In Area I,

where both methane hydrate and carbon dioxide hydrate are thermodynamically stable, the replacement process is inhibited. In other word, when the temperature and pressure fall within this region (i.e., Area I), methane hydrates and carbon dioxide hydrates coexist within the sediments. In Area III, carbon dioxide hydrates cannot form, and the pre-existing methane hydrates in the sediment will also dissociate into water and methane as a result of thermal stimulation or depressurization. In this case, the dissociation of methane hydrates is not driven by carbon dioxide replacement. Finally, when the bottom-hole temperature and pressure fall within Area IV, methane hydrates remain stable, whereas carbon dioxide hydrates cannot form. This behavior is opposite to the expected chemical reaction pathway considered in this study.

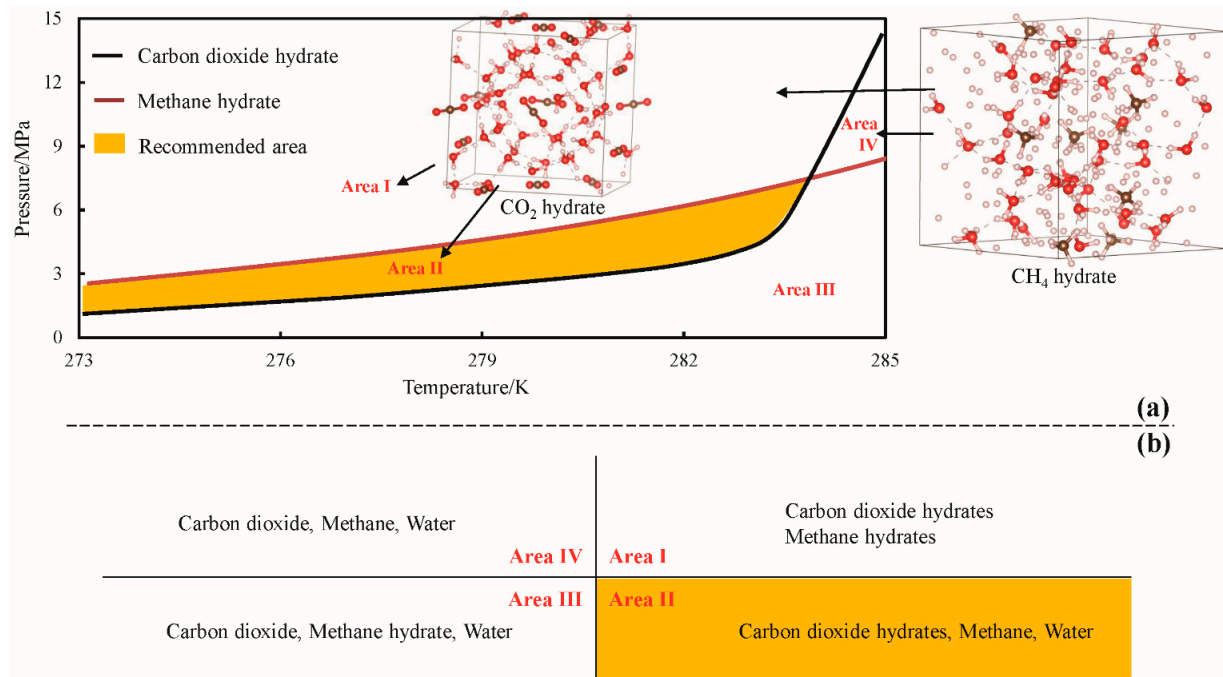


Figure 5. (a) Phase equilibrium curves of methane hydrate and carbon dioxide hydrate in pure water; (b) Substances present in the four area.

However, it can be seen that this region exhibits an irregular shape, and cannot be adequately defined using only temperature–pressure window. Thus, the preliminary strategy of characterizing this temperature–pressure region by analogy with the safe mud weight window in drilling operations proved to be impractical [52–54]. In the present work, the influence of various factors can only be represented by presenting irregular regions corresponding to specific temperature and pressure combinations. Herein, the area of the recommended region was also quantified through custom code implementation, and the Matlab R2023a code was presented in Appendix A [55,56].

Figure 6 presents the result obtained by applying this method to the example shown in Figure 5. During the Monte-Carlo sampling, 50,000 points were distributed across the entire domain. The points located within the recommended region are marked in green, while those in the remaining areas are marked in red (see Figure 6a). The final statistical result shows that 4568 points fall within the recommended region, accounting for approximately 9.14% of the total points. Accordingly, the calculated size of the recommended area is 10.9632 K·MPa. To minimize the influence of randomness, three independent calculations were performed for each case, and the average value was adopted. Based on the example presented in Figure 5, the final size of the recommended area is 10.9680 K·MPa. This parameter provides a quantitative indicator of the size of the

recommended bottom-hole temperature and pressure combination distribution area in hydrate development using the combined CO₂ replacement and inhibitor injection strategy. A larger value of this parameter indicates a broader range of available bottom-hole temperature–pressure combinations, thereby facilitating both design and implement of hydrate development operations [57].

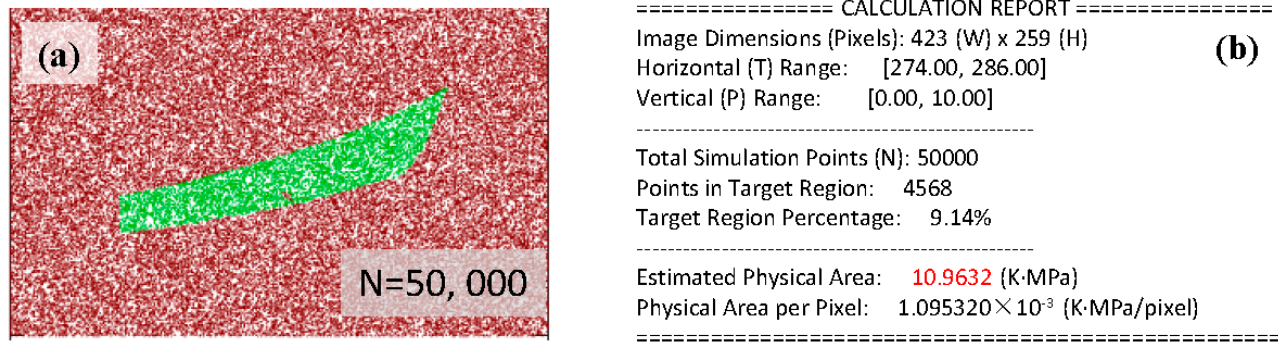


Figure 6. (a) Distribution of points based on Monte-Carlo algorithm; (b) Calculation results.

To verify the numerical convergence of the Monte Carlo calculation, additional simulations were performed using different numbers of random points (10,000, 50,000, 100,000, and 500,000). The Monte-Carlo convergence analysis for the calculated recommended area was shown in Table 3. As shown in Table 3, the calculated recommended area increased significantly when the sampling number increased from 10,000 to 50,000, whereas the estimated area remained almost unchanged when the number of points exceeded 50,000. The maximum difference between the results obtained with 50,000 and 500,000 points was only 0.0022 K·MPa, which indicates that 50,000 sampling points were sufficient to achieve numerical convergence.

Table 3. Monte Carlo convergence analysis for the calculated recommended area.

Points Number	Area of the Recommended Area, K·MPa
10,000	10.3567
50,000	10.9680
100,000	10.9595
500,000	10.9610

Also, to evaluate the influence of image resolution on the calculated area, a sensitivity analysis was performed using different image resolutions. As summarized in Table 4, the calculated area gradually converged with increasing image resolution. The area obtained at 96 dpi was 10.6245 K·MPa, whereas the values increased to 10.9680, 10.9758, and 10.9686 K·MPa at 150, 300, and 600 dpi, respectively. The maximum deviation among the tested resolutions was approximately 3.2%, while the difference between 300 and 600 dpi was less than 0.1%. These results demonstrate that the image-based quantification method is insensitive to image resolution when sufficiently high-resolution figures are used. Therefore, the area differences observed among different hydrate systems are unlikely to originate from image resolution effects.

Table 4. Impact of image resolution.

Image Resolution, dpi	Area of the Recommended Area, K·MPa
96	10.6245
150	10.9680

300	10.9758
600	10.9686

In addition, the composite metric expressed in units of K·MPa represents the area enclosed by the temperature-pressure (T - P) trajectory in the phase space. It is important to note that this metric is introduced as a relative comparative index rather than a fundamental physical quantity with absolute meaning. Because its numerical value depends on the selected axis ranges and scaling of the T - P plot, direct quantitative comparisons of absolute magnitudes across different sites should be interpreted with caution. This index provides a convenient way to rank the overall thermodynamic driving force and operational severity of hydrate dissociation conditions, but comparisons are best regarded as qualitative unless further normalization is applied.

