Enhancing CO₂ hydrate formation and long-term stability in subseafloor saline sediments through integrated thermal and pressure management for effective CO₂ sequestration

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HIGHLIGHTS

- Thermal and pressure manipulation strategies aimed at optimizing CO₂ hydrate formation and stability were examined
- The evaluation was performed based on incorporating both experimental data, simulation, and theoretical deductions studies.
- The study revealed novel electrical heating systems and different pressure management techniques.
- Thermal and pressure controls, like electrostatic interactions and cycling, impact CO₂ hydrate stability efficiency.
- The findings offer promising approaches for the controlled formation and stability of CO₂ hydrate.

ARTICLE INFO

ABSTRACT

This review examines recent advancements in thermal and pressure management strategies for optimizing CO₂ hydrate formation and stability in subseafloor saline sediments, focusing on their application in carbon capture and storage (CCS). The research synthesizes findings from various studies, exploring how temperature and pressure manipulation, coupled with chemical additives, enhance CO₂ hydrate kinetics, stability, and sequestration efficiency. Novel approaches, such as electrical heating systems and pressure cycling, are discussed for their role in promoting hydrate formation. Challenges, including sediment heterogeneity, salinity variations, and environmental impacts, are critically analyzed. The review concludes by identifying research gaps and suggesting innovative methodologies to improve hydrate-based CCS efficiency. This work provides a comprehensive understanding of the current state and future direction of CO₂ hydrate research, contributing to advancing environmentally sustainable energy practices.

1. Introduction

In recent years, the formation and stability of CO₂ hydrates have garnered significant attention due to their potential in carbon capture and storage (CCS) technologies [1,2]. CO₂ hydrates, or CO₂ clathrates, are ice-like compounds that form from water and CO₂ under specific temperature and pressure conditions [3]. These hydrates have emerged as a promising option for long-term CO₂ storage, offering a secure and environmentally friendly alternative to traditional storage methods. Optimizing CO₂ hydrate formation in sub-seafloor saline sediments is essential due to these geological formations' vast potential storage capacity. Sub-seafloor saline sediments provide an extensive and naturally occurring reservoir for storing CO₂ in hydrates [4]. By focusing on these sediments, we can tap into a substantial storage resource that can sequester large volumes of CO₂ over extended periods. Furthermore, the stability of CO₂ hydrates in sub-seafloor saline sediments is of great

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interest for ensuring the long-term containment of captured CO_2 [4–6]. It is essential to develop strategies for enhancing their formation and stability in this specific environment. Thermal and pressure management strategies are vital in optimizing CO_2 hydrate formation and stability in sub-seafloor saline sediments, as illustrated in Fig. 1. By carefully controlling the temperature and pressure conditions within the sediments, researchers can influence the formation and dissociation of CO_2 hydrates, thereby maximizing their storage capacity and longevity [7]. Thermal management involves manipulating the temperature to promote the formation of CO_2 hydrates, while pressure management focuses on maintaining the appropriate pressure conditions to ensure their stability [8]. Understanding and implementing these strategies are vital for harnessing the full potential of CO_2 hydrate-based storage solutions in sub-seafloor saline sediments.

Previous works have intensely highlighted the potential of optimizing CO_2 hydrate formation and stability in marine sediments via thermal and pressure management. However, there is a need for further investigation into the specific mechanisms and factors influencing CO_2 hydrate formation in sub-seafloor saline sediments because their long-term stability is compromised in the harsh conditions of sediment heterogeneity, high temperature, pressure, and salinity. Understanding the interplay of temperature, pressure, and sediment chemical composition in this context is crucial for developing effective thermal and pressure optimization strategies. The potential for large-scale implementation of these strategies, considering factors such as technological feasibility, economic viability, and environmental impact, has been partially described in manuscripts. This work comprehensively investigated novel thermal and pressure techniques, materials, and approaches for achieving and maintaining optimized CO_2 hydrate formations in sub-seafloor saline sediments. Furthermore, integrating these strategies with existing sub-seafloor engineering practices and technologies is explored to address potential compatibility or operational challenges. The comparison of numerous experimental and simulation results related to optimizing CO_2 hydrate formation and stability in sub-seafloor saline sediments via thermal and pressure management reveals both successes and limitations. Identified research gaps in optimizing CO_2

hydrate formation and stability via thermal and pressure management studies are addressed, and potential interventions are proposed. Furthermore, the impact of geological heterogeneity, salinity, fluid flow dynamics, temperature fluctuations, limitations, and proposed interventions for field applications are discussed in detail. Our findings offer a concrete foundation for future research and application in energy storage and carbon capture domains. As we steer toward an era of environmentally conscientious energy practices, these insights pave the way for advanced hydrate-based technologies that promise increased efficiency and sustainability.

2. Fundamentals of CO_2 hydrate formation

Comprehending the formation mechanisms of CO_2 hydrates is crucial for optimizing their stability and formation in various environmental conditions. This section delves into the molecular interactions, structures, and key factors influencing the kinetics and stability of CO_2 hydrate formations, especially within sub-seafloor saline sediments. By examining the processes at the molecular level, researchers can better comprehend how CO_2 hydrates can be used in carbon capture and storage technologies.

2.1. Molecular mechanisms of CO_2 hydrate formation

In the case of CO_2 hydrate formation, the clathrate structure and CO_2 inclusion mechanisms play a crucial role [9,10]. Water molecules arrange into a lattice structure, forming cages that trap CO_2 molecules [11]. The carbon dioxide (CO_2) inclusion mechanisms involve the formation of these cages, where the CO_2 molecules are encapsulated within the water lattice in a specific arrangement, as shown in Fig. 2. This arrangement is primarily stabilized by van der Waals forces between the CO_2 molecules and the surrounding water lattice, forming CO_2 hydrates [11,12]. Water molecules act as the host structure for CO_2 molecules, providing the framework for forming CO_2 hydrates. The arrangement of water molecules in a lattice structure creates cavities or cages that can accommodate CO_2 molecules. The van der Waals interactions facilitate
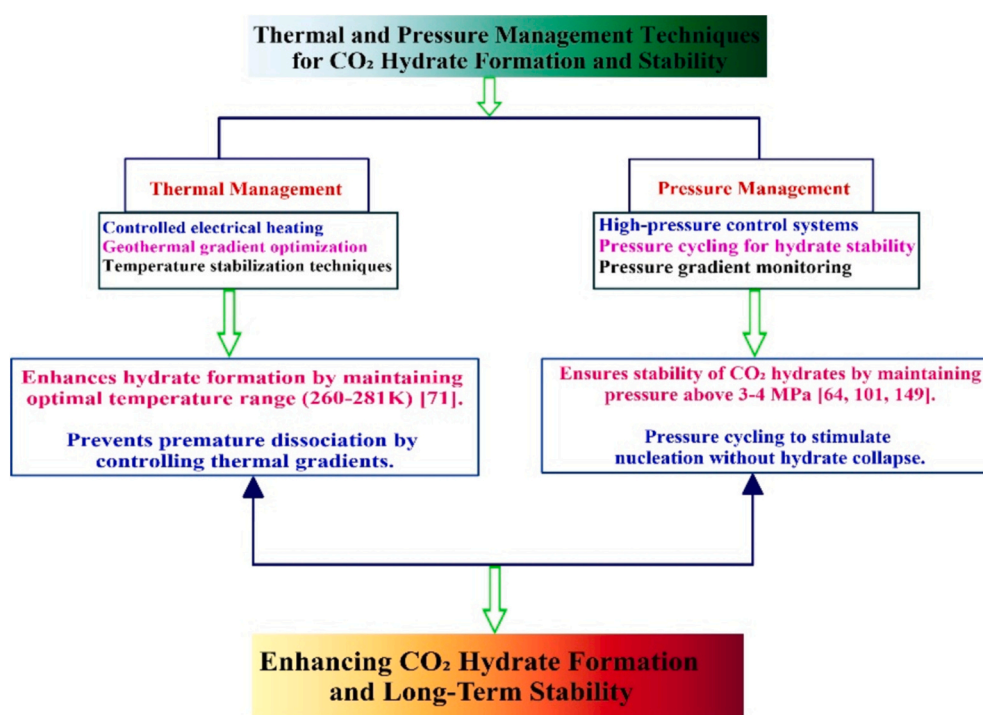

