

Microscopic Insights and Optimization of the CH₄–CO₂ Replacement in Natural Gas Hydrates

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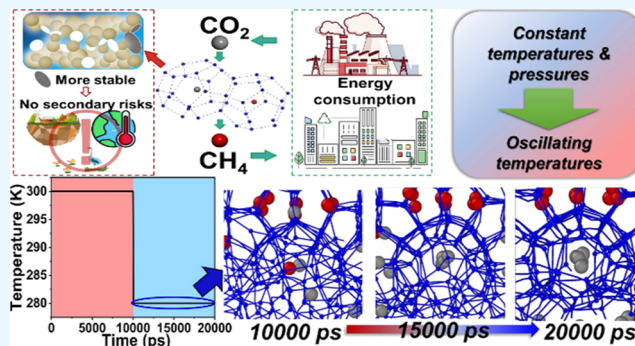
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ABSTRACT: Using the CO₂ replacement method to exploit natural gas hydrates and store CO₂ has great significance in energy access and environmental protection. Herein, the molecular dynamic method is utilized to analyze and evaluate the CH₄–CO₂ replacement at different constant temperatures and pressures. For optimization, various temperature oscillations are introduced in the CH₄–CO₂ replacement. It illustrates that increasing the temperature can improve the amounts of CH₄ escape and CO₂ capture but is unfavorable to the long-term CO₂ storage and hydrate stability. The effects of pressure are not as significant and definite as those of temperature. Appropriate temperature oscillations can achieve comprehensive improvements, which benefit from both the deep diffusion of CO₂ in the higher temperature stage and the rapid rebuilding of CO₂ hydrate within just nanoseconds caused by the memory effects in the lower temperature stage. The results also reveal that the optimal lower temperature duration and frequency should be moderate. Decreasing the lower temperature value can distinctly enhance CO₂ capture and hydrate stability. This study can help understand the mechanisms of CH₄–CO₂ replacement under different temperature and pressure conditions, especially at temperature transitions, and proposes a potentially effective method to achieve large-scale carbon sequestration in the hydrate.



1. INTRODUCTION

The lack of energy has been drawing increasing attention due to the rapid development of industry and society.^{1,2} Meanwhile, there is an obvious conflict that traditional fossil fuels have caused serious pollution after utilization for several decades.^{3,4} In view of the immaturity and instability of new energy sources,^{5–7} increasing attention is being paid to natural gas,⁸ a kind of clean energy that has been proven to be widely stored in natural gas hydrates (NGH). Nowadays, three kinds of hydrates have been found: type I, type II, and type H.⁹ For NGH, it is mainly CH₄ hydrate, which belongs to type I.^{10,11} In the standard case, each cubic meter of NGH can produce 164 cubic meters of methane gas after decomposition, which is why NGH is a kind of significant energy source.¹²

The main extraction methods of NGH are depressurization, thermal stimulation, hydrate inhibitor injection, and the CO₂ replacement method.^{9,10} The principle of the first three methods is to make NGH out of the conditions, where it can stay stable. The principle of the gas exchange method is to replace methane in the NGH by using CO₂.¹¹ Among the four methods mentioned above, depressurization is the most popular, and the other three are often used as auxiliary methods. However, due to the imperfect production technology and complex reservoir characteristics, the first three methods may lead to large-scale uncontrollable decomposition of NGH and further

loss and damage.^{13–15} First, NGH play an indispensable role in geological stability. Hydrate and sand support each other to ensure a stable geologic structure.^{16,17} Without hydrate, geological disasters are inevitable.¹⁸ More seriously, it can set off a series of chain reactions. For instance, undiscovered hydrate reservoirs can be destroyed and release much CH₄, causing greenhouse effects, sea level rise, climate deterioration, and ecological unbalance.^{19,20} Second, the uncontrollable decomposition of NGH produces much gas and water. When they flow out, a lot of sand can be carried out, resulting in the breakdown of facilities and even the shutdown of the whole hydrate exploitation project.^{21,22} In consideration of the risks mentioned above, more and more researchers have begun to realize the significance of the gas exchange method.^{23–25} Different gases can be utilized to replace the CH₄ in hydrate, among which CO₂ is the most widely used gas.^{26,27} For one thing, due to the higher stability of CO₂ hydrate than CH₄ hydrate, the newly formed

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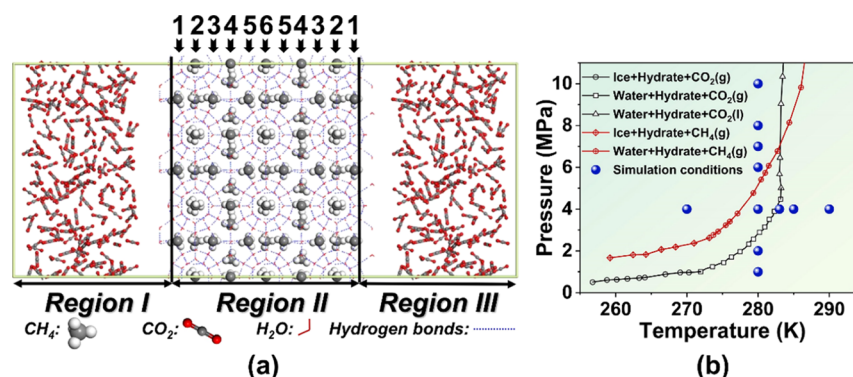


Figure 1. (a) Initial configuration of the simulation system (black arrows: CH₄ molecules at different depths); (b) simulation conditions and phase diagrams of CH₄ hydrate and CO₂ hydrate.

CO₂ hydrate reduces the risk of uncontrollable decomposition of hydrates, sand production, and other secondary disasters mentioned above.^{28,29} For another, the CO₂ replacement method can help not only extract CH₄ from NGH but also realize CO₂ storage and reduce the greenhouse effects. Therefore, a recycle without carbon emissions can be formed, which is supported by the policies of many countries.^{30,31} In addition, the development of the carbon trading market also provides extra benefits for the gas exchange method.^{32,33} At present, many experimental and computational investigations have been performed to verify the feasibility of the CO₂ replacement method in aspects of thermodynamics and kinetics.^{34–38} However, it cannot be ignored that the low replacement efficiency of the gas exchange method limits its application and promotion.^{37,39,40} Possible improving methods mainly include extending the soaking time,⁴¹ using small-molecule gases,^{27,42} changing the phase of CO₂,^{43,44} using hydrate promoters or inhibitors,^{45,46} and selecting the proper temperature and pressure. Therein, selecting the proper temperature and pressure is closest to the field test because it is easy to realize with the assistance of the thermal stimulation method and depressurization method.