It should also be noted that the comparison between logarithmic and polynomial fitting methods performed in the sensitivity analysis revealed that curve fitting itself may introduce noticeable variability in the estimated area. This observation further supports the decision to avoid fitting-based area calculation in the present study and instead employ direct image-based Monte Carlo sampling. Consequently, the reported area values in this work are independent of the selected fitting function. Nevertheless, relatively small differences between recommended areas should be interpreted with appropriate caution because they may still be influenced by experimental uncertainties in the phase-equilibrium curves and image discretization. In contrast, the larger differences reported between different hydrate systems, particularly those associated with the existence or disappearance of the recommended operating window, remain qualitatively robust.

3.2. Differences in Design Results Across Different Sea Areas

Although methane dominates the gas phase following natural gas hydrate dissociation, notable variations in composition are commonly observed, which can be clearly seen from Table 1. It is well known that the phase equilibrium conditions of hydrates are strongly influenced by the composition of guest molecules [58,59]. As a result, differences inevitably arise in the recommended design values of bottom-hole temperature and pressure for hydrate development using the carbon dioxide replacement strategy worldwide.

3.2.1. South China Sea, China

The natural gas hydrates occurring in the Shenhu area of the South China Sea are mainly classified as structure I (sI) hydrates [60]. According to publicly available information, methane generally constitutes over 96% of the gases produced by dissociation of natural gas hydrate in the South China Sea, China. More specifically, analyses of the gas released from the hydrate reservoir indicate that methane accounts for more than 99% of the total gas composition [61,62]. Based on the determination method mentioned above, Figure 7 presents the recommended combinations of bottom-hole temperature and pressure for the GMGS1-SH2, GMGS1-SH3, and GMGS1-SH7 stations in the Shenhu Sea area.

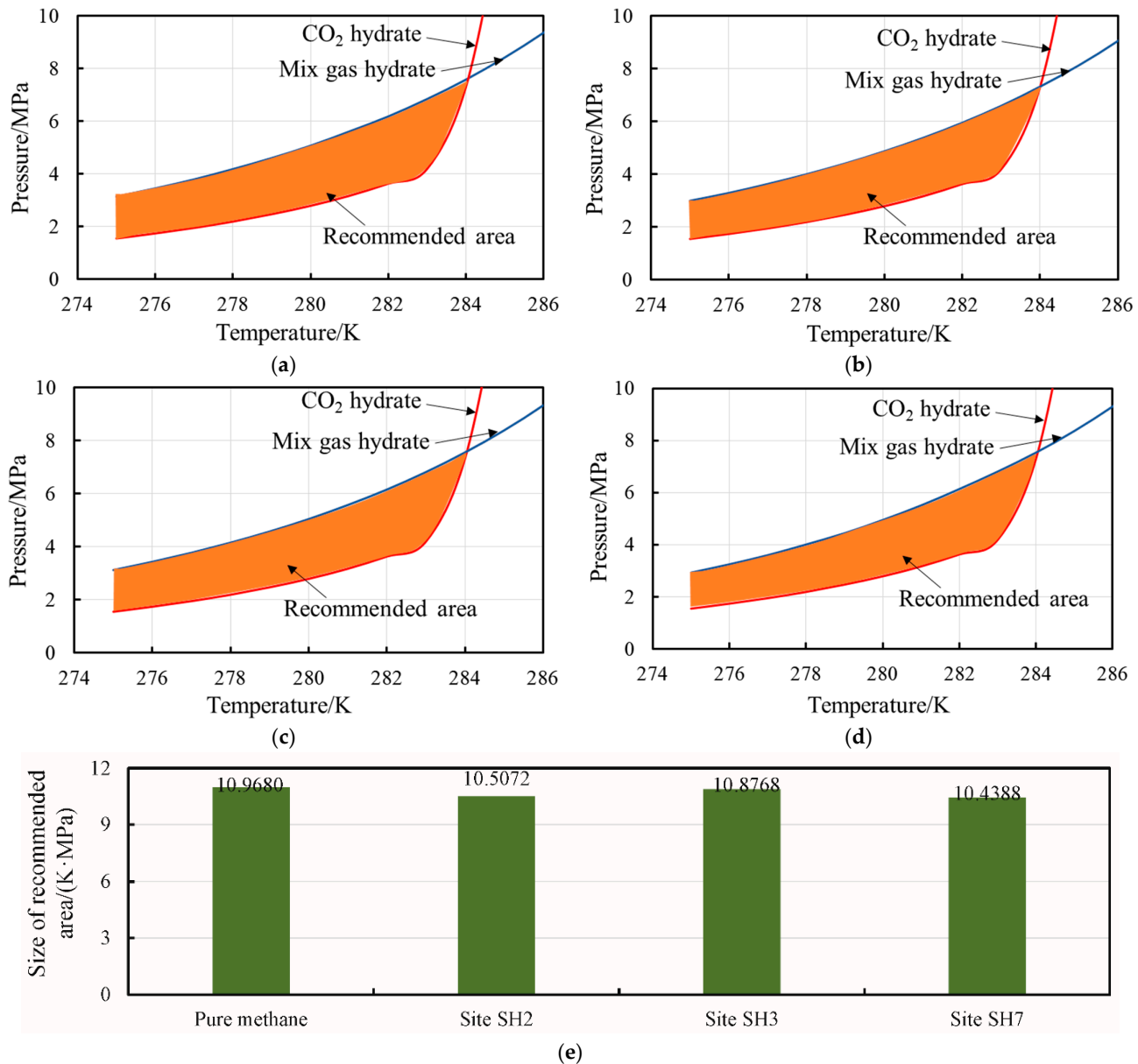


Figure 7. Recommended combinations of temperature and pressure for hydrate reservoirs in South China Sea, China. (a) Pure methane hydrate; (b) Gas hydrate in site GMGS1-SH2; (c) Gas hydrate in site GMGS1-SH3; (d) Gas hydrate in site GMGS1-SH7; (e) Size of recommended area for different cases.

It can be qualitatively seen in Figure 7a–d that the recommended combinations of bottom-hole temperature and pressure for hydrate reservoirs at various sites in the Shenhu area of the South China Sea exhibit similar distributions. This is largely due to the fact that the gas compositions within hydrates are nearly the same for four cases. At sites SH2, SH3, and SH7, methane concentrations exceeded 99%, specifically 99.32%, 99.91%, and 99.68%, respectively [63–65]. In addition, ethane and the remaining gas components are present at very low concentrations. As a result, the phase equilibrium behavior of gas hydrates is largely consistent across these sites. For the four cases, the recommended area sizes for the bottom-hole temperature–pressure combinations are 10.9680, 10.5072, 10.8768, and 10.4388 K·MPa, respectively (see Figure 7e). Nevertheless, slight differences exist among the four cases. The presence of minor components such as

ethane and propane in natural gas hydrates lowers the phase equilibrium pressures. The size of the recommended area will decrease accordingly. The minor differences in the recommended regions among the site SH2, site SH3, and site SH7 are attributed to variations in components such as ethane, propane, and carbon dioxide. For instance, although methane accounts for a slightly higher fraction of natural gas at site SH7, it also contains minor amounts of propane (0.06%) and carbon dioxide (0.16%). By comparison, the dissociation gas at site SH2 lacks both propane and carbon dioxide. As a result, the recommended design domain for SH7 is slightly reduced relative to that for SH2.

3.2.2. Gulf of Mexico, USA

Significant reserves of natural gas hydrates have also been identified in the Gulf of Mexico through exploration [66,67]. However, in contrast to hydrates in the South China Sea, those in the Gulf of Mexico display pronounced variations in gas composition upon dissociation. This is attributable to the presence of both sI and sII gas hydrates in the Gulf of Mexico [68]. The methane concentration in sI hydrate samples from Green Canyon in Gulf of Mexico also exceeds 98%, whereas that in other sII hydrate samples ranges from 70% to 80%. Figure 8 presents the corresponding proportions of different hydrate types at three sites of the Gulf of Mexico. As can be seen in Figure 8, for hydrate-bearing sediments at sites GC185-GC2 and GC415-TVG12, sI hydrates are absent, with only ice and sII hydrates occurring. The proportions of sII hydrates in the hydrate deposits at these two sites are 85.6% and 58.3%, respectively. However, at site Chapopote-GC6, the hydrate-bearing sediments consist exclusively of sI hydrates (66.9%) and ice (33.1%), and sII hydrates are absent. This poses challenges and uncertainties for the design and control of bottom-hole temperature and pressure in hydrate development.