Fig. 1. Schematic diagram illustrating the thermal and pressure management strategies for optimizing CO_2 hydrate formation and stability in subseafloor saline sediments.
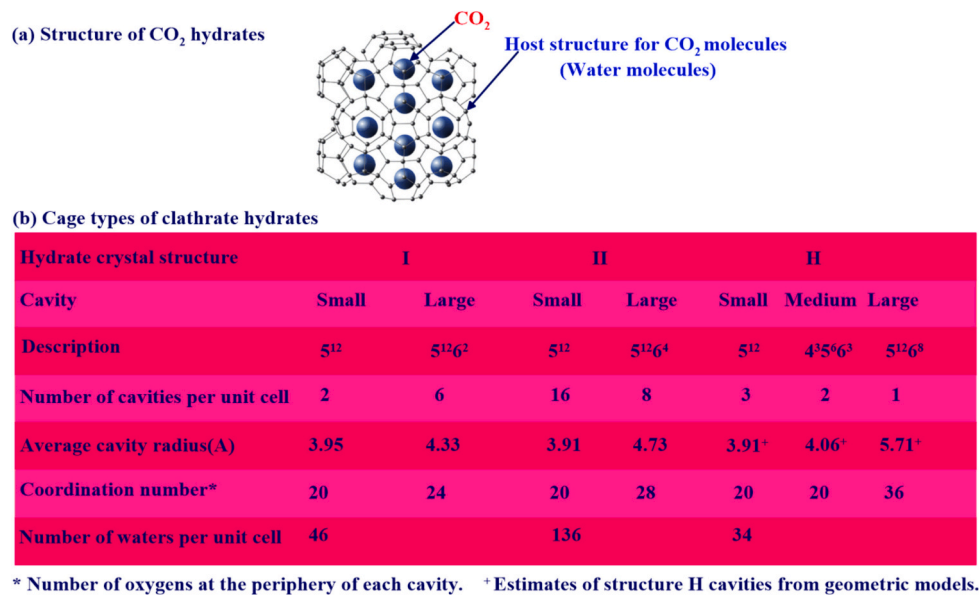
(a) Structure of CO$_2$ hydrates

CO$_2$

**Host structure for CO$_2$ molecules
(Water molecules)**

(b) Cage types of clathrate hydrates

Hydrate crystal structure	I		II		H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius(A)	3.95	4.33	3.91	4.73	3.91$^+$	4.06$^+$	5.71$^+$
Coordination number*	20	24	20	28	20	20	36
Number of waters per unit cell	46		136		34		

* **Number of oxygens at the periphery of each cavity.** $^+$**Estimates of structure H cavities from geometric models.**

Fig. 2. The structure of CO$_2$ clathrate hydrates and cage types [15].

the trapping of CO$_2$ molecules within the hydrate cages, contributing to the overall stability of the CO$_2$ hydrate structure. The hydrogen bonding between water molecules maintains the integrity of the lattice itself but does not directly stabilize the CO$_2$ molecules inside the hydrate cages [13]. As CO$_2$ molecules are trapped within these cages, the water molecules provide a stable environment for CO$_2$ hydrate formation and contribute to the overall stability of the hydrate structure [13,14].

2.2. Influential factors on CO$_2$ hydrate stability and formation kinetics

The stability and kinetics of CO$_2$ hydrate formation are highly dependent on several environmental and chemical factors. This section explores the impact of temperature, pressure, salinity, and sediment composition on the formation and dissociation of CO$_2$ hydrates. By understanding how these factors interact, researchers can develop strategies to enhance the formation efficiency and long-term stability of CO$_2$ hydrates in marine sediment environments.

2.2.1. Impact of temperature, pressure, and salinity on CO$_2$ hydrate formation

In recent research investigations, the impact of temperature, pressure, and salinity on CO$_2$ hydrate stability and formation kinetics has been a focal point [16–18]. These influential factors are crucial in understanding and optimizing CO$_2$ hydrate formation and stability in sub-seafloor saline sediments [18]. Temperature has been revealed to influence CO$_2$ hydrate stability and formation kinetics significantly. Studies have shown that lower temperatures generally promote the formation of CO$_2$ hydrates, as the lower thermal energy facilitates the molecular rearrangement necessary for hydrate formation [17,19]. Liu et al. [20] revealed that a temperature drop from 255 to 235 K significantly reduces the linear growth rate of CO$_2$ hydrates. In contrast, Dhamu et al. [21] reported that the stability of CO$_2$ hydrates in oceanic sediments at depths of 1 km with a higher pressure from 10 MPa and low temperatures between 276.15 and 277.15 K can sustain hydrate stability for extended periods. Yet, the exact temperature conditions for optimal CO$_2$ hydrate formation and stability are subject to further exploration, especially in sub-seafloor saline sediments. Pressure is also a critical factor in CO$_2$ hydrate stability and formation kinetics. Higher pressures can enhance the stability of CO$_2$ hydrates, as they provide the conditions for forming a stable hydrate structure [22,23]. However, molecular simulation investigation by Liu et al. [20] reported that pressure has

little effect on CO$_2$ hydrate formation. Instead, temperature plays a more significant role in the growth rate of hydrates. In contrast, the study by Yang et al. [24] revealed that varying pressures, temperatures, and flow rates can influence CO$_2$ hydrate saturation in porous media. Certain conditions, like stopping CO$_2$ flow, can prevent blockades that may appear frequently at higher pressures. The divergent observations emphasize the need for comprehensive investigations considering multiple factors to elucidate the intricate dynamics of CO$_2$ hydrate formation. In addition, salinity is another factor affecting CO$_2$ hydrate stability and formation kinetics. Research has indicated that salts in sub-seafloor saline sediments can impact the equilibrium conditions and kinetics of CO$_2$ hydrate formation [25]. The interaction between CO$_2$, water, and salt ions influences hydrate formation's thermodynamic and kinetic aspects, making salinity a critical parameter for optimizing CO$_2$ hydrate stability. Also, hydrate formation may lead to increased salinity in the fluids, affecting the properties of the hydrate lattice and the system's overall stability [26]. Thus, the influence of salinity variations provides valuable insights for tailored and controlled CO$_2$ release [27]. The practical significance of optimizing the encapsulation matrix to respond to varying saline conditions, such as nanoparticle-assisted surfactant/ polymer formulations and responsive coating technology, is crucial for enhancing CO$_2$ formation and stability in saline sediment environments [28,29], particularly in the context of carbon capture and storage technologies.

Zhao et al. [30] conducted molecular dynamics simulations to investigate the optimization of CO$_2$ hydrate formation and stability in marine sediments through thermal and pressure management. The simulations used a configuration with a $4 \times 4 \times 3$ sI CO$_2$ hydrate unit cell in a salty solution containing NaCl and water molecules. The force field parameters for water, CO$_2$ molecules, ions, and water–ion interactions were specified to predict CO$_2$ hydrate phase boundaries accurately. The molecular simulations were performed using GROMACS 2022, and the growth process of CO$_2$ hydrate in salty water was evaluated. The study tracked the time evolution of hydrate cages, CO$_2$ molecules in different phases, and ion concentrations in the hydrate phase. The results revealed the three stages of hydrate growth: an initial phase of fluctuation, a steady growth phase, and a dynamic equilibrium phase. The mechanism of ion entry into the hydrate structure was examined, showing that both Na$^+$ and Cl$^-$ ions could enter the hydrate phase, with Cl– revealing a closer association with the hydrate structure. The temperature dependence analysis demonstrated a maximum growth rate at

265 ± 5 K, situated approximately 20 K below the melting point of CO_2 hydrate at 5 MPa, as shown in Fig. 3. This optimal temperature range suggests that seawater desalination through CO_2 hydrate formation is most efficient at temperatures ranging from T_m – 25 K to T_m – 5 K, emphasizing the importance of managing temperature conditions for optimal performance. Conversely, pressure was found to have a negligible effect on the growth rate of CO_2 hydrate within the investigated range, indicating that pressure variations within that range do not significantly impact the mass transfer process in the simulations.

In addition, the study by Zhao et al. [30] demonstrated that the growth rate of CO_2 hydrate slows down with increasing salinity in the solution. The study observed a correlation between the number of ions incorporated into the hydrate structure and the solution's growth rate and salinity. Specifically, sodium ions (Na^+) and chloride ions (Cl^-) were found to enter the hydrate structure, with more Cl^- ions present in the hydrate phase, as shown in Fig. 4. The presence of ions in the hydrate structure was found energetically unfavorable, leading to a slightly distorted hydrate structure. Furthermore, studies have highlighted the role of kinetic control in ion entry into the hydrate phase, suggesting that the trapping of ions in the hydrate structure is related to the dynamic properties of ions in the solution [17,31]. Specifically, the dynamic properties refer to the ability of ions to diffuse and move within the solution [30,32]. Higher temperatures are associated with faster dynamics of ions in the solution, although ions are more easily trapped in the hydrate structure at lower temperatures [30]. This phenomenon can be attributed to the fact that, at lower temperatures, ions diffuse more slowly in the solution, making them more susceptible to being incorporated into the growing hydrate structure, as diagrammatically illustrated in Fig. 5(a). In contrast, ions exhibit rapid diffusion at higher temperatures, as shown in Fig. 5(a), reducing the probability of being trapped in the hydrate phase [30]. Therefore, the kinetic properties of ions, influenced by temperature, play a crucial role in determining the extent to which ions become incorporated into the CO_2 hydrate structure during growth.