Zhang et al.⁴⁷ conducted experiments at different pressures (3.6, 4.0, and 4.5 MPa) and different temperatures (below and above the freezing point) to study how pressure and temperature affect the replacement process. The results indicated that higher pressure and temperature are conducive to improving the average replacement rate and efficiency. Xu et al.⁴⁸ investigated the effects of pressure on the replacement process by in situ Raman analysis. It was found that the replacement rate is positively influenced by the operating pressure. Gambelli and Rossi⁴⁹ carried out eight experimental tests to compare the effects of two different thermal stimulations on the replacement process. They found that increasing the temperature first and then introducing CO₂ required much less thermal energy to finish the replacement process than introducing CO₂ first and then increasing the temperature. Zhang et al.⁵⁰ combined thermal stimulation and gas exchange methods, and the CH₄ replacement percentage of an upper limit of 64.63% was achieved. Li et al.⁵¹ injected mixed CO₂ and N₂ into gas hydrates and found that there was decomposition and replacement in this process at the same time. The results indicated that higher temperature and lower pressure can promote the decomposition and improve the gas recovery efficiency. Mok et al.⁵² investigated the effects of different pressures (10.0–18.5 MPa) and temperatures (274.2–277.2 K) on the CH₄–CO₂ + N₂ replacement process. It was shown that at 274.2 K, the extent of

replacement increased with the injection pressure of CO₂ and N₂. Meanwhile, at a higher temperature, the extent of replacement did not change. Chen et al.⁵³ studied the behavior of methane hydrate during depressurization-assisted CO₂ replacement. They found that depressurization assistance can enhance the CO₂ utilization efficiency. Although many works have been done to test different temperature and pressure conditions, there are still no definite principles and related explanations. Some previous studies have even presented contrary research conclusions, especially on the influencing pattern of pressure.⁵⁴ In addition, most previous researchers focused on experimental studies and observed the macroscopic phenomenon. Few have focused on the micro-mechanisms of the replacement process under different conditions and their differences. This may lead to unclarity on some key issues, such as whether the CO₂ is firmly trapped by the hydrate, or silted in the pore space, or just dissolved in the liquid.

To monitor and explain the microscopic process, the molecular dynamics (MD) simulation is regarded as an effective method, which can provide more general and fundamental insights. Nowadays, MD simulation has been widely utilized in studying various behaviors of NGH.^{55–58} For CO₂ hydrate and CO₂/CH₄ mixed hydrate, MD simulation has also shown satisfying applicability and provided valuable insights.^{59–61} In this work, the MD method is used to analyze and evaluate the CH₄–CO₂ replacement at different constant temperatures (270–290 K) and pressures (1–10 MPa). As a novel optimization strategy, various temperature oscillations are introduced. The effects of the lower temperature duration, the lower temperature value, and the frequency of oscillations are investigated and explained.

2. METHODOLOGY

2.1. Model and Simulation Details. At first, the initial type I hydrate structure is constructed according to previous X-ray analysis,⁶² based on which a 3 × 3 × 3 supercell is built. Then, 200 CO₂ molecules are added to the surfaces of CH₄ hydrate. The total amount of CO₂ molecules is 400 due to the fact that there are two surfaces of CH₄ hydrate. Subsequently, energy minimization is carried out based on the steepest descent, ABNR, and quasi-Newton methods. Finally, the whole model of the simulations is shown in Figure 1a, containing 1242 H₂O molecules, 216 CH₄ molecules, and 400 CO₂ molecules. The simulation model is divided into three regions: region I, region II, and region III. At the initial time, all the CO₂ molecules are in the fluid phase (region I and region III). Meanwhile, the CH₄

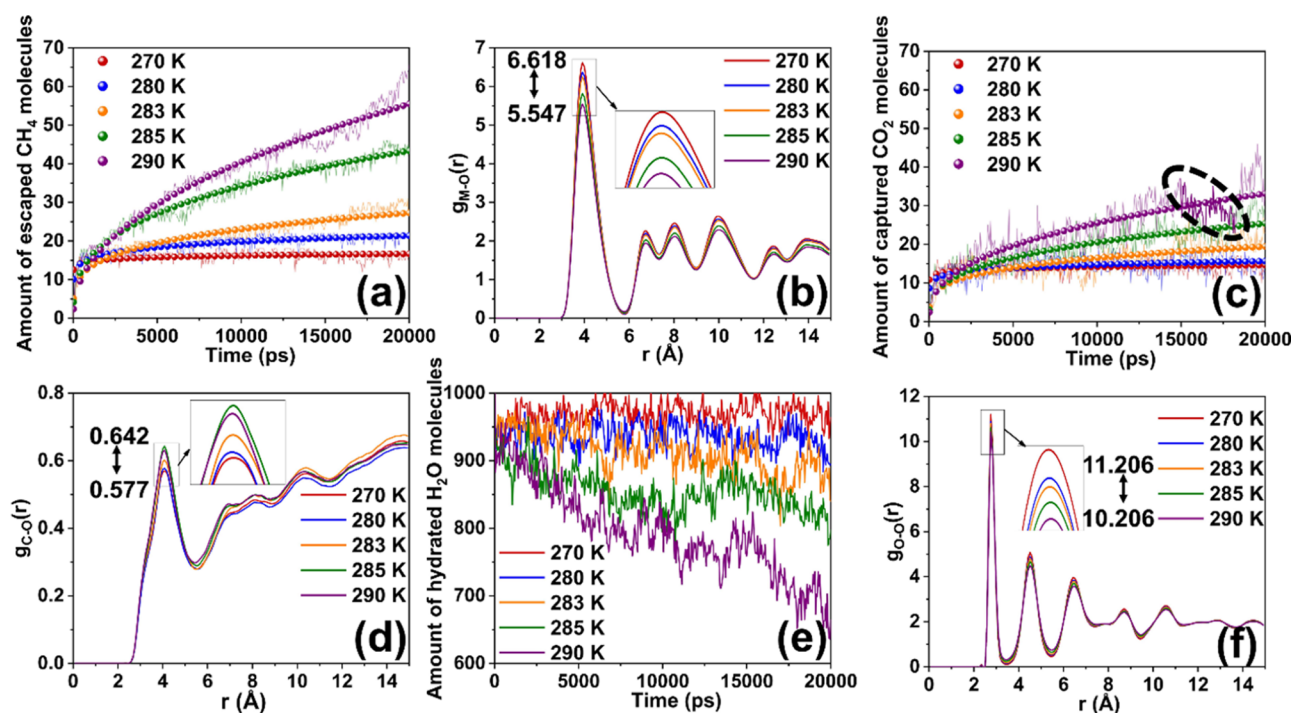


Figure 2. (a) Changes in the amounts of escaped CH_4 molecules over time at different temperatures; (b) RDF curves between CH_4 molecules and H_2O molecules at different temperatures; (c) changes in the amounts of captured CO_2 molecules over time at different temperatures; (d) RDF curves between CO_2 molecules and H_2O molecules at different temperatures; (e) changes in the amounts of hydrated H_2O molecules over time at different temperatures; (f) RDF curves between H_2O molecules at different temperatures.

molecules are arranged at different depths of the hydrate phase (region II).