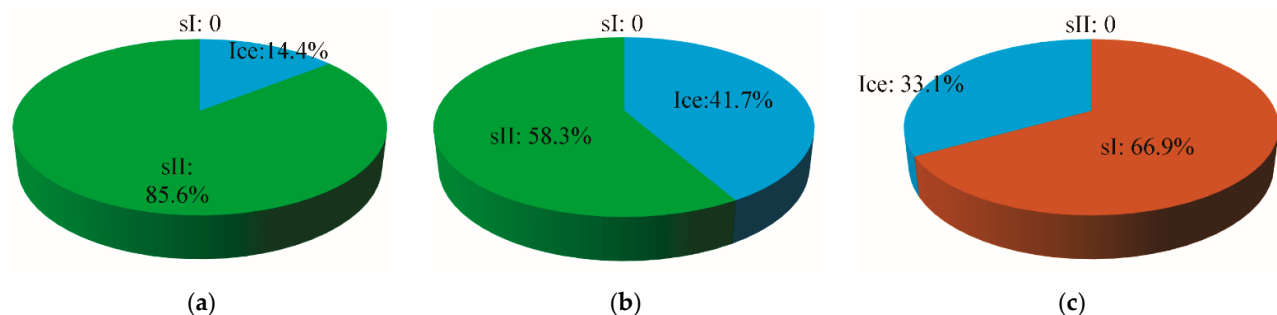


Figure 8. Proportion of hydrate types at various sites in the Gulf of Mexico, USA. (a) Site GC185-GC2; (b) Site GC415-TVG12; (c) Site Chapopote-GC6.

Based on three typical sites in Gulf of Mexico, the recommended combinations of bottom-hole temperature–pressure in hydrate development using the CO₂ replacement strategy were obtained. Figure 9 illustrates the distribution region of recommended temperature–pressure combinations at the three sites, depicted as P–T phase diagrams.

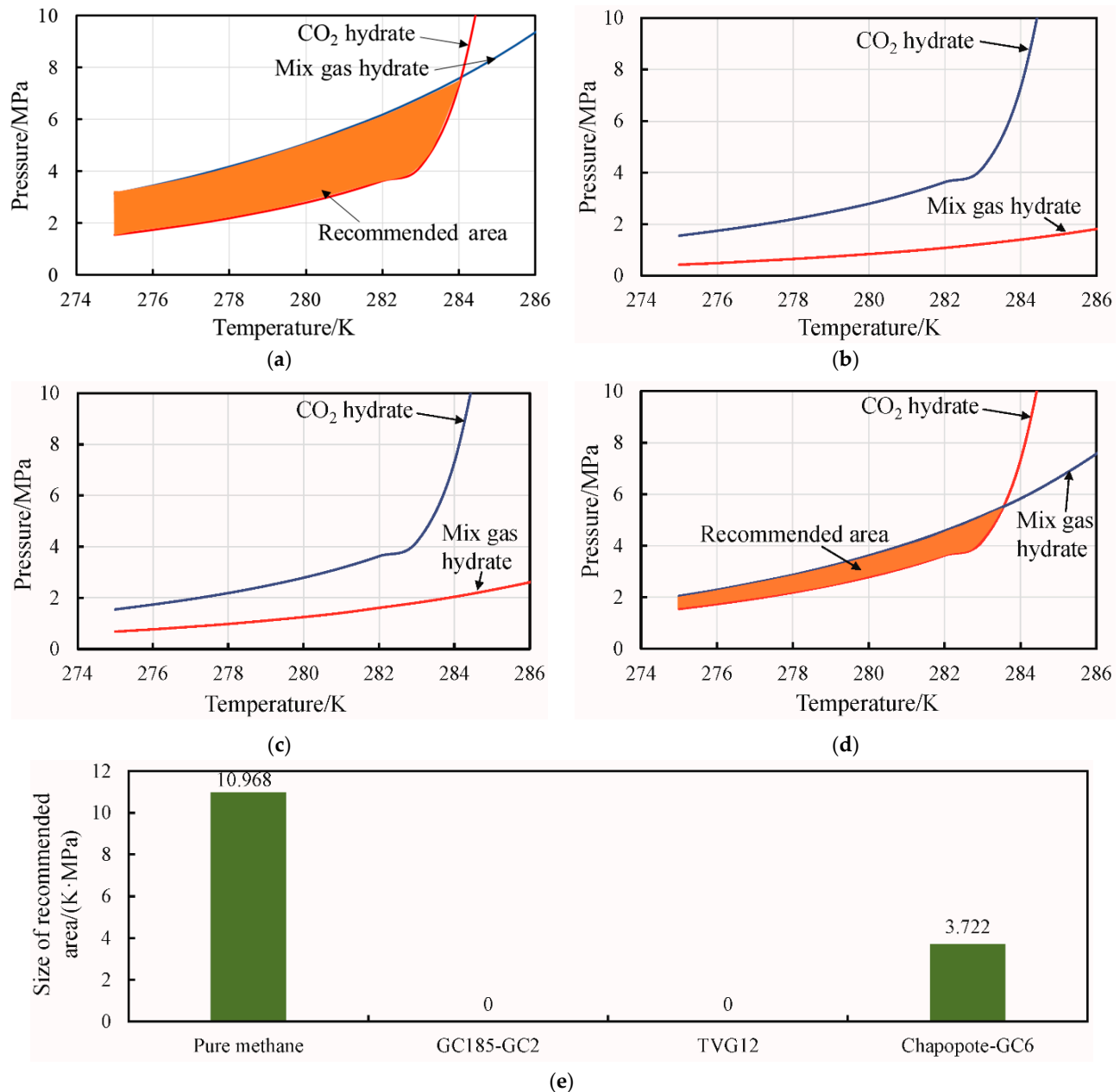


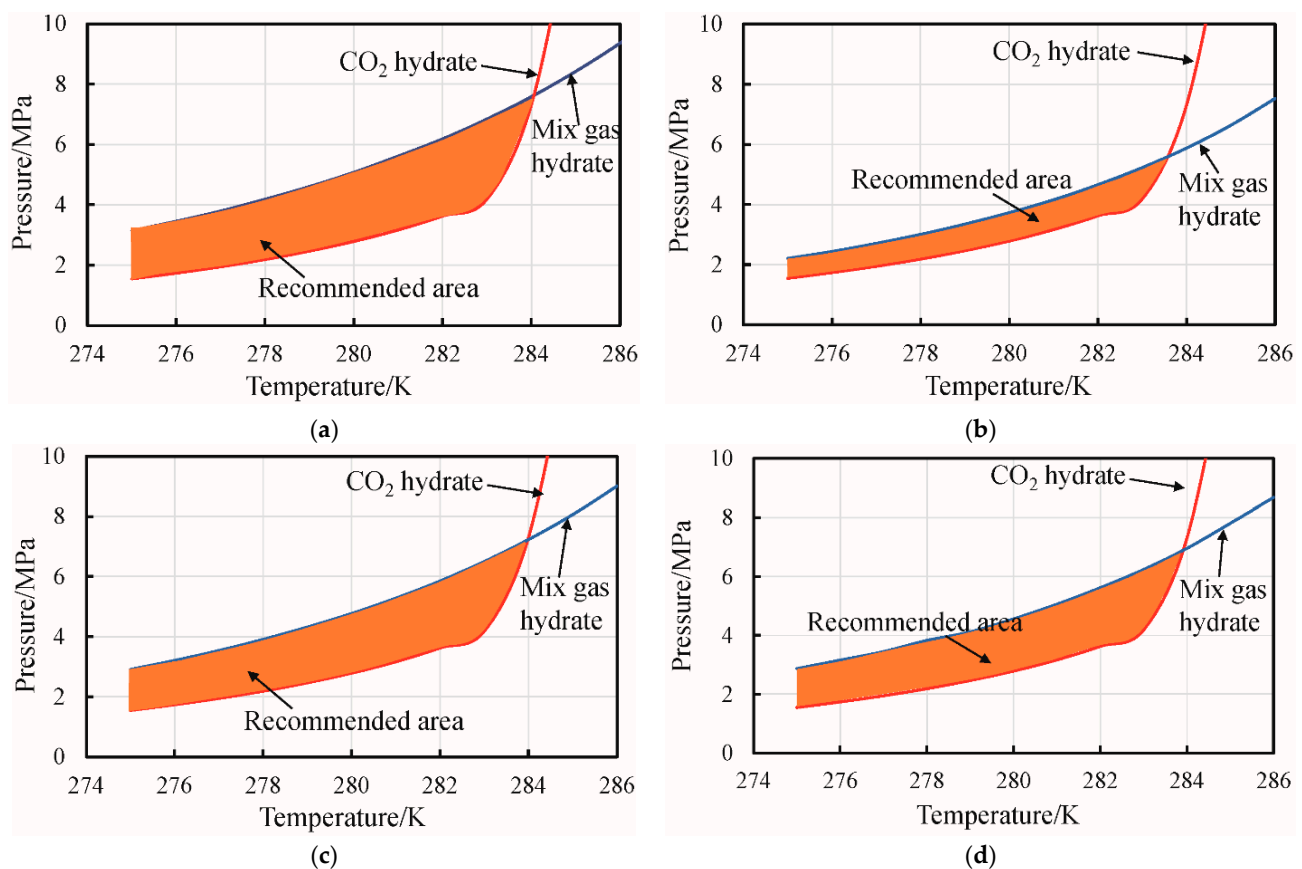
Figure 9. Recommended combinations of temperature and pressure for hydrate reservoirs in Gulf of Mexico, USA. (a) Pure methane hydrate; (b) Gas hydrate in site GC185-GC2; (c) Gas hydrate in site GC415-TVG12; (d) Gas hydrate in site Chapopote-GC6; (e) Size of recommended area for different cases in Gulf of Mexico.