The investigation by Liu et al. [20] provides a detailed molecular-level sympathetic view of hydrate cage arrangement and growth. The study unveiled insightful findings regarding the impact of temperature, pressure, and salinity on CO_2 hydrate formation and stability. Contrary to expectations, pressure exerted limited influence on the growth of CO_2 hydrate crystals, suggesting that increased pressure primarily enhanced the formation of hydrate nuclei rather than individual crystal growth. Temperature, however, emerged as a critical factor, significantly affecting CO_2 hydrate growth rates. Lower temperatures delayed initial growth despite an increased driving force. CO_2 concentration played a key role, with higher concentrations facilitating faster CO_2 hydrate formation and resulting in higher cage crystallinity. The findings revealed that NaCl concentration in the system impairs CO_2 hydrate formation and stability, reducing the formation rate and inhibiting cage growth, as shown in Fig. 6. The figure shows that the growth rate of both D-cage and T-cage from pure water was initially highest, resulting in a more significant overall number of newly formed cages than systems with NaCl. Observably, during the initial 400 ns of growth, as the NaCl concentration rose from 3.5 to 20 wt%, there was a slight decline in the growth rate of CO_2 hydrate and the total count of formed cages, indicating that lower salinity areas are preferable for CO_2 hydrates formation, stability and storage potential in subseafloor saline sediments.

According to the study by Liu et al. [20] on the inhibitory effect of salt ions revealed that salt ions could not infiltrate the water cages or be absorbed into the cage faces during the hydrate formation process, likely due to the fundamental properties of the molecular structure of hydrates and the electrostatic interactions involved. The water cages in the hydrate structure have a specific arrangement and geometry, creating an environment that may not be conducive to including salt ions [8,33]. The ions likely face electrostatic repulsion from the water molecules within the cages, preventing their integration into the crystal lattice. Additionally, the size and charge of salt ions may not align with the openings and binding sites of the hydrate cages, making it energetically unfavorable for the ions to penetrate or become absorbed. The inability
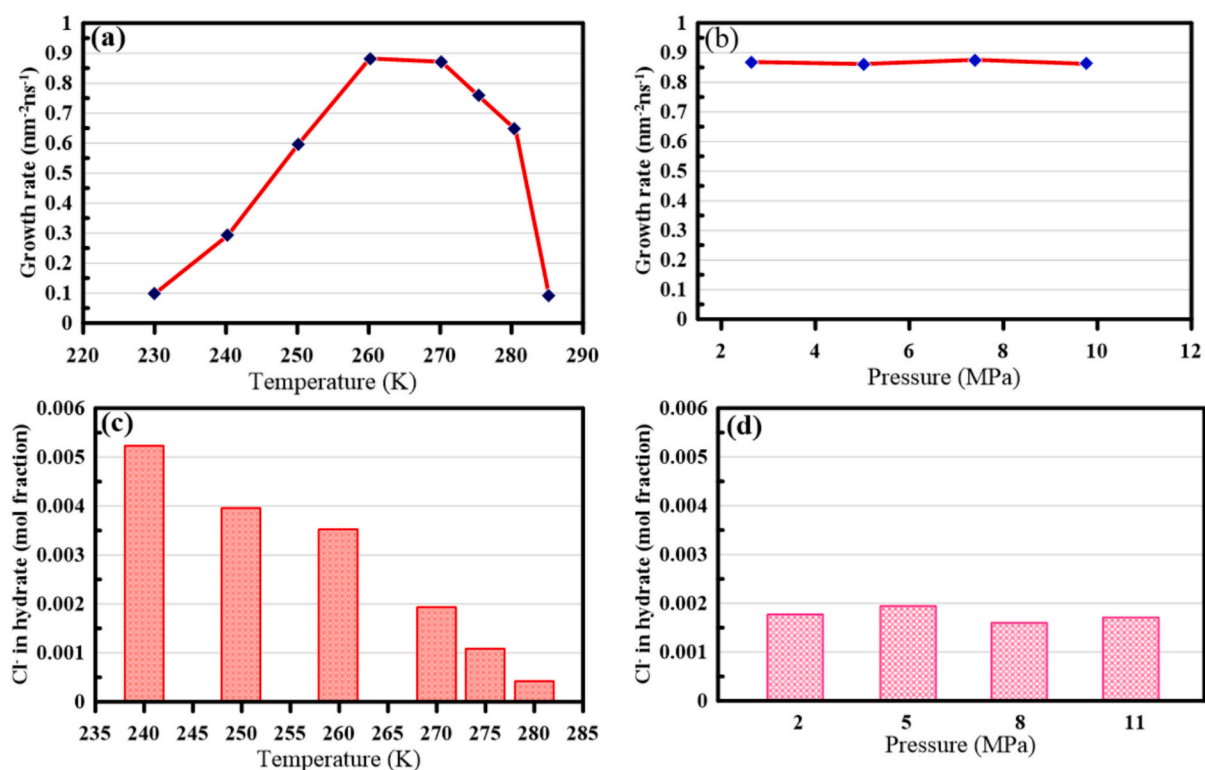

Fig. 3. Temperature and pressure dependence analysis of CO_2 hydrate growth rate. (a, b) The growth rate of CO_2 hydrate in NaCl solution to temperature and pressure dependencies. (c, d) depict Cl^- concentration's temperature and pressure dependencies in the newly formed hydrate phase [30].
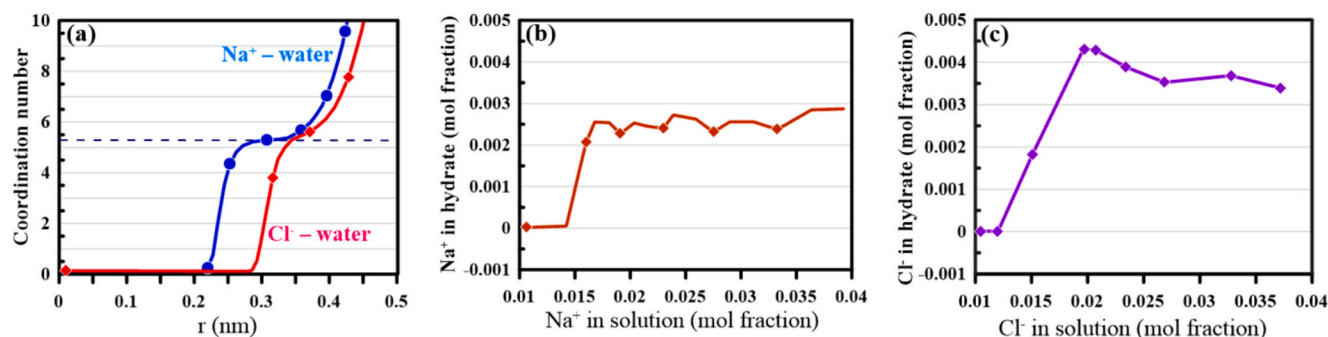
Fig. 4. Relationship between ion incorporation, salinity, and hydrate structure distortion. (a) Coordination of the number of water molecules surrounding ions in the solution phase at 260 K and 5 MPa. (b, c) correlation between solution salinity and ion concentration in the newly formed hydrate phase [30].
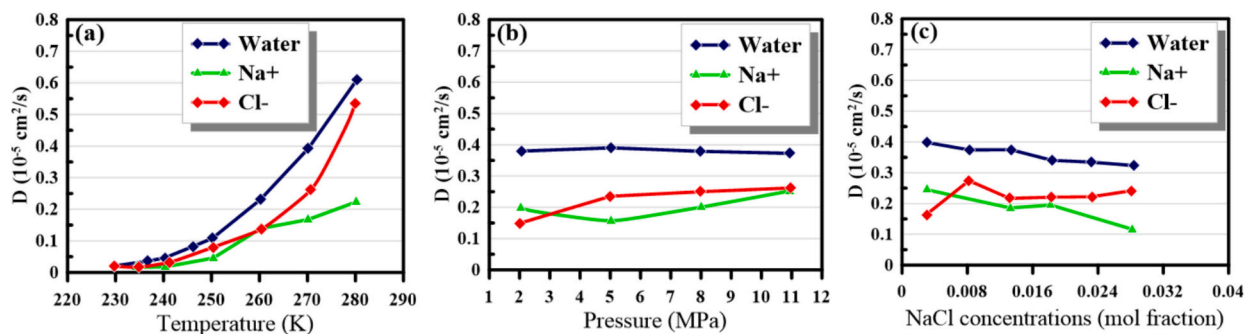

Fig. 5. Influence of temperature on ion diffusion and incorporation into CO_2 hydrate structure during growth with respect to pressure and ion concentrations. (a) temperature, (b) pressure, and (c) varying NaCl concentrations [30].
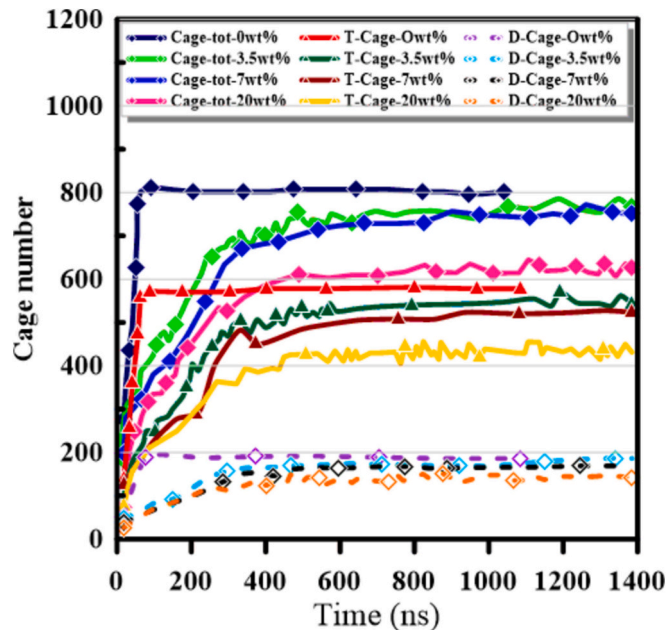