For MD simulation, it is vital to ensure the accuracy of the potential energy functions. In this work, the TIP4P/Ice model⁶³ is used for H_2O , which is more accurate to simulate the solid water phase than the previous TIP4P model.⁶⁴ The OPLS-AA model⁶⁵ is utilized for CH_4 , which considers five points of methane molecules rather than a single point. In this way, more accurate results can be obtained than using single-point models such as OPLS-UA.^{64,66} The EPM2 model⁶⁷ is applied to CO_2 . Previous investigations have been conducted to verify that the models used in this work are almost the most superior models to reproduce the real properties of hydrate.^{66,68,69} For atoms in different molecules, the Lorentz–Berthelot mixing rule is used to determine their parameters of Lennard-Jones potentials. MD simulations of 20,000 ps under the *NPT* ensemble are carried out with a time step of 1 fs. The rigid bonds and angles are fixed by the SHAKE algorithm.⁷⁰ The velocity-Verlet algorithm is used to calculate Newton's equation of motion. The cutoff for short-ranged interactions is set to 15 Å, and the long-ranged Coulomb interactions are calculated by the PPPM algorithm. Periodic boundary conditions are applied in all directions. The simulation conditions and typical phase equilibrium diagrams of CH_4 hydrate and CO_2 hydrate⁷¹ are shown in Figure 1b. All the MD simulations are carried out by LAMMPS, an open-source program.⁷²

2.2. Evaluation and Description of CH_4 – CO_2 Replacement. Evaluation metrics need to be determined first to evaluate the CH_4 – CO_2 replacement. According to the unique significance of the CO_2 replacement method, in this work, the performances of the CH_4 – CO_2 replacement processes are evaluated in three aspects: CH_4 production, CO_2 sequestration, and hydrate stability. Correspondingly, the escape of CH_4

molecules, the capture of CO_2 molecules, and the maintenance of the hydrate cage structure need to be monitored and evaluated on the microscale. It is worth mentioning that the better the hydrate cage structure is maintained, the better the hydrate stability is maintained, and the better the formation can be cemented and supported by hydrate.⁵⁴ In order to achieve the evaluation and elucidate the micro-mechanisms, the dynamic position distributions of different molecules, the radial distribution functions (RDFs), the Chill+ structure identification algorithm,³⁹ and the hydrate configurations are selected to characterize the replacement processes.

Depending on the degree of the CH_4 – CO_2 replacement, CH_4 molecules at different depths are replaced by CO_2 molecules. In accordance with the literature,⁶⁹ in this work, the CH_4 molecules that spread into region I and region III are regarded to have escaped. And the CO_2 molecules that spread into region II are considered to have been captured. The position of different molecules is determined by a self-made code.

The RDFs can describe the relative spatial distribution between two types of particles, and they can be calculated as eq 1.

$$g(r) = \frac{V}{N_A N_B} \left(\sum_{i=1}^{N_A} \frac{n_i b(r)}{4\pi r^2 \Delta r} \right) \quad (1)$$

where N_A and N_B represent the total numbers of particles A and B, respectively. V stands for the total volume of the simulation box. $n_i b(r)$ denotes the number of particle B in the space between concentric spheres that is r far from particle A.

The Chill+ structure identification algorithm³⁹ distinguishes water structures such as free water, ice, and NGH through the topological relation between H_2O molecules. It can identify the type of water structure to which a single H_2O molecule belongs

to and count the amount of hydrated H₂O molecules that form gas hydrate in the whole simulation system. Combined with the configurations of hydrate, the structural changes of hydrate can be monitored intuitively.

3. RESULTS AND DISCUSSION

3.1. CH₄–CO₂ Replacement Process at Different Temperatures. At different temperatures, the changes in the amount of escaped CH₄ molecules over time are shown in Figure 2a. The semitransparent and thin lines represent raw data obtained by a self-made code. For clearer expression, the raw data are fitted based on a power function, and the fitting curves are presented by solid dots. The power function has a similar trend to the Avrami model and the shrinking core model, which are well-known physical models for crystallization kinetics and the CH₄–CO₂ replacement process.⁷³ It can be seen that the amount of escaped CH₄ molecules increases with temperature. Moreover, the RDFs between CH₄ molecules and H₂O molecules at different temperatures are calculated and exhibited in Figure 2b. It shows that the RDF peaks at 4 Å (from 6.618 to 5.547) become lower with the increase in the temperature, which indicates that more CH₄ molecules escape from the center of hydrate cages.

At different temperatures, the changes in the amounts of captured CO₂ molecules over time are presented in Figure 2c. Same to the escape of CH₄ molecules, the results show that the amounts of captured CO₂ molecules also increase with temperature. And it is worth noting that two different variation trends are observed in both Figure 2a,c. With regard to 270 and 280 K, the amounts of escaped CH₄ molecules and captured CO₂ molecules increase at first and then tend to level off. Taking the case at 270 K as an example, Figure 3a displays the

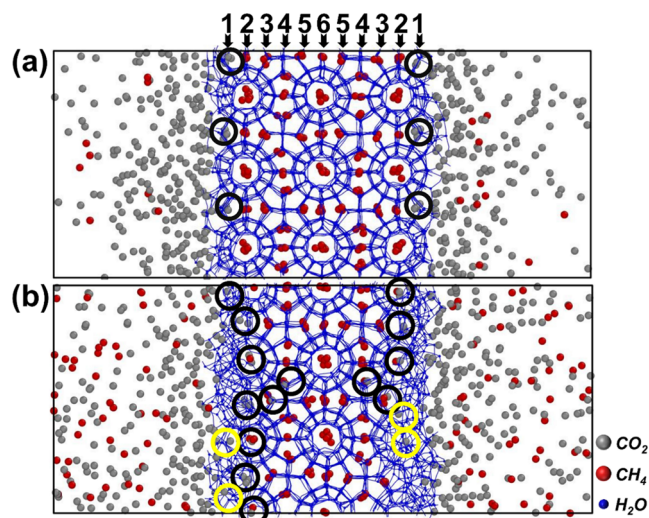


Figure 3. (a) Configuration after 20,000 ps at 270 K; (b) configuration after 20,000 ps at 290 K.