As observed in Figure 9, for the site of the GC185-GC2 and GC415-TVG12, the phase equilibrium curves of CO₂ and the mixed gas do not intersect at any temperature (see Figure 9b,c). In other words, for both cases, no suitable combination of bottom-hole temperature and pressure can be recommended to support methane production from gas hydrates using a CO₂ replacement strategy. Accordingly, as shown in Figure 9e, the size of the recommended area corresponding to both cases is zero. More specifically, at the site of GC185-GC2 and GC415-TVG12, the application of a single CO₂ replacement strategy for methane hydrate exploitation is not feasible. For the site Chapopote-GC6, the phase equilibrium curves of the mixed gas hydrate and carbon dioxide hydrate intersect in the low-temperature range. This cross region represents the recommended

distribution area of bottom-hole temperature and pressure combinations to enable effective hydrate development based on a carbon dioxide replacement strategy. In addition, the region size obtained via the Monte Carlo method is 3.722 K·MPa, which is 33.94% of the corresponding value for pure methane hydrates. Therefore, methane hydrate development in the Gulf of Mexico based on a carbon dioxide replacement strategy is more challenging than that in the South China Sea. In addition, based on the results shown in Figures 8 and 9, it can be concluded that a single CO₂ replacement method is not recommended for hydrate reservoirs dominated by sII hydrate. This limitation arises from the fact that no temperature–pressure combination can concurrently enable formation of CO₂ hydrates while promoting dissociation of natural gas hydrates [69,70].

3.2.3. KG Basin, India

Analyses of gas compositions from all sites in the KG Basin indicate that microbial methane is the dominant component, accompanied by small amounts of microbial ethane [71–73]. It should be noted that substantial differences in gas composition are observed across the sites. Gas hydrates at most sites in the KG Basin are structure I (sI) hydrates and are suitable for development using a carbon dioxide replacement strategy [74]. In this study, three sites—KG-Hyd41, KG-3B25X, and KG-Hyd71—were selected as representative cases to investigate the distribution of recommended bottom-hole temperature and pressure combinations, which was shown in Figure 10.



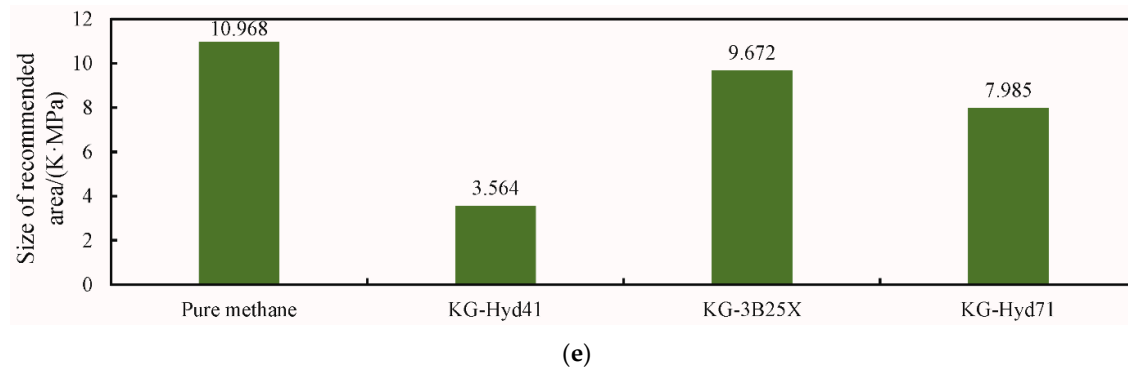


Figure 10. Recommended combinations of temperature and pressure for hydrate reservoirs in KG Basin, India. (a) Pure methane hydrate; (b) Gas hydrate in site KG-Hyd41; (c) Gas hydrate in site KG-3B25X; (d) Gas hydrate in site KG-Hyd71; (e) Size of recommended area for different cases in KG Basin, India.

As can be seen in Figure 10, significant differences are observed in the recommended areas among the various sites in this basin. At the site KG-Hyd41, carbon dioxide constitutes 36.61% of the gas mixture; nevertheless, methane still predominates at 63.38%. That is to say, the gas hydrates occurring at this site is still classified as a structure I (i.e., sI) hydrate. A recommended area for the combination of bottom-hole temperature and pressure for hydrate development via a carbon dioxide displacement strategy still exists, although it is smaller than that under the pure methane hydrate condition [75]. At this site, the application of a carbon dioxide replacement strategy for natural gas hydrate development is constrained by a limited range of viable bottom-hole temperature–pressure combinations (see Figure 10b). The size of this area is 3.564 K·MPa, corresponding to 32.49% of that for the case of pure methane hydrate. Furthermore, both the temperature range and pressure range applicable to development design are narrower than those for pure methane hydrates. For the KG-3B25X site, the mixed gas is dominated by methane (93.62%), accompanied by minor amounts of ethane (1.30%), nitrogen (3.35%), and carbon dioxide (1.73%). The gas hydrates at this site remains a typical structure I (sI) hydrate. Owing to the high methane content, the recommended area of temperature–pressure combinations at this site is large, approaching that of pure methane hydrates. Its size is 9.672 K·MPa, which is 88.18% of that for the case of pure methane hydrate. Such a large area can provide substantial flexibility for the design and selection of bottom-hole pressure–temperature combinations in hydrate development using carbon dioxide replacement strategy. For site KG-Hyd71, although the methane content remains high (92.58%), the carbon dioxide content is also elevated (7.41%), resulting in a smaller size of the recommended area compared with the KG-3B25X site.