Fig. 6. Influence of sodium chloride (NaCl) concentration on CO_2 hydrate cage formation and stability at 255 K, 30 MPa [20].

of salt ions to infiltrate the water cages or interact with the cage faces reinforces the inhibitory effect on CO_2 hydrate growth. However, adding more salt ions could delay the progression of CO_2 hydrate growth [17]. Furthermore, the experiments conducted by Husebø J et al. [26] using bentheim sandstone as a porous medium demonstrates that higher initial salinity leads to longer induction times and less hydrate

formation, which is attributed partly to the lower energy state of the system. The study indicates that, for low initial salinity, the porous media may restrict further hydrate formation before reaching the thermodynamically stable salinity threshold for hydrate. This observation implies that the physical structure of the pore system interacts with temperature and pressure dynamics, impacting the overall process of hydrate formation. The experiments suggest that the residual free water's salinity after hydrate formation is a limiting factor for additional hydrate growth, particularly when the initial salinity exceeds 4.0 wt% NaCl.

While molecular simulations suggest the potential for Na^+ and Cl^- ions to enter the hydrate phase, with Cl^- ions exhibiting a closer association with the hydrate structure, as seen in the study by Zhao et al. [30], experimental findings reveal a different outcome. Liu et al. [20] revealed that the inhibitory effect of salt ions on hydrate formation is due to the hydrate lattice's electrostatic interactions and molecular structure, which prevent ions from infiltrating the water cages. Specifically, during the hydrate formation process, the water cages maintain a specific geometric arrangement that repels salt ions, limiting their integration into the crystal structure. This discrepancy between simulation and experimental results reflects the complexity of ion behavior in hydrate systems, where theoretical possibilities shown in simulations may not always be observed in real-world experimental conditions. As a result, while simulations provide valuable insights into the mechanisms of ion association with hydrate phases, practical evidence shows that salt ions are typically excluded from the hydrate structure during formation. Thus, the findings are complementary, offering a comprehensive understanding of ion interactions with hydrate structures. Together, these approaches provide a more holistic view, acknowledging that the complexities of molecular interactions can vary depending on the conditions and methodologies used. This balanced understanding allows for better predictions and strategies when working with hydrate systems in practical applications.

2.2.2. Impact of sediment heterogeneity and sediment chemical composition

The influence of sediment heterogeneity and chemical composition on CO_2 hydrate stability and formation kinetics has been the subject of significant research investigations. Sediment heterogeneity, encompassing grain size, mineral composition, and pore structure variations, has impacted CO_2 hydrate formation and stability in marine sediments [34]. Studies have revealed that sediment heterogeneity can significantly influence the distribution and availability of water and CO_2 within the sediment matrix, affecting the conditions for hydrate formation [4,34]. Pore size and connectivity variations can lead to the heterogeneous distribution of CO_2 and water, influencing the local thermodynamic conditions and hydrate formation kinetics [35]. Kou et al. [36] identified a non-uniform distribution of gas hydrate in pores, with smaller particle sizes contributing to increased heterogeneity, challenging the notion that gas hydrate distribution in smaller pores might be underestimated. Temperature variations influenced hydrate distribution characteristics, leading to the evolution of hydrate growth habits. Further, Kou et al. [36] introduced a novel metric, the "hydrate heterogeneity degree," to characterize and quantify the heterogeneity of gas hydrate distribution under different conditions of grain particle size and sample temperature, as shown in Eq.1–3. Essentially, the hydrate heterogeneity degree provides a numerical value that reflects the degree of heterogeneity in gas hydrate distribution within the sediment. The findings revealed changes in these factors influence the degree of heterogeneity, as diagrammatically described in Fig. 7, offering a valuable tool for researchers to precisely analyze and describe the spatial variability of gas hydrate within sediment samples.

$$C_{Sh} = \sigma_{Sh} = \sqrt{S_{Sh}} \tag{1}$$

$$\sigma_{Sh} = \sqrt{\sum_{i=1}^{n} (S_i - \overline{S_{Sh}})^2 \Big/ (m-1)} \tag{2}$$

$$\overline{S_{Sh}} = \sum_{i=1}^{n} S_{Sh} \Big/ m \tag{3}$$

From Eq.1–3, the hydrate heterogeneity degree (C_{Sh}) is defined as a function of the standard deviation of saturation (σ_{Sh}), the hydrate saturation at layer i (S_i), the mean hydrate saturation, $\overline{S_{Sh}}$, and the number of layers (*m*). This proposed hydrate heterogeneity degree
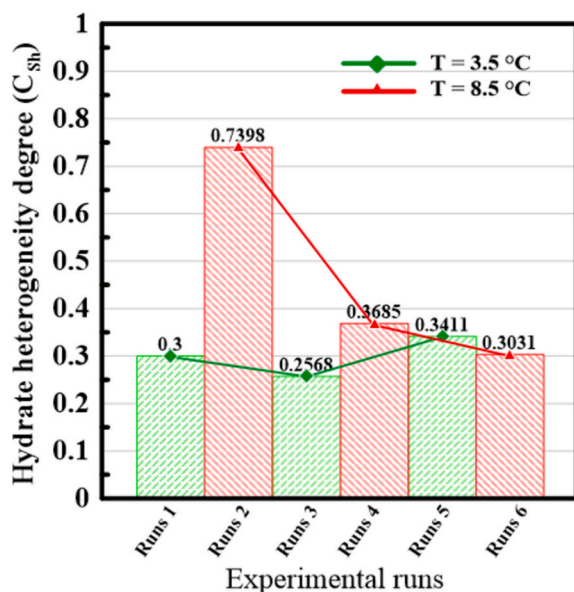

Fig. 7. Heterogeneity levels of gas hydrate within samples from six experimental trials [36].

quantifies the variability or dispersion of hydrate saturation within a specific layer relative to the average hydrate saturation across the entire region. As a non-dimensional parameter, the heterogeneity degree ranges from 0 to 1, with a smaller value indicating minimal differences in hydrate saturation for each layer and a tendency toward a more homogeneous gas hydrate distribution, and vice versa.

As depicted in Fig. 7, there is a subtle distinction in the hydrate heterogeneity degrees between experimental runs 1 and 3. Notably, the hydrate heterogeneity degree in run 5 surpasses that in runs 1 and 3, confirming the heightened heterogeneous distribution of gas hydrate in smaller pores. The heterogeneity degrees of experimental runs 1 and 3 reveal an increase as the temperature rises from 3.5 °C to 8.5 °C. For instance, the heterogeneity degree in experimental run 1 experiences a significant surge from 0.3 to 0.7398 in run 2, likely attributed to the vigorous dissociation of gas hydrate. However, with a further increase in temperature to 8.5 °C, the degree of heterogeneity in experimental run 5 decreases to 0.3031 in run 6. The abnormal rise in heterogeneity degree from run 5 to run 6 is attributed to hydrate reformation during the temperature increase in experimental run 6. Overall, the variations in heterogeneity degree observed in experimental runs 5 and 6 highlight that the hydrate distribution in small pores tends to become more homogeneous with increasing temperature.

Furthermore, the chemical composition of sediments has been found to play a critical role in influencing CO_2 hydrate stability and formation kinetics. The presence of minerals with specific surface properties, such as clays or zeolites, can affect the nucleation and growth of CO_2 hydrates within the sediment matrix [37]. Additionally, interactions between CO_2, water, and mineral surfaces can impact hydrate formation's thermodynamic and kinetic aspects [37,38]. Gurjar et al. [39] reported that clay, specifically bentonite, has a profound impact, significantly reducing CO_2 storage capacity. Via his laboratory experiment, observation revealed that as the clay content increases, there is a substantial decrease in the storage capacity, as shown in Fig. 8, with 8 wt% clay resulting in approximately 75 % reduction compared to the non-clay experiment. The hydrate inhibition effect of clay is attributed to its water absorption and swelling properties, leading to a reduction in sediment porosity and, consequently, slower hydrate formation kinetics.