configuration of the simulation system at the last moment. It can be seen that the replacement process stops at the surface of CH₄ hydrate even though 20,000 ps has been spent. This phenomenon can be attributed to that the CO₂ hydrate formed on the surface is very stable at 270 and 280 K, which leads to the termination of the replacement process. On the one hand, the possibility of the further decomposition of internal CH₄ hydrate is reduced by the stable CO₂ hydrate because the decomposition

of hydrate must start from the surface.⁷⁴ Therefore, lots of CH₄ molecules in the deeper cannot be released. On the other hand, stable CO₂ hydrate plays a role as a mass transfer barrier, which stops the replacement process. The CH₄ molecules in the deeper cannot be replaced by the CO₂ molecules. As a result, both the escape of CH₄ and the capture of CO₂ stop after a period of time.

In terms of 283, 285, and 290 K, however, it is demonstrated that the changing curves of escaped CH₄ molecules and captured CO₂ molecules still keep increasing rather than level off after a period of time. Taking the case at 290 K as an example, the final configuration in Figure 3b reveals that the replacement process does not stop at the surface of the CH₄ hydrate but proceeds to the deeper part. The reason can be that the CO₂ hydrate becomes relatively unstable at 283, 285, and 290 K. For one thing, therefore, internal CH₄ hydrate has opportunities to further decompose and release amounts of CH₄ molecules. For another, the unstable CO₂ hydrate leads to a weaker mass transfer barrier, which makes it easier for CH₄ molecules in the deep to escape. Meanwhile, the CO₂ molecules in the region I and region III can diffuse into the deeper of hydrate phase to easily replace the CH₄ molecules. However, it needs to be noted that the relative instability of CO₂ hydrate caused by higher temperatures can also bring about negative effects on the capture of CO₂. Much of the newly formed CO₂ hydrate decomposes after a period of time and releases CO₂ molecules. Some of the released CO₂ molecules return to the region I and region III again, which can be inferred from the sudden drops of the changing curves circled in Figure 2c. Additionally, based on the Chill+ structure identification algorithm,³⁹ the yellow circles in Figure 3b mark a few CO₂ molecules captured by amorphous H₂O molecules rather than more stable hydrate cages, though these CO₂ molecules still stay in region II. Moreover, Figure 2d exhibits the RDFs between CO₂ molecules and H₂O molecules at different temperatures. It can be seen that the peaks at 4 Å become higher (from 0.577 to 0.642) with the temperature between 270 and 285 K, but the peak at 290 K is lower than the peak at 285 K. All these results show that excessive temperature is not conducive to CO₂ storage in the form of standard CO₂ hydrate, meaning that the capture of CO₂ may be temporary.

In order to evaluate the maintenance of the hydrate cage structure, the changes in the amounts of hydrated H₂O molecules over time at different temperatures are calculated by the Chill+ algorithm³⁹ and shown in Figure 2e. It is demonstrated that the amount of hydrated H₂O molecules becomes less with the rising temperature. Moreover, the RDFs between H₂O molecules at different temperatures are displayed in Figure 2f. It is indicated that the RDF peaks at 2.5 Å (the distance between H₂O molecules in hydrate) become lower (from 11.206 to 10.206) with temperature. The decrease of this feature peak means that the H₂O molecules tend not to be arranged in the form of gas hydrate. The reasons for the above results could be twofold. On the one hand, it is supposed that higher temperatures make CH₄ molecules leave the hydrate cages very rapidly, but the CO₂ molecules cannot occupy the empty hydrate cages in a timely manner. Then, the empty hydrate cages get broken without the support of CO₂ molecules. On the other hand, the CO₂ hydrate is relatively unstable at higher temperatures. Therefore, some of the newly formed CO₂ hydrate decomposes after a period of time, and the hydrate cages are broken. In short, it is detrimental to the maintenance of hydrate stability before and after the replacement process.

Overall, the amounts of CH₄ production and CO₂ capture can be improved at higher temperatures, where CO₂ hydrate