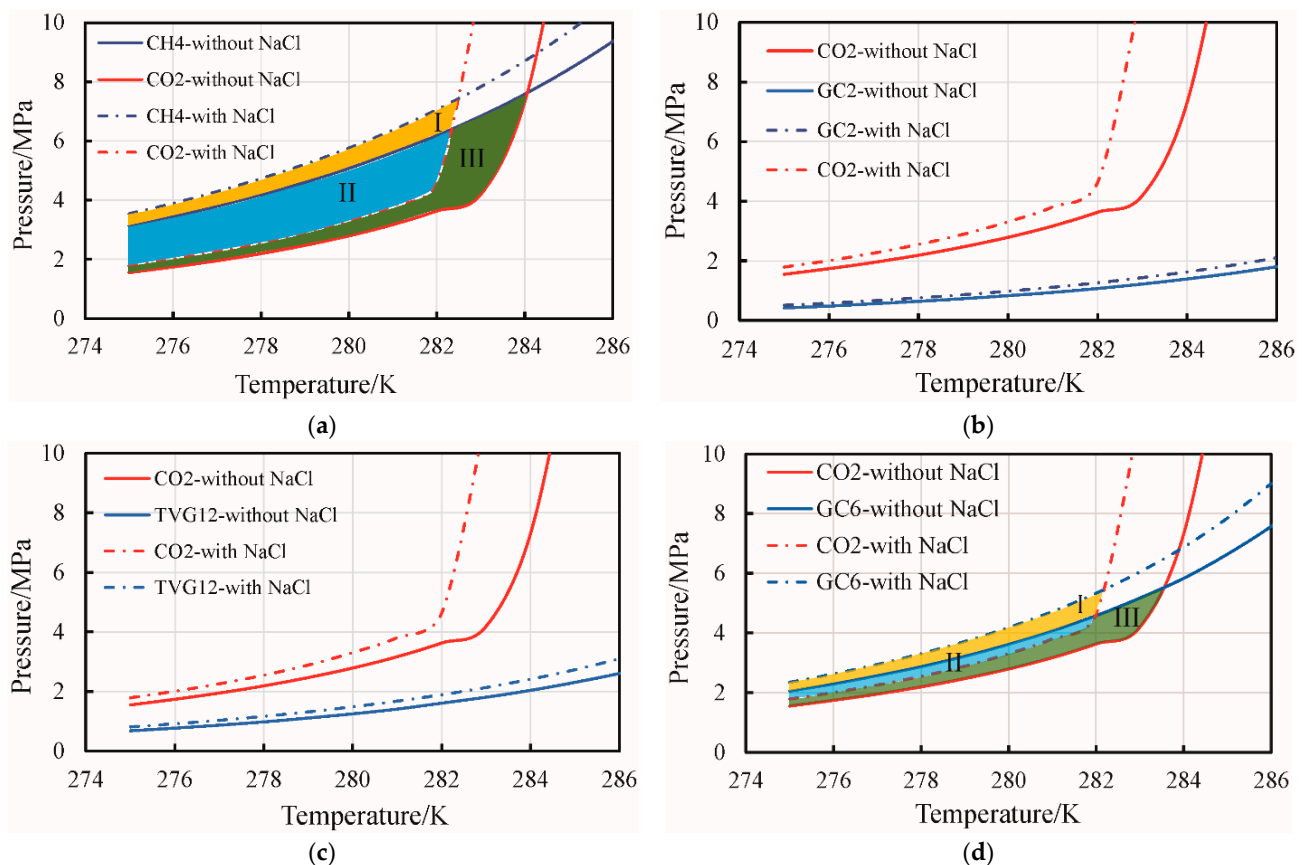
The above analysis suggests that the carbon dioxide replacement strategy may not be suitable for hydrate development in various regions worldwide. Overall, based on the representative gas compositions investigated in this study, the CO₂ replacement strategy shows better applicability for sI hydrates than for sII hydrates. However, the applicability of this strategy may vary depending on reservoir-specific gas composition, particularly the contents of methane and other guest molecules. [75]. Nevertheless, variations in gas composition in hydrates strongly impact the difficulty of designing and controlling the bottom-hole temperature–pressure combinations for hydrate development using this strategy [76,77].

It should be noted that the gas compositions used in this study represent specific sampling locations and may not completely reflect the spatial heterogeneity within natural hydrate reservoirs. Variations in guest gas composition, especially methane and

carbon dioxide contents, can modify the phase equilibrium behavior and consequently influence the size of the recommended temperature–pressure window. For example, an increase in CO₂ concentration in the original hydrate system may reduce the difference between CH₄ hydrate and CO₂ hydrate equilibrium conditions, thereby narrowing the operational window for CO₂ replacement. Conversely, hydrate reservoirs dominated by methane generally provide a wider temperature–pressure range for CO₂ replacement. Therefore, although the present results reveal the controlling role of hydrate structure and gas composition, site-specific evaluation considering compositional uncertainty remains necessary before field application.

3.3. Role of Inhibitor in Changing Size of Recommended Area

The injection of chemical additives, particularly inhibitors, can change phase equilibrium conditions of hydrates, which may in turn modify the size of the recommended area described in the above analysis [78–80]. In some cases, the use of chemical additives may enable the application of carbon dioxide replacement strategy for the exploitation of sII-type hydrates [81]. In this section, the effects of NaCl, as a thermodynamic inhibitor, are analyzed using three cases from the Gulf of Mexico (Section 3.2.2). Figure 11 presents the corresponding results for a NaCl concentration of 3.0 wt%.



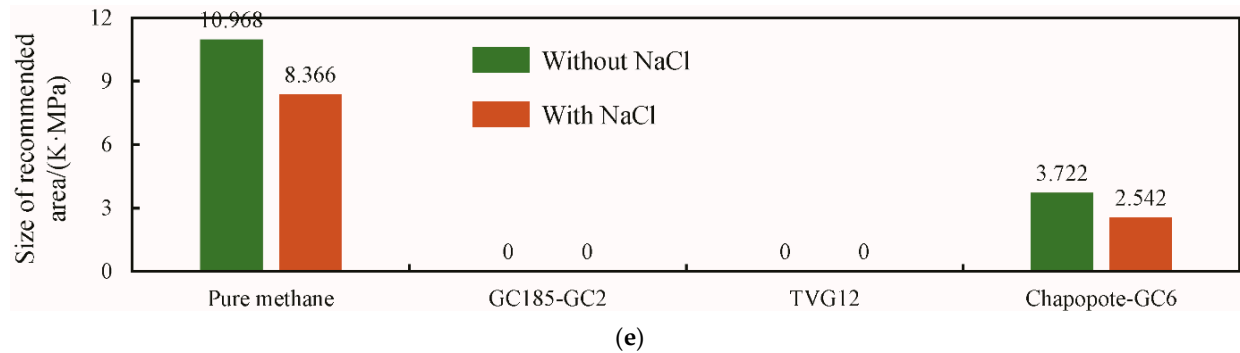


Figure 11. Recommended combinations of temperature and pressure for hydrate reservoirs in Gulf of Mexico, USA with or without NaCl solution (3.0 wt%) injection. (a) Pure methane hydrate; (b) Gas hydrate in site GC185-GC2; (c) Gas hydrate in site GC415-TVG12; (d) Gas hydrate in site Chapopote-GC6; (e) Size comparison of recommended area with or without NaCl Solution Injection (3.0 wt%).

As can be seen in Figure 11a, although inhibitors can enhance the dissociation rate of gas hydrates, their injection may, to some extent, narrow the recommended area of bottom-hole pressure–temperature combinations. That is to say, the combined carbon dioxide replacement and inhibitor injection strategy can improve gas production efficiency, but at the cost of greater difficulty in design and control of bottom-hole temperature–pressure. In Figure 11a, the combined area of Regions I and II represents the recommended area after the addition of 3.0 wt% NaCl solution. However, the recommended area corresponds to the sum of Regions II and III before addition of NaCl solution. In this case, the intersection of the recommended area before and after NaCl solution addition corresponds to Region II. Thus, the effect of NaCl addition on the recommended area can be determined by comparing the areas of Regions I and III. Obviously, the area of region III is larger than that of region I. This directly confirms the above conclusion that the addition of inhibitors increases the difficulty of designing and controlling bottom-hole pressure and temperature during hydrate development using a carbon dioxide replacement strategy. For pure methane hydrates, the quantitative results shown in Figure 11e indicate that the recommended area decreases by 2.602 K·MPa after NaCl addition compared with the case without NaCl. Experimental results from the site of Chapopote-GC6 also demonstrate the same pattern. For the case of site Chapopote-GC6, the recommended area decreases by 1.180 K·MPa after NaCl addition compared with the case without NaCl. This result further confirms the above conclusion. At the sites GC415-TVG12 and GC185-GC2, the addition of NaCl solution results in a greater separation between the phase equilibrium curves of the two gases (i.e., carbon dioxide and mixed gas). The recommended area, which is initially zero, remains unchanged at zero after the addition of NaCl solution.

In this case, when a combined carbon dioxide replacement and inhibitor injection strategy is used for hydrate development, the selection of bottom-hole temperature and pressure requires more professional design and control [82–84]. This is because some pressure-temperature combinations designed for a single CO₂ replacement strategy are not suitable for the combined CO₂ replacement and inhibitor injection strategy.

4. Simulation of Methane Production and Carbon Sequestration

To further evaluate the accuracy and scientific rigor of the above experimental results, corresponding numerical simulations were conducted. In this section, methane production and CO₂ sequestration during hydrate development were investigated using

the carbon dioxide replacement strategy [85–88]. All simulation experiments in this study were carried out in a reaction vessel using a carbon dioxide displacement strategy for methane hydrate development.

It should be clarified that while Section 2.1 describe the overall physical dimensions of the laboratory-scale reactor vessel (radius 15.0 cm, height 50.0 cm), the numerical model in this Section utilizes a simplified core domain (length 30 cm, diameter 10 cm) to verify the underlying replacement mechanisms. This geometric simplification is designed to focus exclusively on the effective hydrate-bearing porous matrix while eliminating boundary dead-volume effects (such as fluid caps and bottom buffers) and optimizing computational efficiency. The simplified simulation domain directly represents the core reactive zone of the experimental system, ensuring the mechanistic findings are highly relevant to the laboratory observations.