2.2.3. Effects of additives or nucleation promoters on kinetics

Additives, such as sodium dodecyl sulfate (SDS) or polyvinylpyrrolidone (PVP), can enhance the local hydrogen-bonding network among water molecules or help construct mass transfer channels, thereby improving the nucleation and growth of CO_2 hydrates [17]. Kinetic promoters, such as tetra-n-butylammonium bromide (TBAB) or tetra-n-butylammonium chloride (TBAC), can also improve the kinetic properties of CO_2 hydrate formation [9]. Similarly, thermodynamic promoters, such as tetrahydrofuran (THF) or cyclopentane, can efficiently occupy hydrate cages under moderate temperature and pressure conditions, enhancing the stability and formation of CO_2 hydrates [9]. Studies have explored using additives, such as nanoparticles or surfactants, to enhance the nucleation and growth of CO_2 hydrates within sub-seafloor saline sediments [4,25,40]. These additives have been observed to influence the interfacial properties of the CO_2-water-mineral system, promoting the formation of stable hydrate structures [4,28]. Research has revealed that the restrained selection and application of nucleation promoters can significantly impact the kinetics of CO_2 hydrate formation, offering opportunities to optimize the stability and efficiency of hydrate formation processes. Nucleation promoters have been revealed to alter the thermodynamic conditions for CO_2 hydrate formation, leading to improved kinetics and stability [41,42]. Introducing nucleation promoters with specific chemical properties, such as natural or synthetic surfactants, nanoparticles, or organic compounds, has been shown to accelerate nucleation rates and enhance the growth of CO_2 hydrates under controlled conditions [43,44]. These promoters can effectively alter the interfacial properties of the CO_2-water-mineral system, thereby influencing the kinetics and stability of
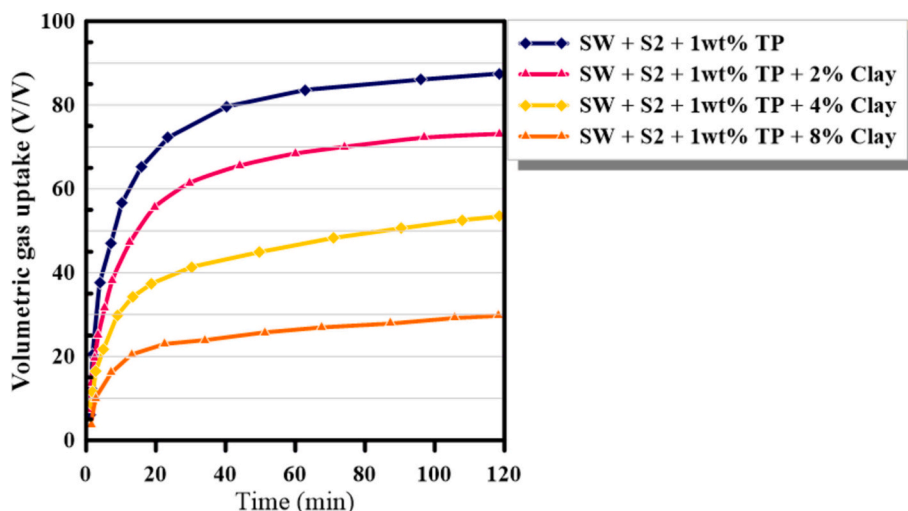
Fig. 8. Influence of clay (bentonite) content with respect to sand in the sediment on CO_2 storage capacity in hydrate formation. SW is saline water, S2 is Silica sand, and TP is L-tryptophan [39].

CO_2 hydrate formation in sub-seafloor saline sediments. Li et al. [45] reported the intricate dynamics of CO_2 hydrate formation and the consequential impact of additives, specifically graphene oxide (GO) nanoparticles and sodium dodecyl sulfate (SDS) surfactant, on the kinetics of this process. One notable revelation is the significant promoting effect observed with the complexation of GO and SDS, highlighting a pronounced influence on the rate and efficiency of CO_2 hydrate formation. The investigation reveals that the composition ratio and mass fraction of the GO and SDS complex system play key roles in influencing hydrate formation. The optimal promotion mass fraction is identified as 0.005 % GO +0.2 % SDS, demonstrating a remarkable reduction in hydrate formation time by 69.7 % compared to pure water and 12.2 % compared to a single 0.005 % GO system. As per this observation, the combination of SDS and GO seems to strengthen the system's heat and mass transfer characteristics, fostering a conducive environment for the rapid formation of hydrates. The uniform dispersion of GO in the presence of SDS provides more nucleation points, enhancing the system's ability to capture gas efficiently. Consequently, this leads to a faster and more stable system temperature, a more pronounced pressure drop, a significant increase in gas consumption, and a substantial reduction in generation time. In addition, Li et al. [45] introduced a chemical affinity model to elucidate the driving force behind the chemical reaction involved in hydrate formation. Fig. 9 shows the procedural steps for computing the parameters within the chemical affinity model algorithm. The model can accurately correlate experimental parameters with time and provides a reliable tool for predicting hydrate formation in GO and SDS systems. The simplicity and efficacy of the chemical affinity model make it a valuable resource for understanding and predicting the kinetics of CO_2 hydrate formation, offering insights that could extend to the broader exploration of additives and nucleation promoters in hydrate formation processes.

Srivastava et al. [46] investigated the impact of amino acid kinetic promoters and a surfactant on the kinetics of CO_2 hydrate formation, explicitly focusing on dissociating CO_2 gas hydrates (GH) at a high temperature of 90 °C. Four hydrophobic food-grade amino acids, such as cysteine, valine, leucine, and methionine, and one surfactant (lecithin) were considered as potential kinetic promoters for CO_2 GH. A combination of these amino acids was explored to assess its impact on the percentage of CO_2 retention during GH formation. The findings indicated that the stability of GH decreased with an increase in temperature, but the addition of promoters, especially leucine + methionine + lecithin, significantly enhanced CO_2 uptake during GH formation. In addition, Srivastava et al. [46] assessed the economic viability of using amino acids (leucine and methionine) as kinetic promoters for CO_2 GH
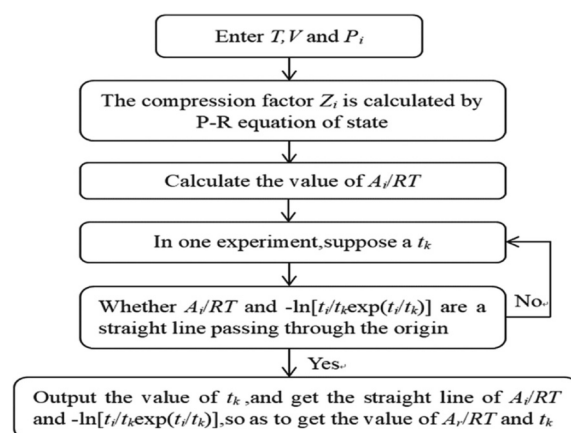

Fig. 9. The procedural steps for computing the chemical affinity model algorithm. Where, Ai-Affinity at state i, Ar-Proportionality constant, t_i-Time it takes to get to state i, and s, t_k-Time it takes to get to k, n_{ci}-Number of moles of gas consumed at t_i, n_{cf}-Total number of moles of gas consumed, R-ideal gas constant, T-Temperature (K), P-Pressure (Pa), Z-Gas compression factor, and i-State at the time I [45].

production by calculating the number of moles consumed and comparing it with the molecular weight of the amino acids. The results demonstrated that leucine and methionine are economically feasible, consuming only 0.003 g per mole in each cycle of CO_2 GH production. Further optimization experiments revealed that an optimum amount of 0.5 % by weight of leucine or methionine contributes to higher CO_2 entrapment at room temperature. Increasing the amount beyond 1 % could not significantly enhance CO_2 gas uptake, suggesting that a specific threshold is required for the proper functioning of amino acids as kinetic promoters. According to the study by Phan et al., [47] reported detailed findings from the computational study investigating the effects of nitrogen-containing heterocyclic compounds, specifically aziridine, pyrrolidine, and tetrahydrofuran (THF) on the kinetics of CO_2 hydrate formation. The analysis of hydrate growth kinetics revealed that aziridine and pyrrolidine could act as effective thermodynamic and kinetic promoters for CO_2 hydrate formation. The study observed an exponential growth of hydrate cages at lower temperatures (269.1 K), and the results indicated that, at this temperature, aziridine outperformed both pyrrolidine and THF in enhancing the kinetics of CO_2 hydrate formation. The simulations showed that, even though aziridine and pyrrolidine did

not compromise the storage capacity of CO_2 hydrates, they significantly influenced the hydrate growth rates. Notably, aziridine exhibited a higher growth rate than pyrrolidine and THF at 269.1 K, suggesting its potential as an efficient CO_2 hydrate promoter.