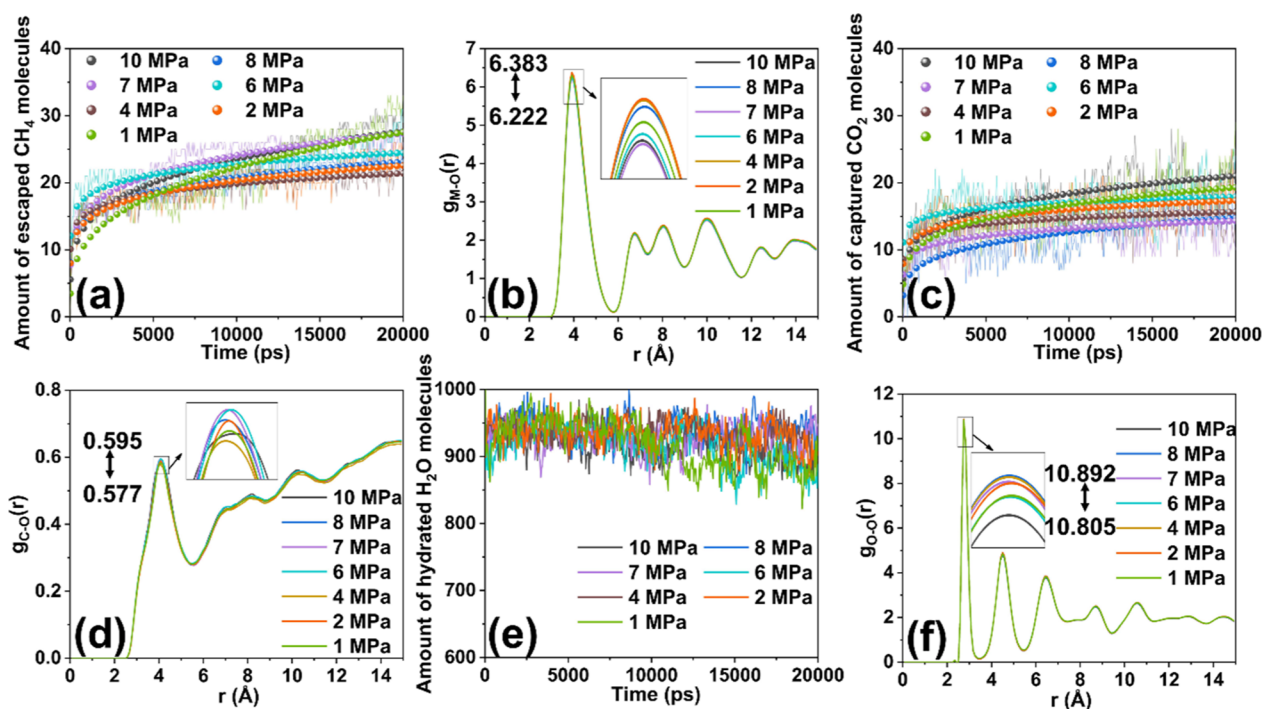


Figure 4. (a) Changes in the amounts of escaped CH₄ molecules over time at different pressures; (b) RDF curves between CH₄ molecules and H₂O molecules at different pressures; (c) changes in the amounts of captured CO₂ molecules over time at different pressures; (d) RDF curves between CO₂ molecules and H₂O molecules at different pressures; (e) changes in the amounts of hydrated H₂O molecules over time at different pressures; (f) RDF curves between H₂O molecules at different pressures.

becomes relatively unstable and forms a weaker mass transfer barrier. In this work, however, an unlimited increase in temperature is not regarded as a perfect way to facilitate the CH₄–CO₂ replacement process. At higher temperatures, the sequestration of CO₂ tends to be unstable, which means that the observed CO₂ capture may be temporary. Also, the hydrate's stability will decrease, leading to a weaker ability to ensure geological stability. Briefly, there is a conflict in selecting the proper temperature. In order to handle this conflict, choosing a middle temperature as a compromise can be feasible.

3.2. CH₄–CO₂ Replacement Process at Different Pressures. At the same temperature of 280 K and different pressures, the changes in the amounts of escaped CH₄ molecules captured CO₂ molecules, and hydrated H₂O molecules with time are shown in Figure 4a,c,e. Furthermore, the RDF curves between different particles at different pressures are calculated and shown in Figure 4b,d,f. It can be seen that the various curves intersect and overlap with each other, and the differences are not obvious. It is indicated that the effect of pressure on the replacement process is not as significant as that of temperature, and the conclusion is also consistent with previous computational and experimental studies.^{64,75,76} However, it is worth emphasizing that the insignificance is relative to the effects of temperature but not absolute. On a larger and longer scale than that of this work, pressure is still an important and non-negligible factor.⁵⁴

Figure 5 exhibits the average amounts of escaped CH₄ molecules, captured CO₂ molecules, and hydrated H₂O molecules from 19,500 to 20,000 ps at different pressures to evaluate the final performance. In terms of the differences that can be observed, the effect of pressure appears to be not monotonic but fluctuating. There are no definite principles detected. A possible reason might be that pressure plays a role in

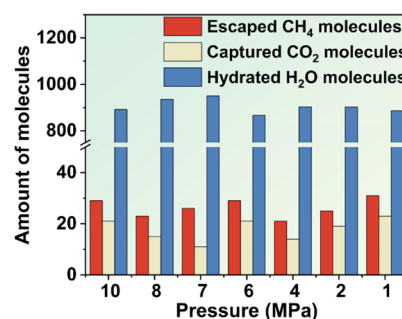


Figure 5. Average amounts of escaped CH₄ molecules, captured CO₂ molecules, and hydrated H₂O molecules from 19,500 to 20,000 ps at different pressures.

the replacement process in two different ways between 1 and 10 MPa. For one aspect, higher pressure can increase the local concentration of CO₂ molecules according to the ideal gas state equation, promoting the diffusion of CO₂ molecules into the solid phase (CH₄ hydrate) based on Fick's law. Then, these CO₂ molecules can replace CH₄ molecules in the hydrate more easily. For another aspect, it is supposed that lower pressure has a similar but weaker effect with higher temperature. At low pressure, both CH₄ hydrate and CO₂ dioxide hydrate become relatively unstable. Subsequently, the mass transfer barrier becomes weaker, improving the replacement process. As the pressure changes, however, it is difficult to determine which of the above aspects plays a dominant role, so the effects of pressure do not show a clear pattern.

3.3. Mechanisms and Evaluation of Temperature Oscillation Cases. Considering the unclear and weaker effects of pressures mentioned above, temperature conditions are hoped to be further optimized. For constant temperatures, no

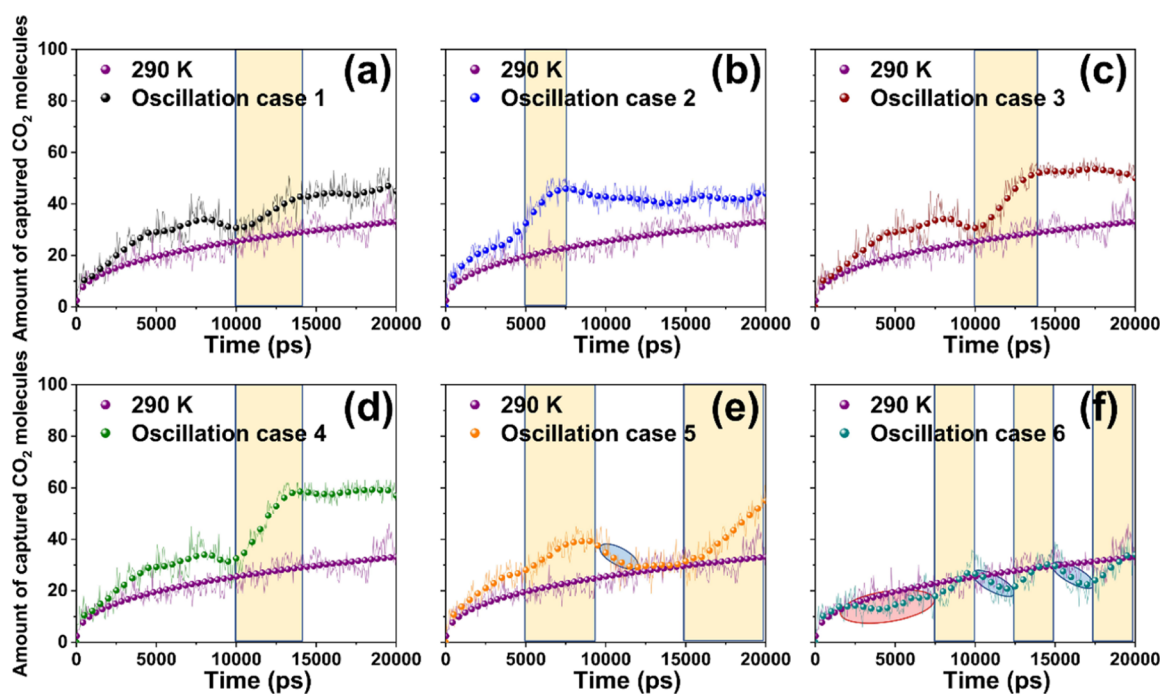


Figure 8. Changes in the amounts of captured CO₂ molecules over time for (a) oscillation case 1, (b) oscillation case 2, (c) oscillation case 3, (d) oscillation case 4, (e) oscillation case 5, and (f) oscillation case 6.