4.1. Description of the Zero-Dimensional Reactor Model

As mentioned above, all simulations in this study are investigating the cases inside the reaction vessel. Therefore, the geometric model used in this study, as shown in Figure 12, is a cylindrical domain with a length of 30 cm and an internal diameter of 10 cm. In this study, a zero-dimensional (0D) model was employed to analyze the temporal evolution of each component, without accounting for spatial variation. Continuous injection of carbon dioxide is prone to causing significant pore clogging, which may hinder effective mass transfer. Fortunately, the periodic “injection–equilibrium” strategy facilitates diffusion-dominated transport, which helps to enhance the replacement rate. In the simulation, carbon dioxide is injected into the reaction vessel through the injection port at a segmented flow rate, and the piecewise function is shown in Figure 13. The total simulation time is about 3 days (i.e., 71 h). As can be seen from Figure 13, the injection of carbon dioxide was carried out in five stages throughout the entire simulation process. However, the duration of each stage is inconsistent. Although a cylindrical geometry is illustrated in Figure 12, the numerical model developed in this study is a zero-dimensional (0D) model. The cylindrical configuration is only used to represent the physical reactor and define the total system volume, rather than as a spatial computational domain. No spatial discretization or transport equations were solved in the radial or axial directions. Instead, the reactor was treated as a homogeneous control volume, and the temporal evolution of pressure, temperature, gas composition, hydrate formation, and methane production was calculated based on mass and energy balances.

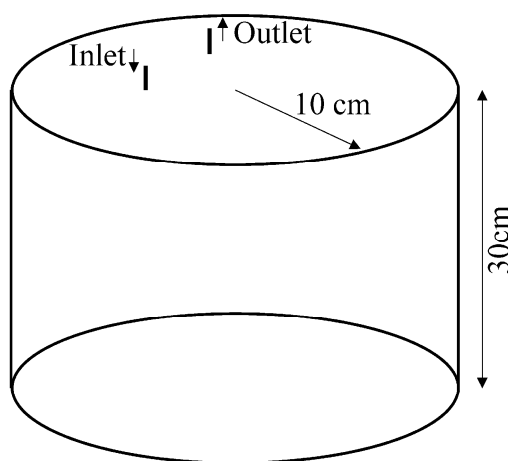


Figure 12. Schematic representation of the reactor configuration used in the zero-dimensional model.

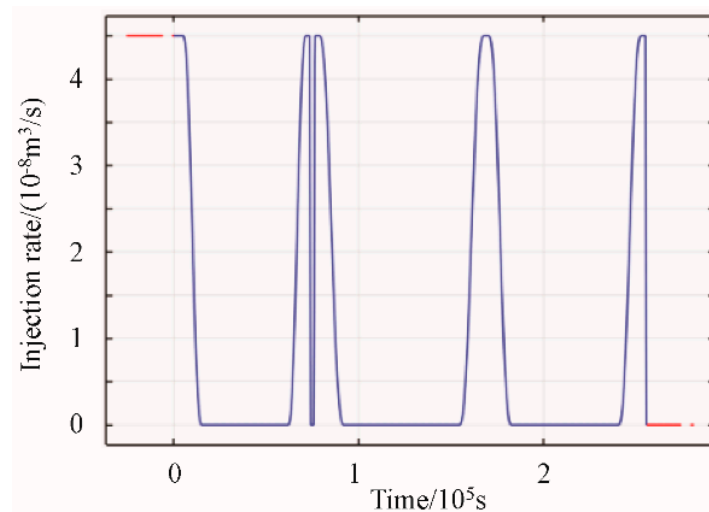


Figure 13. Segmental function for injection rate of carbon dioxide in simulation.

A series of basic data used to implement the simulation are presented in Table 5. In the simulation, the following chemical reactions were involved [89–91].

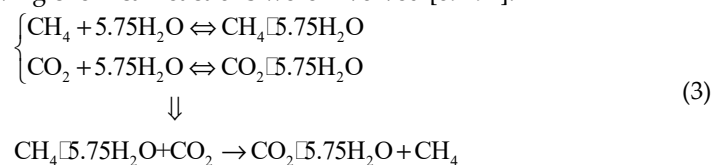


Table 5. Basic parameters used for simulation.

Parameters	Unit	Value	Parameters	Unit	Value
Heat capacity of methane hydrate	268	J/(K·mol)	Activation energy of CH ₄ hydrate	81,000	J/mol
Heat capacity of water	74.16	J/(K·mol)	Activation energy of CO ₂ hydrate	102,900	J/mol
Heat capacity of CO ₂ hydrate	328	J/(K·mol)	Initial concentration of water	42,800	mol/m ³
Heat capacity of methane	47.69	J/(K·mol)	Initial saturation of CH ₄ hydrate	33	%
Heat capacity of CO ₂	106.62	J/(K·mol)	Initial temperature of reactor	283.15	K
Heat capacity of sand	44.40	J/(K·mol)	Initial pressure	8.0	MPa
Enthalphy of CH ₄ hydrate	54,200	J/mol	Sediment porosity	0.65	-
Enthalphy of CO ₂ hydrate	82,000	J/mol	Dissociation rate constant of CH ₄ hydrate	0.006	mol/(s·m ³)
Molar density of methane hydrate	8000	mol/m ³	Dissociation rate constant of CO ₂ hydrate	0.008	mol/(s·m ³)
Water density	1010	kg/m ³	Thermal conductivity of sediment	3.3	W/(m·K)
Thermal conductivity of CH ₄ hydrate	0.62	W/(m·K)	Thermal conductivity of water	0.583	W/(m·K)
Thermal conductivity of CO ₂ hydrate	0.49	W/(m·K)	Thermal conductivity of CH ₄	0.05	W/(m·K)
Injection rate of CO ₂	4.5 × 10 ⁻⁸	m ³ /s	Thermal conductivity of CO ₂	0.10	W/(m·K)

4.2. Model Validation

To evaluate the applicability of the proposed model, the simulation results were compared with previously reported investigation results for CO₂ injection into methane hydrate systems. Gharasoo et al. (2019) investigated methane recovery and CO₂ sequestration through CO₂ injection and provided measurements of methane release and CO₂ retention [92]. Therefore, the dataset was selected as a benchmark for model evaluation. Based on one case investigated in Reference [92], namely 13 MPa and 275.15 K, a comparison was performed and the applicability of the investigation model was evaluated, and the comparison results are shown in Figure 14.

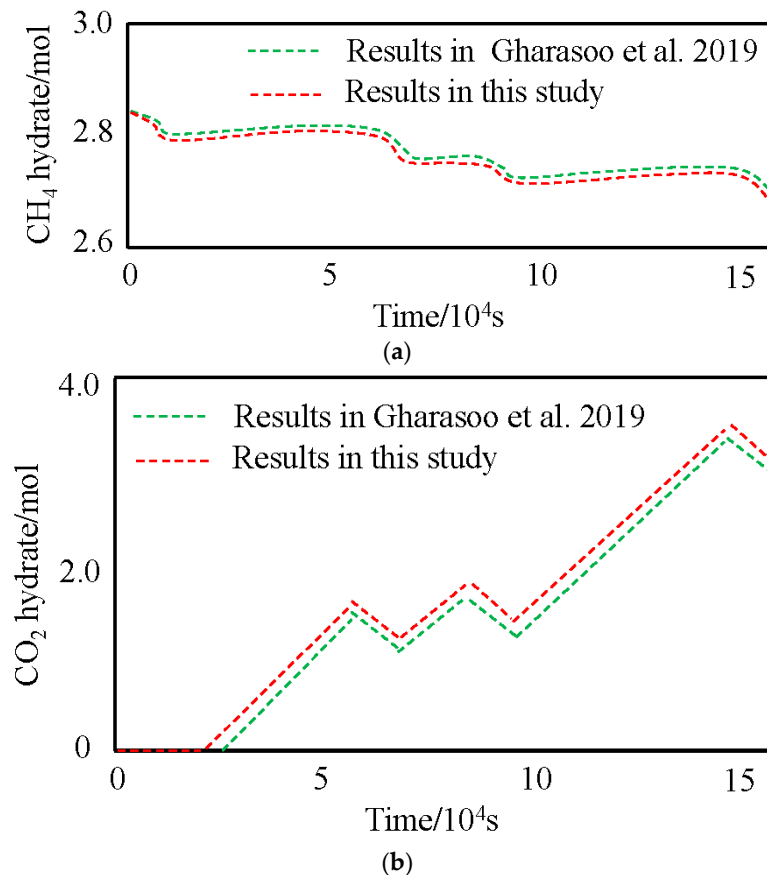


Figure 14. Evolution of carbon dioxide hydrate in reaction vessel [92]. (a) CH₄ hydrate; (b) CO₂ hydrate.