In addition, Farhang et al. [48] examined the influence of sodium halide additives on CO_2 hydrate stability and formation kinetics under stirred conditions. Sodium iodide at a high concentration (500 mM) showed limited enhancement, contrasting with varied effects observed for sodium chloride and sodium fluoride. Gas consumption analysis revealed concentrations above 350 mM, resulting in gas uptake similar to pure water, with a crucial transition concentration identified at around 50 mM for all sodium halides. The comparison of different sodium halides showed that sodium iodide demonstrated the best performance in terms of CO_2 conversion, outperforming sodium bromide, sodium chloride, and sodium fluoride. Further, Farhang et al. [48] revealed significant insights into induction time, growth rate, and surface potential during CO_2 hydrate formation. Comparing sodium halides, sodium iodide and sodium bromide exhibited shorter average induction times, while sodium fluoride and sodium chloride showed considerably longer times. The growth rate for CO_2 hydrates formed in the presence of aqueous salt solutions peaked at around 50 mM concentrations for all sodium halides, emphasizing the crucial role of this transition concentration in facilitating faster hydrate formation kinetics. Surface potential measurements demonstrated a negative charge on hydrate particles, with the highest absolute value observed at the transition concentration of 50 mM, indicating the importance of surface interactions in enhancing gas transport and hydrate formation. However, researchers encounter persistent challenges in optimizing CO_2 hydrate formation for practical applications. Despite achieving a conversion and storage capacity of 18.34 ± 3.21 % and 49.02 ± 0.06 (volume ratio), respectively, the study acknowledges that these results fall short of industrial expectations. The complex interplay of factors influencing hydrate kinetics, including the impact of sodium halide additives, presents hurdles in achieving higher gas uptake. Therefore, there is a need for continued research efforts to overcome these challenges and enhance the efficiency of CO_2 hydrate formation, which is crucial for its application in areas such as gas storage and transportation.

3. Sub-seafloor sediments: Characteristics and challenges

The study of sub-seafloor sediments is critical in understanding their role in carbon capture and storage, particularly in the formation and stability of CO_2 hydrates. This section delves into the unique properties of sub-seafloor saline sediments, essential for optimizing CO_2 hydrate formation. It also addresses the challenges faced in these deep-sea environments, where extreme conditions can significantly impact the efficiency of hydrate formation processes. By examining the characteristics of these sediments, researchers can better tailor strategies for effective carbon storage and mitigate the impacts of climate change.

3.1. Properties of sub-seafloor saline sediments

The porosity and permeability characteristics of sub-seafloor saline sediments are crucial for optimizing CO_2 hydrate formation and stability [2,4,49]. Porosity, the measure of void spaces in the sediment, plays a fundamental role in determining hydrate storage capacity. Higher porosity increases hydrate molecules' accommodation, influencing the overall capacity for CO_2 hydrate formation [49]. The permeability of these sediments, representing their ability to transmit fluids, is equally significant. It dictates the ease with which fluids can flow through the sediment matrix, affecting the distribution and growth of hydrate formations [2,49]. A comprehensive analysis of porosity and permeability helps identify ideal locations within sub-seafloor sediments for implementing thermal and pressure management strategies optimizing CO_2 hydrate formation.

The chemical composition of sub-seafloor saline sediments is diverse and includes various minerals and salts that significantly influence the hydrate stability thermodynamic conditions. Notably, the presence of minerals such as clays, silicates, and carbonates can impact the formation and stability of hydrates [50–52]. Specific salts, including sodium chloride (NaCl), magnesium sulfate ($MgSO_4$), and potassium chloride (KCl), among others, also contribute to the overall composition, playing a crucial role in hydrate stability zones [53,54]. Each mineral and salt present in sub-seafloor sediments introduces distinct interactions and reactions with water and gases, affecting the equilibrium conditions for hydrate formation. Identifying regions rich in certain minerals and salts becomes essential for pinpointing areas with optimal conditions for CO_2 hydrate stability. Moreover, understanding the chemical composition provides valuable insights into the potential inhibitors or promoters for hydrate formation. Some minerals may act as inhibitors, impeding the growth of hydrates in sub-seafloor saline sediments. Notably, clay minerals like kaolinite and illite possess structures that physically hinder the aggregation of water and gas molecules crucial for hydrate stability [55]. Additionally, sulfate minerals such as gypsum and anhydrite can compete with water molecules, disrupting the hydrate formation process [56]. On the other hand, some minerals function as promoters, facilitating the stability of hydrates. Silicate minerals, including specific zeolites, provide suitable frameworks for hydrate nucleation and growth, enhancing stability [57]. Salt minerals, such as potassium chloride, can also act as promoters by influencing the thermodynamic conditions necessary for hydrate formation [54].

Characterizing the chemical environment of sub-seafloor sediments is integral to effectively tailoring thermal and pressure management techniques. By adapting strategies based on the specific mineral and salt composition, scientists can enhance CO_2 hydrate stability and reduce the risk of dissociation. This knowledge is key for successfully implementing carbon capture and storage strategies in marine environments, as it allows for targeted and efficient utilization of sub-seafloor resources while minimizing environmental impacts.

3.2. Unique challenges in CO_2 hydrate formation

The formation of CO_2 hydrates in deep-sea conditions presents numerous challenges that significantly impact the efficiency and stability of the process. The extreme environmental conditions in sub-seafloor regions, characterized by high pressures and low temperatures, pose a formidable hurdle to successfully forming CO_2 hydrates. At depths exceeding a few hundred meters, the pressure can reach several hundred atmospheres, increasing difficulty in achieving the conditions for hydrate formation [58]. Moreover, the low temperatures prevalent in these deep-sea environments demand precise thermal management strategies to initiate and sustain the hydrate formation process [59,60]. The interplay between high pressure and low temperature necessitates a nuanced understanding of their combined effects on the kinetics and thermodynamics of CO_2 hydrate formation. Overcoming these deep-sea conditions requires innovative engineering solutions and a comprehensive grasp of the underlying physical principles governing hydrate formation at such depths.

In addition to the inherent challenges posed by deep-sea conditions, interactions with the seabed and sediment introduce further complexities to CO_2 hydrate formation. The heterogeneous nature of sub-seafloor sediments influences the hydrate formation process in unique ways, presenting sediment-specific hindrances. The presence of mineral components, varying grain sizes, and heterogeneous permeability profiles within the sediment matrix can impede the migration of CO_2 and affect the overall efficiency of hydrate formation [61,62]. Furthermore, sediment-water interactions play a crucial role in determining the stability and distribution of hydrates within the geological formations [63]. These complex seabed interactions are prevailing for optimizing CO_2 hydrate formation and stability, as they enable the development of tailored approaches that address sediment-specific challenges. Thus, unravelling the intricacies of deep-sea sediment dynamics is essential for

advancing the field of CO_2 hydrate research and ensuring the viability of sub-seafloor hydrate storage as a carbon capture and storage strategy.

4. Thermal management techniques for optimizing CO_2 hydrate formation

The effective management of thermal conditions is critical for optimizing the formation and stability of CO_2 hydrates in sub-seafloor saline sediments. Given the unique challenges posed by the deep-sea environment, including high pressures and low temperatures, innovative thermal management techniques are essential. This section explores various strategies that can be employed to manipulate thermal conditions, thereby enhancing the efficiency of CO_2 hydrate formation.

4.1. Thermal manipulation strategies

Controlled heating methods are essential in optimizing CO_2 hydrate formation and stability in sub-seafloor saline sediments. One prominent approach involves using electrical heating systems, as diagrammatically illustrated in Fig. 10 [64]. By applying controlled electrical currents, researchers can precisely manage the temperature within the sediments, facilitating the controlled formation and dissociation of CO_2 hydrates. This method allows for a fine-tuned manipulation of the thermal conditions, enabling scientists to study and optimize the hydrate formation process with high precision [64,65]. Additionally, microwave heating is another noteworthy technique employed in this context. Microwave energy can be selectively delivered to specific regions of sub-seafloor sediments, promoting efficient heating and enhancing the kinetics of CO_2 hydrate formation [66]. Bin Wang [66] revealed that microwave heating can provide timely and sufficient energy for hydrate formation and dissociation from hydrate deposits, significantly improving energy efficiency and gas generation rates. The findings indicate that the operational strategy for microwave heating can be optimized to achieve better hydrate formation and dissociation performance, making it a promising method for CO_2 hydrate formation in sub-seafloor saline sediments. The controlled nature of electrical and microwave heating methods provides researchers with valuable tools to investigate and optimize the underlying mechanisms governing CO_2 hydrate stability. In contrast to controlled heating methods, utilizing geothermal gradients for localized heating offers a unique and environmentally friendly strategy [2,67]. This approach capitalizes on the natural temperature gradients in sub-seafloor environments. By strategically placing heat sources in specific locations within the sediments, researchers can

harness geothermal energy to induce localized heating [68,69]. This minimizes the need for external energy inputs and aligns with sustainable practices. Utilizing geothermal gradients provides a cost-effective and energy-efficient alternative, demonstrating the potential for harnessing naturally occurring thermal resources to optimize CO_2 hydrate formation and stability in sub-seafloor saline sediments [69,70]. Researchers exploring thermal manipulation strategies can benefit from considering both controlled heating methods and the innovative use of geothermal gradients to advance CO_2 hydrate. This study discussed the approach of electrical heating systems in optimizing CO_2 hydrate formation and stability in marine saline sediments.