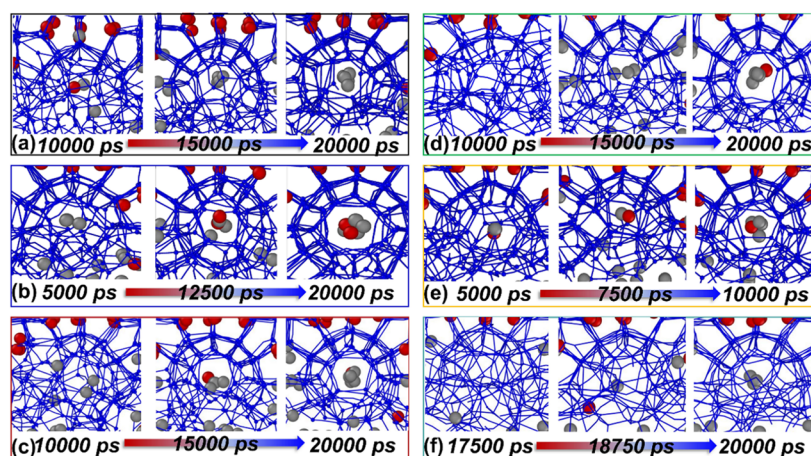


Figure 9. Rapid rebuilding of CO₂ hydrate in the lower temperature stage of temperature oscillations.

increases when the temperature is 300 K. And it stops almost immediately when the temperature becomes lower. According to the previous results in this work, the reason is that the mass transfer barrier formed by CO₂ hydrate becomes very stable when the temperature becomes lower than 280 K. An internal CH₄ hydrate cannot decompose, which immediately prevents the escape of CH₄ molecules. It is worth mentioning that the amount of escaped CH₄ molecules may decrease slightly during the lower temperature stage. This is because some of the escaped CH₄ molecules could be captured again by the hydrate cages.

As for the capture of CO₂, it can be seen in Figure 8 that the amount of captured CO₂ molecules increases at the initial higher temperature stage. Similar to the cases at constant temperatures, the increase in this stage is mainly caused by the diffusion of CO₂ molecules into the hydrate phase. Interestingly, at the lower temperature stage, as marked by the light-yellow rectangles in Figure 8, the amount of captured CO₂ molecules continues to rise for a period of time, showing a delayed response to

temperature changes. It is supposed that the increase in this stage is mainly caused by the rebuilding of CO₂ hydrate. Figure 9 illustrates parts of the rebuilding process of CO₂ hydrate under different temperature oscillation cases. It can be seen that the intact hydrate cages are broken and produce incomplete hydrate cage structures after the higher temperature stage. When the temperature reduces to the lower, CO₂ hydrate can stay stable. Because of the memory effects of hydrate,⁷⁴ it is easy for CO₂ molecules and these incomplete hydrate cage structures to rebuild CO₂ hydrate rapidly within only nanoseconds. In short, the capture of CO₂ at oscillation temperatures benefits from both the diffusion of CO₂ in the higher temperature stage and the rebuilding of CO₂ hydrate in the lower temperature stage. In addition, it should be noted from the blue circle in Figure 8e,f that when the temperature returns to the higher level, the amount of captured CO₂ molecules decreases for a period of time due to the decomposition of CO₂ hydrate. Subsequently, the diffusion process of CO₂ molecules and the rebuilding

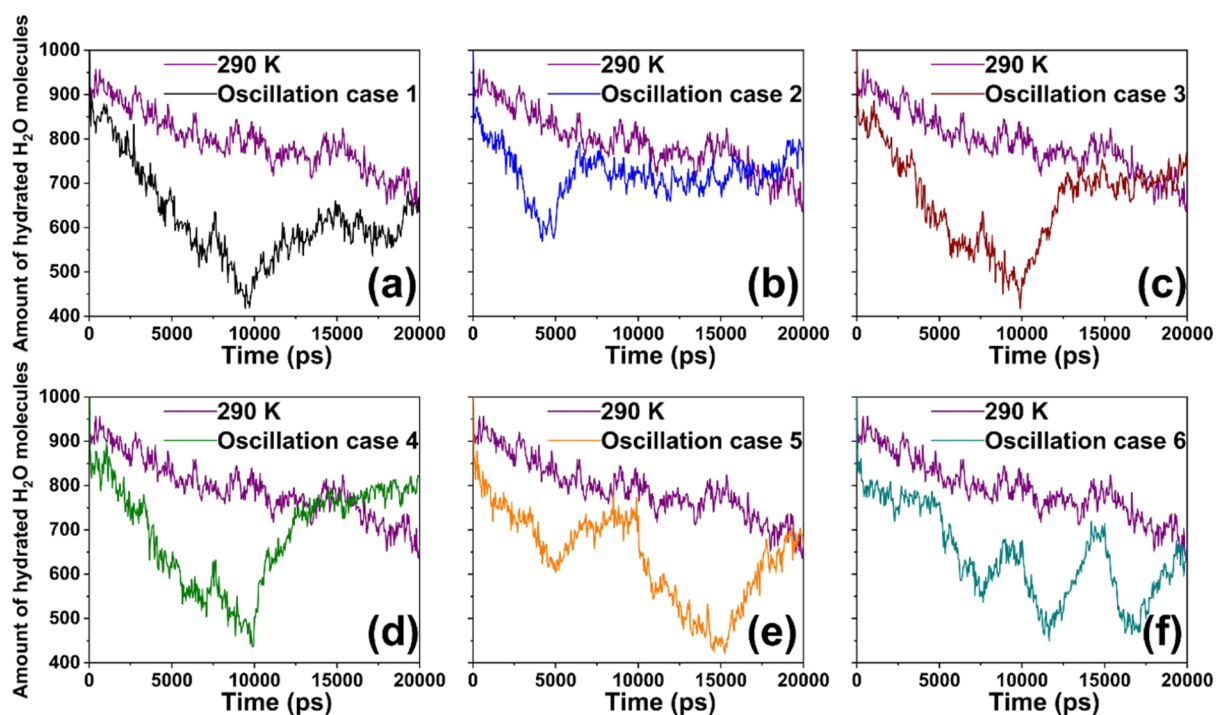


Figure 10. Changes in the amount of hydrated H₂O molecules over time for (a) oscillation case 1, (b) oscillation case 2, (c) oscillation case 3, (d) oscillation case 4, (e) oscillation case 5, and (f) oscillation case 6.