As shown in Figure 14, the evolution trends of CH₄ hydrate dissociation and CO₂ hydrate formation predicted by the present model are highly consistent with the results reported in Ref. [92]. Both models capture the same variation characteristics during the CO₂–CH₄ hydrate replacement process, including the gradual reduction of CH₄ hydrate and the continuous formation of CO₂ hydrate. The predicted values exhibit only minor discrepancies throughout the simulation period, indicating that the proposed model can accurately describe the hydrate phase transition behavior induced by CO₂ injection.

Nevertheless, slight differences can still be observed between the two results. Specifically, the CH₄ hydrate amount predicted in this study is marginally lower than that reported in Ref. [92], whereas the calculated CO₂ hydrate amount is slightly higher. These deviations are mainly attributed to the different hydration numbers adopted in the two models. In the present study, a hydration number of 5.75 was used, corresponding to the ideal structure-I hydrate with complete occupation of hydrate cages, while a value of 6.0 was adopted in Ref. [92], representing a more practical hydrate structure with incomplete cage occupancy. Since the hydration number determines the molar relationship between guest molecules and water molecules in hydrate phases, a lower hydration number indicates that fewer water molecules are required to form hydrate per mole of guest gas. Consequently, compared with the model using a hydration number of 6.0, the present model slightly increases the conversion of water molecules into CO₂ hydrate and promotes the release of CH₄ molecules during the replacement process, resulting in a slightly higher CO₂ hydrate formation and a slightly lower CH₄ hydrate amount.

The maximum deviation between the two simulations remains limited, suggesting that the influence of hydration number within the range of 5.75–6.0 on the overall hydrate evolution is relatively small. Therefore, the good agreement with previous results verifies the accuracy and reliability of the proposed numerical model for simulating CO_2 – CH_4 hydrate replacement processes.

4.3. Evolution of Carbon Dioxide Hydrates

Figure 15 shows the evolution curve of the total amount of carbon dioxide hydrates present in the reaction vessel. As can be seen in Figure 15, the growth of carbon dioxide hydrate was extremely slow, with a brief stagnation observed during the initial 5520 s. The injection of carbon dioxide increased the reactant concentration. Meanwhile, the high-temperature carbon dioxide led to a rapid increase in the local temperature within the reaction vessel, which exceeds the stable region of gas hydrates. At this stage, the experimental system is dominated by physical gas accumulation, while phase transition kinetics is inhibited by the elevated temperature. When the injection of carbon dioxide was stopped after 5520 s, the temperature inside the reaction vessel was reduced to 8 °C, and a strong subcooling driving force was formed. During the period from 5520 s to 71,520 s in simulation, a dense carbon dioxide hydrate envelope layer had not yet formed on the surfaces of the sand particles. At this stage, mass transfer resistance is minimal, allowing the displacement reaction to proceed with maximum efficiency. Therefore, the evolution curve in Figure 15 exhibits an approximately linear growth of carbon dioxide hydrate during this stage [93,94].

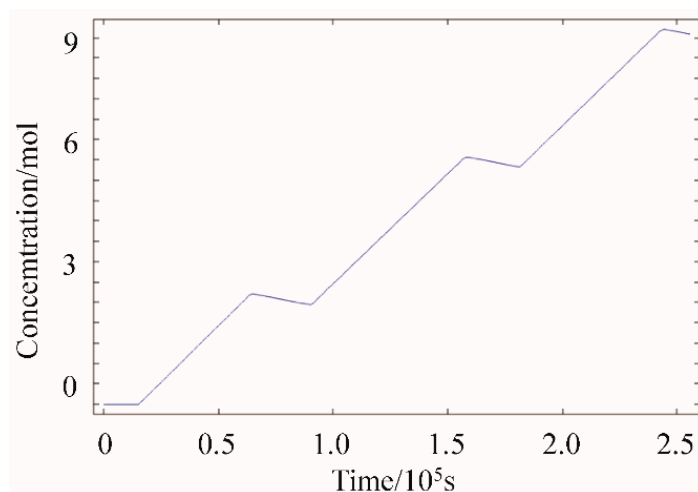


Figure 15. Evolution of carbon dioxide hydrate in reaction vessel.

The period from 71,520 s to 78,840 s represents a brief secondary strengthening phase. Within this stage, the simulation system not only failed to sequester additional carbon dioxide but also released previously fixed portion of carbon dioxide back into the gas or liquid phase. It can be seen that two carbon dioxide injection events were carried out during this stage. Although the injection is intermittent, the porous medium (sand bed) in reaction vessel exhibits significant thermal inertia [95–97]. The heat generated during the first injection was not fully dissipated during the short static period of 2220 s, and the subsequent injection introduced elevated temperatures once again. As a result, the temperature inside the reaction vessel remains consistently above the equilibrium temperature of carbon dioxide hydrate at the corresponding pressure. After this, the amount of carbon dioxide hydrate transitioned from the previous thermal dissociation stage to sustained growth stage during the period from 78,840 s to 167,520 s (about 24.6

h). During this period, the reaction vessel achieved efficient heat dissipation through the external cooling jacket wrapped around it. The temperature inside the reaction vessel rapidly falls back below the phase equilibrium temperature of carbon dioxide hydrate. The increasing supercooling provides sufficient thermodynamic driving force for formation of carbon dioxide hydrate [98–100].

In the following 2940 s, an additional carbon dioxide injection was applied in the model, and the amount of carbon dioxide hydrate in reaction vessel decreased again. The reason is that although high pressure favors hydrate stability in this stage, high temperature destruction for carbon dioxide hydrates dominates absolutely under these conditions [101–103]. An instantaneous heat influx destabilizes carbon dioxide hydrates, which results in partial endothermic dissociation of previously formed hydrate [104,105].

Beyond 174,600 s, the carbon dioxide hydrate in the reaction vessel experienced steady further formation after undergoing the previous stage of thermal dissociation. This is the final stage of the simulation. A substantial amount of highly active free water was released in the preceding stage. These water molecules rapidly reacted with high-pressure carbon dioxide to form new hydrate crystals driven by the strong supercooling [106,107]. In total, about 9.05 mol of carbon dioxide hydrate was formed in the reaction vessel.

Table 6 provides statistics on the key parameters of the simulation process, including the total injected CO₂, retained CO₂, CO₂ sequestration efficiency, and methane recovery factor. As can be seen in Table 6, a total of 29.486 mol CO₂ was injected into the reaction vessel during the entire simulation period, while 12.46 mol CO₂ was effectively retained in the system, corresponding to a CO₂ sequestration efficiency of 42.25%. The results indicate that a considerable proportion of the injected CO₂ was successfully captured through the hydrate formation and retention processes, demonstrating the effectiveness of the CO₂ replacement strategy for carbon storage [106–108]. Meanwhile, the methane recovery factor reached 40.30%, suggesting that CO₂ injection not only contributes to carbon sequestration but also promotes methane production from hydrate dissociation [109,110]. It should be noted that the retained CO₂ amount (12.46 mol) is higher than the amount of CO₂ converted into hydrate phase (9.05 mol), indicating that a fraction of CO₂ was retained in other forms, such as dissolved CO₂ in the aqueous phase. Therefore, evaluating only the hydrate-bound CO₂ may underestimate the overall carbon sequestration capacity [111–113].

Table 6. Quantitative evaluation of methane recovery and CO₂ sequestration performance during the simulation process.

Parameters	Value	Unit
Total injected CO ₂	29.486	mol
Retained CO ₂	12.46	mol
Storage efficiency	42.25	%
Methane recovery	40.30	%

4.4. Temperature Evolution During CO₂ Replacement Process

Temperature evolution within the reaction vessel provides important insights into the coupling relationship between CO₂ injection, hydrate phase transition, and heat transfer during the replacement process [114–116]. As shown in Figure 16, the temperature exhibits a periodic fluctuation behavior corresponding to the segmented CO₂ injection strategy. At the beginning of the simulation, the temperature rapidly increases from approximately 281 K to 291.5 K, followed by a rapid decrease to approximately 283.5 K. Similar temperature fluctuations occur during subsequent CO₂ injection stages, with the

maximum temperature reaching approximately 292 K, whereas the system temperature remains relatively stable at approximately 283.5 K during the non-injection periods.

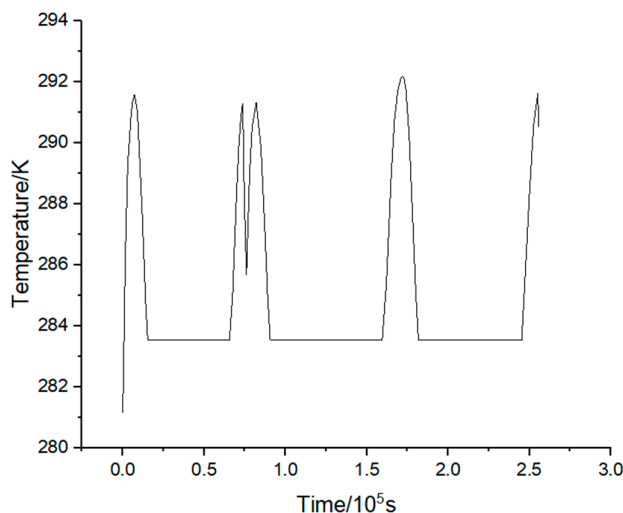


Figure 16. Temperature evolution during CO₂ replacement process in the reaction vessel.