4.1.1. Electrical heating systems for optimizing CO_2 hydrate formation and stability

Investigation findings have revealed a specific "intensity window" of electric field strengths ranging from 0.2 to 0.6 V/nm that significantly promotes the growth of CO_2 hydrate crystals [65]. Electric fields within the intensity window enhance the solubility of CO_2 molecules, offering a mechanism for promoting CO_2 hydrate growth [65]. The dual effect—altering water molecule alignment and increasing solubility—contributes to the overall optimization of CO_2 hydrate formation. The alignment of water molecules under the influence of the electric field has been identified as a crucial factor, leading to the formation of cage-like structures and reducing the diffusion ability of free water [65,71]. This alignment facilitates the growth of CO_2 hydrate crystals within the identified intensity window. Meng et al. [65] thoroughly investigated the effects of electrical fields on CO_2 hydrate formation and stability through molecular dynamics simulations. Minimal impact on CO_2 hydrate growth was observed at lower field strengths (0.1 V/nm), while higher field strengths beyond the intensity window led to the complete decomposition of CO_2 hydrate, as shown in Fig. 11—a temperature-dependent relationship, indicating different optimal electric field strengths for CO_2 hydrate-promoting growth at various temperatures.

CO_2 hydrate structural analyses, including examining F4 order parameters, mean square displacement (MSD), and hydrate cages, provide detailed insights into the system's molecular structure and dynamics changes in electrical heating systems [65,72]. The F4 order parameter represents alterations in the structural characteristics among water molecules during hydrate formation, offering insights into the proximity of the hydrogen bonding network to the crystal structure [65,73]. This parameter can be determined analytically by computing the dihedral angle formed by two neighboring water molecules within the system, as
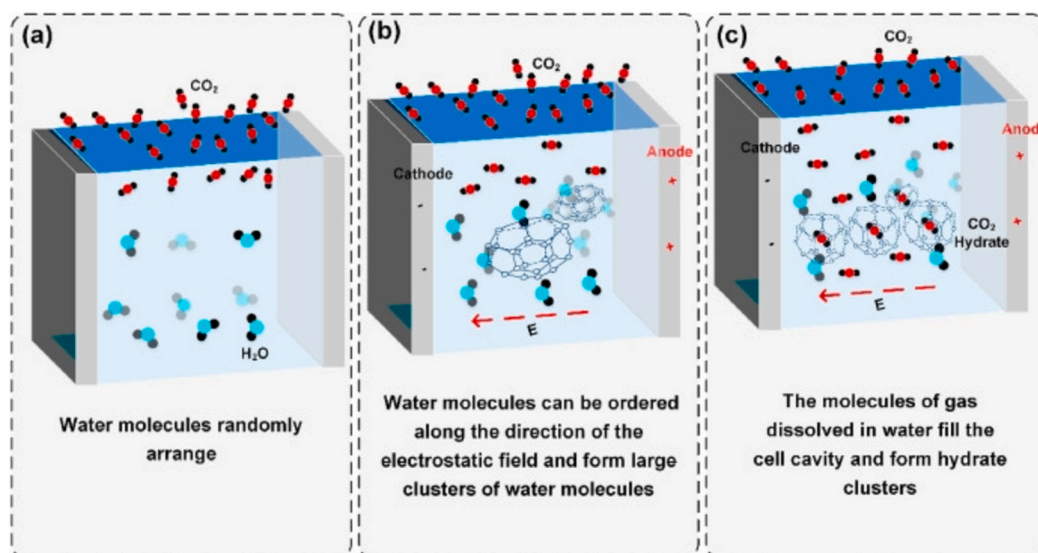

Fig. 10. The formation of CO_2 hydrate under the influence of an electrostatic field [64].
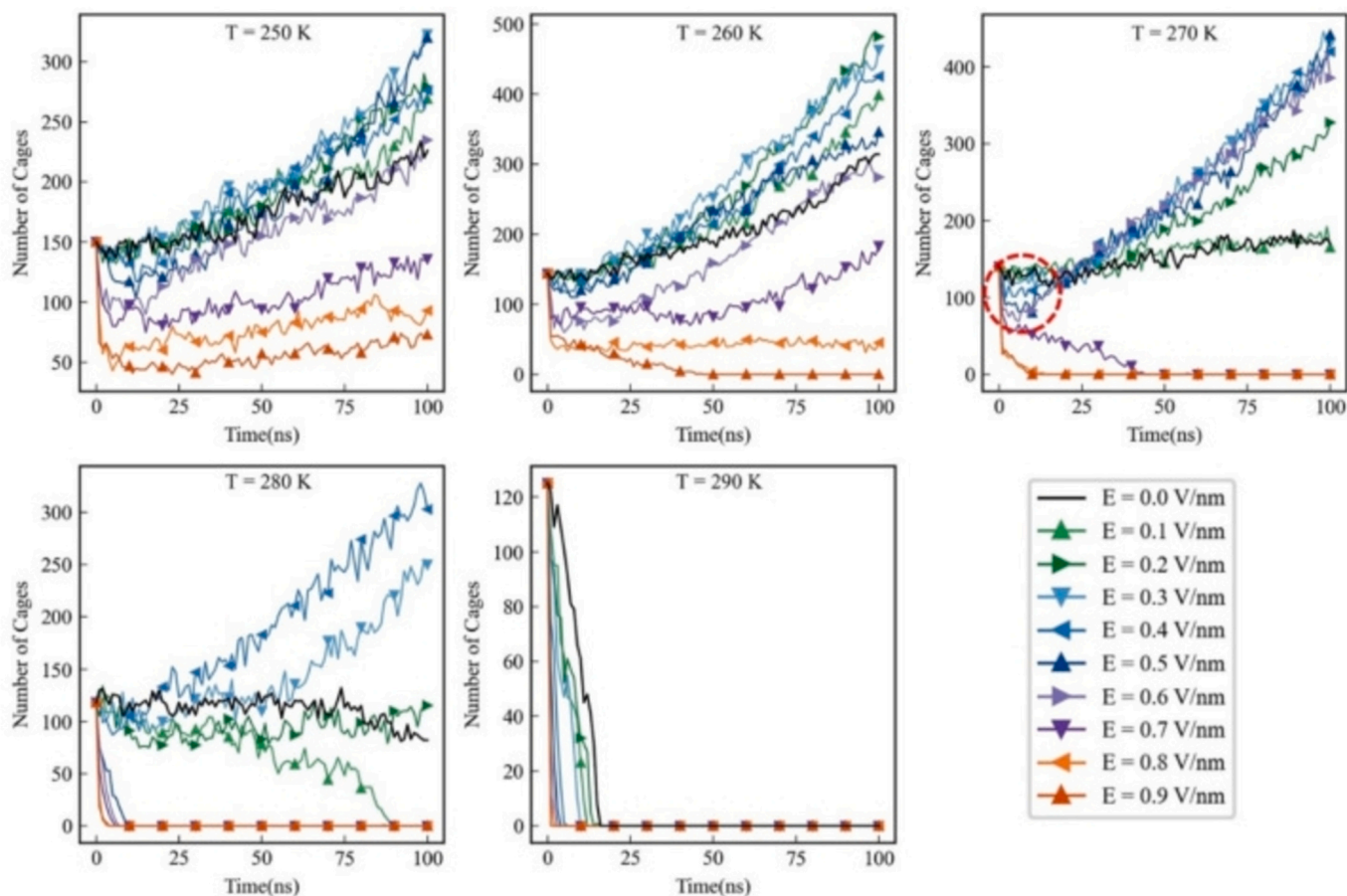
Fig. 11. Changes in the number of CO$_2$ hydrate cages across varying temperature (K) and electrical field (V/nm) conditions. The red dotted circle at $T = 270$ K graph shows the fluctuating phase observed at the beginning of the simulation [65]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

specified in Eq. (4) [65]. The mean F4 order parameter values for water molecules in hydrate, liquid water, and ice are recorded as 0.7, −0.04, and − 0.4, respectively [65,74,75]. The positive value for hydrate indicates a stronger correlation between water molecules than liquid water, while the negative values for liquid water and ice suggest weaker correlations [65,76]. These values align with the expected behavior of water molecules in different phases. It's important to note that these values are approximate and can vary based on specific conditions and experimental methods. However, the provided values are consistent with the typical behavior of water molecules in different states.

$$F_4 = {}^1\!/_n \sum_{i=1}^{n} cos(3\varphi_i) \qquad (4)$$

In Eq.4, indicating the F4 order parameter, φ_i represents the torsional angle of H—O⋯O—H, and n denotes the number of oxygens–oxygen pairs among water molecules located within a radius of a selected molecule. Fig. 12 depicts the variation curves of F4 over simulation time for different temperatures (K) and electrical field systems (Vnm) as observed from Meng et al. [65] investigations on the effects of electrical fields on CO$_2$ hydrate formation and stability. According to this figure, The F4 values in the system reveal an increase compared to those without an electric field within the intensity window at diverse temperatures. The curve maintains a constant slope, indicating a consistent CO$_2$ hydrate growth rate. However, at the electric field intensity that induces hydrate decomposition, the F4 of the system experiences a rapid decrease to −0.04, signifying the complete decomposition of the hydrate crystals within the system at that specific moment. Notably, when the electric field strength is excessively high, the F4 of the system drops below −0.04, suggesting that water molecules in the system have

initiated a transformation into an ice structure at this particular juncture.