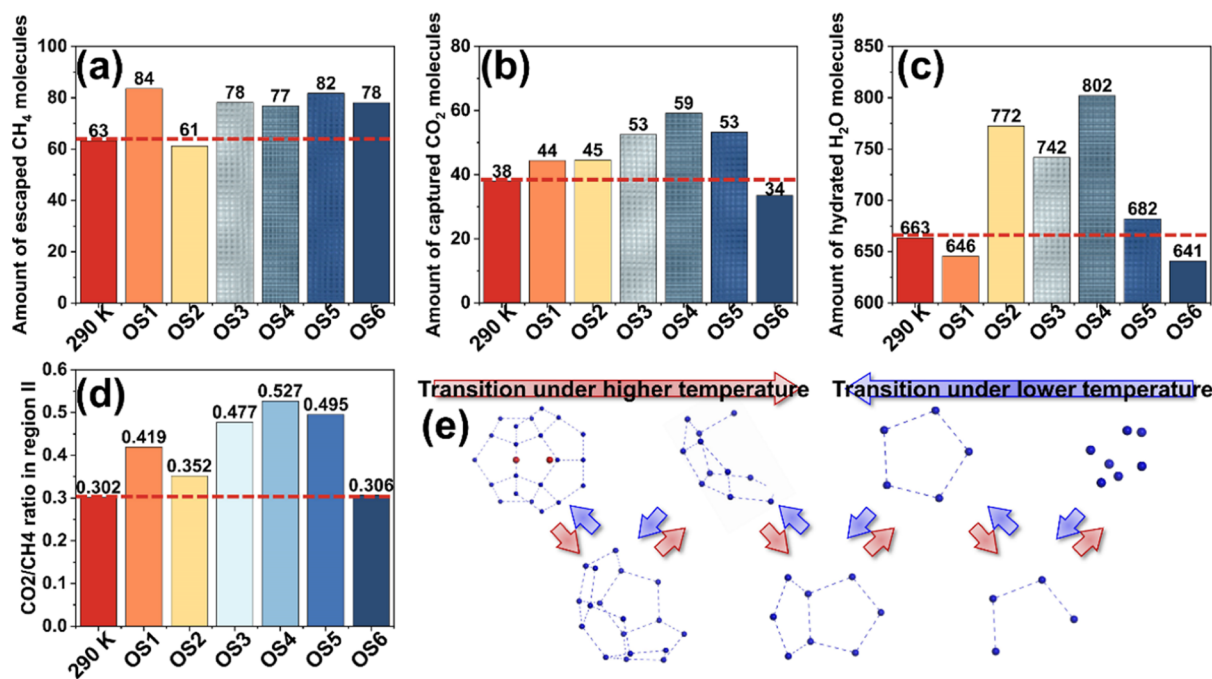


Figure 11. (a) Average amounts of escaped CH₄ molecules from 19,500 to 20,000 ps of different cases; (b) average amounts of captured CO₂ molecules from 19,500 to 20,000 ps of different cases; (c) average amounts of hydrated H₂O molecules from 19,500 to 20,000 ps of different cases; (d) average CO₂/CH₄ ratio in region II from 19,500 to 20,000 ps of different cases; (e) different degrees of damaged hydrate structures in the system.

process of CO₂ hydrate are repeated, resulting in a zigzag upward trend of captured CO₂ molecules. However, a noteworthy anomaly exhibited in the red circle in Figure 8f is that the CO₂ capture does not rise between 2500 and 5000 ps and does not fall between 5000 and 7500 ps, which is inconsistent with the patterns found above. It is due to the fact that at the beginning of the replacement, not enough incomplete hydrate structures are produced. At this time, CO₂

capture depends mainly on the CO₂ diffusion rather than the rebuilding of CO₂ hydrate. Therefore, in this stage, a temperature decrease is unfavorable to the CO₂ diffusion and CO₂ capture, but a temperature returning is advantageous.

In terms of the maintenance of the hydrate cage structure, Figure 10 shows that the amounts of hydrated H₂O molecules decrease rapidly when the temperature is 300 K but increase when the temperature drops to a lower temperature. It indicates

that hydrate structures are repaired in the lower temperature stage. The repairment is the inevitable result of CH₄ hydrates stopping to decompose and CO₂ hydrates rebuilding. Therefore, the rebuilding process caused by temperature oscillations can also be conducive to the maintenance of hydrate stability. In addition, it is worth noting that the hydrate structures are repaired to different extents under different kinds of temperature oscillations.

In order to quantitatively evaluate the replacement processes under different oscillating temperatures and constant temperatures, Figure 11a–c displays the average amounts of escaped CH₄ molecules, captured CO₂ molecules, and hydrated H₂O molecules from 19,500 to 20,000, respectively. Furthermore, the average CO₂/CH₄ ratios in region II range from 19,500 to 20,000 ps and are exhibited in Figure 11d. The ratio can be regarded as a comprehensive indicator that describes the extent of conversion of CH₄ hydrate to CO₂ hydrate during the replacement process. Overall, all oscillating temperatures can improve the CH₄–CO₂ replacement process in certain aspects. Especially, the CH₄–CO₂ replacement process is comprehensively improved in oscillation cases 3, 4, and 5. Also, it is worth noting that the average temperatures of these oscillating temperatures are lower than 290 K. Therefore, it might mean that these oscillating temperatures can help obtain more CH₄, capture more CO₂, and maintain the hydrate stability better but need no additional thermal energy input, which may reduce the cost effectively.

3.4. Effects of the Lower Temperature Duration. From Figure 11, it can be seen that temperature oscillations are effective, but the aspects and strengths of their effects are different, which are supposed to be determined by the different oscillation waveforms. In order to explore the patterns, different temperature oscillation cases are compared and discussed.