The transient temperature increase during CO₂ injection is mainly attributed to the introduction of relatively high-temperature CO₂ and the associated thermal disturbance caused by gas compression and mixing [117–120]. When the injected CO₂ enters the reaction vessel, the increased temperature reduces the subcooling degree of the system. Consequently, the thermodynamic driving force for CO₂ hydrate formation decreases, which explains the limited hydrate growth observed during the early injection stage [121,122]. This phenomenon is consistent with the evolution characteristics of CO₂ hydrate shown in Figure 15, where hydrate formation is initially inhibited during the temperature increase period.

After CO₂ injection is terminated, the external cooling system gradually removes the accumulated heat, causing the temperature to return to approximately 283–284 K. At this stage, the increased subcooling degree provides a stronger driving force for hydrate nucleation and growth. For example, when the temperature decreases from the peak value of approximately 292 K to the stable value of 283.5 K, the temperature reduction exceeds 8 K, significantly enhancing the thermodynamic stability of CO₂ hydrate. Therefore, the intermittent injection mode effectively avoids continuous thermal accumulation and creates favorable low-temperature conditions for CO₂ sequestration [123–125].

In addition, temperature variation has a dual influence on methane recovery and carbon dioxide storage. A moderate increase in temperature is beneficial for CH₄ hydrate dissociation because it shifts the system away from methane hydrate stability conditions, thereby promoting methane release. However, excessive temperature increase may inhibit CO₂ hydrate formation because the stability of CO₂ hydrate is highly sensitive to temperature. Therefore, the temperature evolution observed in this study represents a dynamic balance between methane production and CO₂ sequestration. Maintaining the reaction temperature close to 283–284 K after each injection stage is favorable for maximizing CO₂ fixation while ensuring continuous methane recovery.

From an engineering perspective, the temperature response demonstrates that thermal management is a critical factor in CO₂ replacement-based hydrate exploitation [126,127]. Continuous CO₂ injection without sufficient heat dissipation may cause excessive temperature accumulation and reduce hydrate conversion efficiency [128]. In con-

trast, the intermittent injection strategy adopted in this study enables periodic temperature recovery and maintains sufficient subcooling conditions, thereby improving the overall efficiency of methane production and CO₂ sequestration [129,130].

5. Conclusions

The main conclusions are summarized as follows:

- (1) In hydrate development using carbon dioxide replacement strategy, the bottom-hole pressure at a given temperature must exceed the phase equilibrium pressure of carbon dioxide hydrate while remaining below that of natural gas hydrate. These combinations of bottom-hole temperature and pressure can ensure the rapid dissociation of natural gas hydrates to produce natural gas, while also promoting the formation of carbon dioxide hydrates for carbon sequestration. This area where these temperature and pressure combinations are located is precisely the recommended region for designing bottom-hole temperature and pressure.
- (2) The results obtained from representative cases indicate that the CO₂ replacement strategy is more favorable for sI-type hydrate reservoirs, whereas its application in sII-type reservoirs may face greater thermodynamic constraints. Nevertheless, the feasibility of CO₂ replacement should be further evaluated considering the specific gas composition and spatial heterogeneity of individual hydrate reservoirs.
- (3) Although inhibitor injection can theoretically promote the dissociation of gas hydrates and the production of natural gas, it brings difficulties to the design of bottom-hole temperature and pressure in development engineering. The balance between the enhancement of gas production by inhibitor injection and the difficulties they bring to the design of bottom-hole temperature and pressure is an important focus for future work.

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Conflicts of Interest: The authors affirm that there are no existing financial conflicts or personal associations that might seem to have biased the findings presented in this document.

Appendix A

In this study, a Monte Carlo method was adopted to estimate the areas of regions with irregular geometries. The Monte Carlo algorithm used to compute the area of irregular shapes is fundamentally a statistical sampling method, in which mathematical problems are converted into probabilistic experiments. When a large number of random points are uniformly distributed within a geometric domain of known area, some of these points will fall within the target irregular region. The fraction of points located within the target irregular region corresponds to the ratio of the irregular region's area to the total area. Based on this principle, the following matlab code was developed.

%% Area Calculation and Distribution Visualization Based on Monte Carlo Algorithm

```

clear; clc; close all;
%% 1. Read and Pre-process Image
img = imread('*****.png'); % Ensure the filename is correct
[rows, cols, ~] = size(img);
% 2. Color Recognition (Extract Orange Region)
% Based on the provided image, the orange region has distinct RGB features
R = img(:,:,1); G = img(:,:,2); B = img(:,:,3);
% Thresholds are adjusted to cover the orange region based on typical pixel values
mask = (R > 180 & G > 100 & B < 100);
% 3. Set Physical Coordinate Range (Based on image axes)
T_range = [274, 286];
P_range = [0, 10];
Total_Area = (T_range(2) - T_range(1)) * (P_range(2) - P_range(1));
% 4. Monte Carlo Simulation
N = 50,000; % Set to 50 k for smooth plotting; can be increased to 1 M for higher precision area calculation, which can be changed
rand_col = randi([1, cols], N, 1);
rand_row = randi([1, rows], N, 1);
% Pre-allocate logical index
is_inside = false(N, 1);
for i = 1:N
    if mask(rand_row(i), rand_col(i)) == 1
        is_inside(i) = true;
    end
end
% 5. Calculate Results
in_count = sum(is_inside);
ratio = in_count/N;
Estimated_Area = ratio*Total_Area;
% 6. Plotting and Distribution Visualization
figure('Color', 'w', 'Position', [100, 100, 1000, 450]);
% Subplot 1: Original Mask/Image (Verify if extraction is accurate)
subplot(1, 2, 1);
imshow(img); hold on;
title('Original Image & Coordinate Reference');
% Subplot 2: Monte Carlo Point Distribution
subplot(1, 2, 2);
% Plot points outside the region (Red, faded)
plot(rand_col(~is_inside), rows - rand_row(~is_inside), '.', 'Color', [0.5, 0, 0], 'MarkerSize', 1);
hold on;
% Plot points inside the target region (Green)
plot(rand_col(is_inside), rows - rand_row(is_inside), '.', 'Color', [0, 0.7, 0], 'MarkerSize', 2);
title(['Monte Carlo Distribution (N = ' num2str(N) ')']);
xlabel('Pixel X-coordinate'); ylabel('Pixel Y-coordinate');
legend('Outside Region', 'Inside Target Region', 'Location', 'northeastoutside');
axis equal;
% --- Detailed Calculation Report Output ---
fprintf('\n===== CALCULATION REPORT =====\n');
fprintf('Image Dimensions (Pixels): %d (W) x %d (H)\n', cols, rows);

```

```

fprintf('Horizontal (T) Range:      [%0.2f, %0.2f]\n', T_range(1), T_range(2));
fprintf('Vertical (P) Range:      [%0.2f, %0.2f]\n', P_range(1), P_range(2));
fprintf('-----\n');
fprintf('Total Simulation Points (N): %d\n', N);
fprintf('Points in Target Region:      %d\n', in_count);
fprintf('Target Region Percentage:      %0.2f%%\n', ratio * 100);
fprintf('-----\n');
% Physical meaning of a single pixel (Optional reference)
pixel_area_physical = Total_Area/(rows * cols);
fprintf('Estimated Physical Area:      %0.4f (K·MPa)\n', Estimated_Area);
fprintf('Physical Area per Pixel:      %0.6e (K·MPa/pixel)\n', pixel_area_physical);
fprintf('===== \n');

```

Notably, It is worth noting that while the composite unit 'K·MPa' does not represent a standard thermodynamic state variable, it serves as a geometric operational criterion in the T-P projection space. Mathematically, this area quantifies the total allowable parameter space (safe operating envelope) bounded by the upper and lower equilibrium constraints. A larger 'K·MPa' value fundamentally reflects a wider temperature-pressure tolerance window, indicating higher operational flexibility and resistance to downhole pressure/temperature fluctuations during field injection. To keep this metric intrinsically comparable across different sites, the reference temperature boundary (275 K) and the thermodynamic convergence points are strictly standardized in all cases. This standardization eliminates the influence of arbitrary axis scaling.

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