Oscillation case 1 and oscillation case 2 have different lower temperature durations. It can be obviously observed from Figure 11a,c that extending the lower temperature duration can decrease the amount of escaped CH₄ molecules and increase the amount of hydrated H₂O molecules. By comparing Figure 7a,b, it can be attributed to that the longer lower temperature duration means the shorter higher temperature duration, leading to a shorter time for CH₄ molecules to escape. Thus, the amount of escaped CH₄ molecules decreases. Meanwhile, as shown in Figure 10a,b, the shorter higher temperature stage can break up fewer hydrate cage structures and the longer lower temperature stage can repair more hydrate cage structures. Therefore, the amount of hydrated H₂O molecules rises. In addition, from Figure 11b, it is noteworthy that the amount of captured CO₂ molecules does not change much and even slightly increases after extending the lower temperature duration in oscillation case 2. This is because the capture of CO₂ requires both the higher temperature to break the mass transfer barrier and the lower temperature to rebuild the CO₂ hydrate. Extending the lower temperature duration limits the diffusion of CO₂ molecules but enhances the reconstruction of CO₂ hydrate. For the same reason, it is not thought that the amount of captured CO₂ molecules always keeps unchanged with the extending of the lower temperature duration. Considering a limiting case where the low temperature persists for one full period, that is, the case at a constant temperature of 280 K, the amount of captured CO₂ is much lower than that of the oscillation case 1. Overall, it is thought that the lower temperature duration should be moderate but not extreme to use the complementary effects of high temperature and low

temperature and to avoid the serious drawbacks of them. Besides, because CH₄ production and hydrate stability may be production indicators of varying importance and the effects of lower temperature duration on them are completely opposite, the lower temperature duration needs to be further determined for a given situation and specific goals.

3.5. Effects of the Lower Temperature Value.

Oscillation case 1, oscillation case 3, and oscillation case 4 have different lower temperature values. As shown in Figure 11a, it is indicated that reducing the lower temperature value can marginally decrease the amount of escaped CH₄ molecules. The results may be due to the fact that the lower temperatures make it easier for a few escaped CH₄ molecules to return to hydrate cages like CO₂ molecules. Moreover, reducing the lower temperature value can rise the amount of captured CO₂ molecules and hydrated H₂O molecules, as displayed in Figure 11b,c. The underlying reason might be that the lower temperatures can make fuller use of the memory effects of hydrates.⁷⁴ In detail, the intact hydrate cages are broken and produce incomplete hydrate cage structures at high temperatures. Since the destruction of the hydrate structure is gradual, there are different degrees of damaged hydrate structures in the system, as exhibited in Figure 11e. It is supposed that the lower temperatures have a more powerful ability to allow the more severely damaged hydrate structures to be reconstructed with CO₂ molecules into intact CO₂ hydrates. As a result, decreasing the lower temperature value can help the capture of CO₂ molecules and maintain the hydrate cage structures.

3.6. Effects of the Oscillation Frequency. The oscillation frequencies of oscillation case 1, oscillation case 5, and oscillation case 6 are 0.05, 0.1, and 0.2 GHz, respectively. With the oscillation frequency rising, the amount of escaped CH₄ molecules slightly reduces, as shown in Figure 11a. It can be attributed to the fact that a start-up time is required for the decomposition of hydrates and the escape of CH₄ molecules. During the start-up time, no CH₄ molecules escaped. The higher the frequency, the more starts and the longer the start-up time consumed. As a result, the amount of escaped CH₄ molecules decreases slightly. With regard to the capture of CO₂ molecules and the maintenance of hydrate cage structures, as shown in Figure 11b,c, the frequency of 0.1 GHz produces the best performance among the three frequencies. The reason is that it best balances the diffusion of CO₂ molecules and the rebuilding of CO₂ hydrate and thus benefits the most. For the lower frequency (0.05 GHz), the continuous time of higher temperature is longer, and the hydrate cage structures are more seriously damaged, as exhibited in Figure 11e. Therefore, the memory effects of hydrate⁷⁴ are weakened, and the rebuilding of CO₂ hydrate becomes more difficult. For the higher frequency (0.2 GHz), the continuous time of higher or lower temperature is too short, leading to that the CO₂ molecules have no enough time to finish the diffusion to the deeper of the hydrate phase, and the CO₂ hydrate has no enough time to finish the rebuilding process. In other words, both of the two kinds of behaviors that can enhance CO₂ capture are inhibited by the higher frequency. Therefore, the oscillation frequency should be moderate (0.05–0.2 GHz) to produce the best optimization effects, and it is close to 0.1 GHz. This is an ideal intrinsic frequency determined by the fundamental properties of gas hydrate. For real production, it is worth noting that the oscillation frequency is difficult to reach as high as that optimal frequency. Therefore, on a macroscopic level, it is possible that the higher the oscillation frequency, the better the replacement effect, which can be supported by

previous work.⁷⁷ The previous work⁷⁷ reported that increasing the decompression frequency could effectively improve CH₄ recovery and CO₂ storage.

Summarizing all temperature oscillation cases, it can be found that the key to improving CH₄–CO₂ replacement is fully enhancing the cooperation between the diffusion of CO₂ molecules and the rebuilding of CO₂ hydrate. Furthermore, it is worth noting that though temperature oscillation within several nanoseconds may be hard to achieve, the physical-chemical mechanisms and the regularity found in our paper are not limited to the smaller time scale reported by our work but can also provide a benchmark and important guidance for larger-scale real exploitation.

4. CONCLUSIONS

In this work, the MD method is used to investigate the CH₄–CO₂ replacement at different constant temperatures and pressures. Temperature oscillations are introduced in the replacement process as an optimization strategy. The main conclusions of this work are as follows:

- Increasing the temperature can improve the amounts of CH₄ escape and CO₂ capture but is unfavorable to long-term CO₂ storage and hydrate stability. In comparison, the effects of pressure are not as significant and definite as those of temperature.
- Under temperature oscillations, the CH₄–CO₂ replacement benefits from both the deep diffusion of CO₂ in the higher temperature stage and the rapid rebuilding of CO₂ hydrate within just nanoseconds caused by the memory effects in the lower temperature stage.
- Compared with the constant temperature, temperature oscillations can achieve various improvements, including obtaining more CH₄, storing more CO₂, maintaining the hydrate stability better, and saving cost.
- For temperature oscillations, the lower temperature duration and the oscillation frequency should be moderate to produce the optimization effects. Decreasing the lower temperature value can distinctly improve the CO₂ capture and the maintenance of hydrate stability.

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Notes

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