In addition, mean square displacement (MSD) is employed to investigate CO$_2$ hydrate growth under the influence of an electric field by tracking the average squared distance traveled by individual CO$_2$ molecules over time, as described in Eq.5 [65]. The MSD analysis provides insights into the diffusion behavior and mobility of CO$_2$ molecules within the hydrate structure, offering valuable information on the impact of the electric field on CO$_2$ hydrate formation and growth [77]. This approach enables researchers to assess the effectiveness of electric field promotion in enhancing CO$_2$ hydrate formation and better understand the underlying mechanisms driving the process. Meng et al. [65] reported that within the identified intensity window of electric field strengths (0.2–0.6 V/nm), the MSD is lower than systems without an electric field, signifying a reduced diffusion coefficient of free water. This reduction is associated with the alignment of water molecules induced by the electric field, forming cage-like structures and promoting the growth of CO$_2$ hydrate crystals. When the MSD increases at higher electric field strengths, particularly beyond the intensity window, it indicates enhanced diffusion and the decomposition of CO$_2$ hydrate crystals.

$$MSD = R(t) = \langle |\overrightarrow{r}(i) - \overrightarrow{r}(0)|^2 \rangle = {}^1\!/_N \sum_{i=1}^{N} \langle |R_i(t) - R_i(t_0)|^2 \rangle \qquad (5)$$

In the given expression, R(t) represents the mean squared displacement (MSD) at a specific moment in time. $R_i(t_0)$ denotes the position of particle i at the initial time t_0, and N represents the total number of particles within the system.

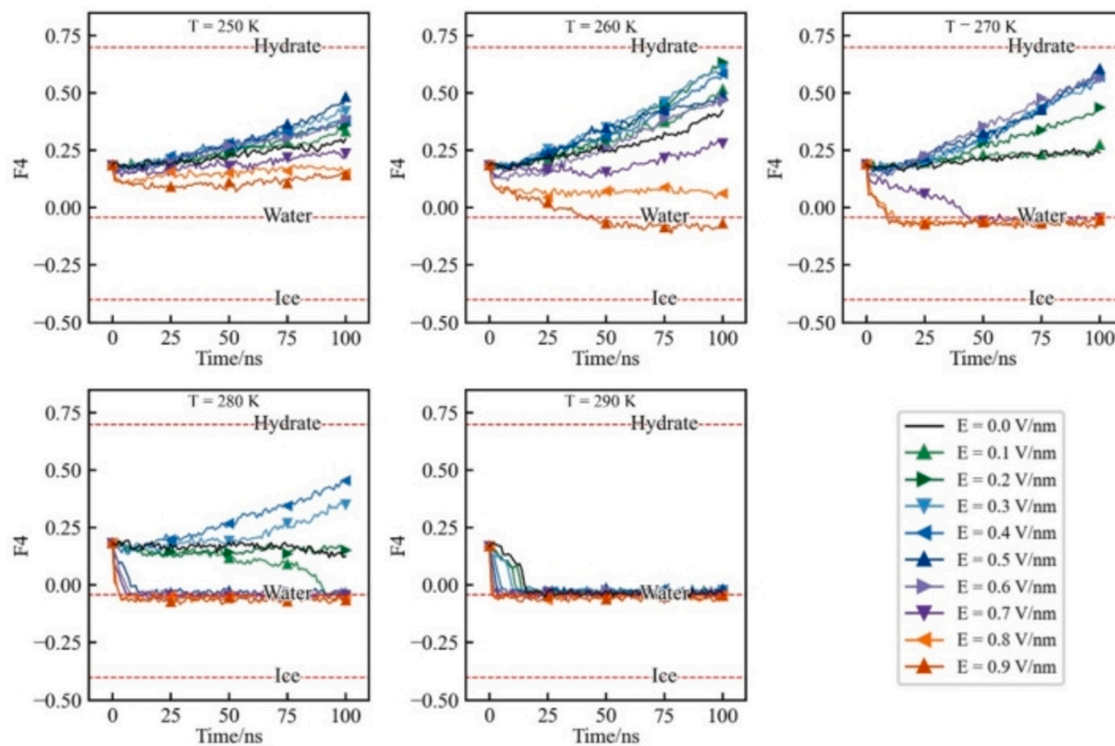Further, the study by Zhao et al. [64] reported that applying a 150 V

Fig. 12. F4 structural order parameters at different temperatures (K) and electrical field (Vnm) conditions [65].

electrostatic field in the freshwater system significantly enhances CO_2 hydrate formation by approximately 54.5 % compared to conditions without an electrostatic field. This improvement is attributed to the electrostatic field's ability to facilitate the aggregation of water molecules into large clusters, thereby promoting the formation of CO_2 hydrate. However, the study revealed that the electrostatic field does not influence the final gas consumption during CO_2 hydrate formation, as described in Table 1, indicating that its impact is more prominent in the early and intermediate stages of the process. The electrostatic field revealed a dampening effect on hydrate formation in the memory water system, where residual hydrate cage fragments remained after decomposition. Despite this, the overall hydrate formation in the memory water system is still optimized over the fresh water system, as shown in Table 1. In this context, the electrostatic field's influence on memory water indicates its ability to disrupt the hydrate formation process. In addition, Zhao et al. [64] revealed that in the saltwater system, an

electrostatic field influences the entire CO_2 hydrate formation process. After the dissolution stage, the field enhances CO_2 hydrate formation, but the intense collision between ions and nuclei under a strong electrostatic field inhibited hydrate growth. Moreover, the electrostatic field influences ion distribution in the solution, promoting hydrate formation in specific directions, as shown in Fig. 13.

4.1.1.1. CO_2 hydrate formation and stability monitoring via electrostatic field application. The application of electrostatic fields allows real-time monitoring of CO_2 hydrate stability and formation. Researchers have developed innovative techniques for non-invasive tracking of hydrate formation dynamics within saline sediments by leveraging electrostatic field measurements. This has provided critical data for modeling and predicting subsurface hydrate behavior, offering new insights into the temporal evolution of CO_2 hydrate stability under varying thermal and pressure conditions. Stern et al. [71] investigated the effects of electrical conductivity on CO_2 hydrate formation and stability. By synthesizing disc-shaped CO_2 hydrate samples under specific pressure-temperature (P-T) conditions, the researchers aimed to understand the electrical behavior during the formation cycles. Impedance measurements were conducted using a specialized electrical conductivity cell with Ag-foil electrodes, allowing for a detailed analysis of the electrical properties of CO_2 hydrate. The findings revealed that CO_2 hydrate exhibited frequency-dependent impedance during synthesis cycles, with distinct differences observed compared to CH_4 hydrate, as shown in Fig. 14. This finding signifies a nuanced electrical behavior unique to CO_2 hydrate compared to CH_4 hydrate. In the context of optimizing CO_2 hydrate formation, this finding suggests that the electrical properties of the hydrate are dynamic and influenced by the synthesis process. The frequency-dependent nature of impedance implies variations in how CO_2 hydrate responds to electrical signals at different frequencies during its formation. For several reasons, understanding these distinct differences in electrical behavior is crucial for optimizing CO_2 hydrate formation. First, it provides insights into the kinetics and mechanisms involved in forming. The frequency dependence may reflect changes in the microstructure, connectivity, or distribution of CO_2 hydrate crystals

Table 1
Conditions for hydrate formation in various systems under the influence of an electrostatic field [64].

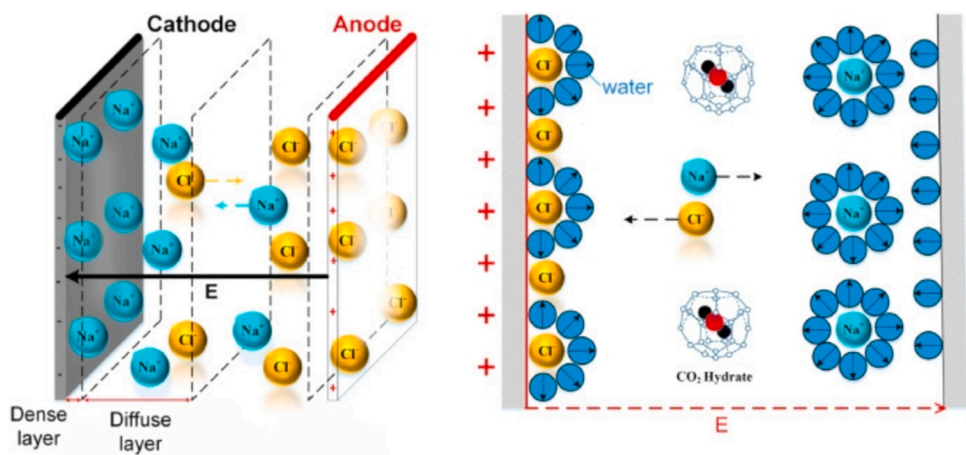| Case	System	Voltage (V)	Pressure (MPa)	Temperature (K)	Gas consumption (mmol/mol)
1	Fresh	(No electrodes)	3.00	274.15	20.05
2		0.00	3.00	274.15	20.26
3		30.00	3.00	274.15	20.29
4		75.00	3.00	274.15	20.28
5		150.00	3.00	274.15	20.34
6		150.00	3.50	274.15	28.56
7	Memory	0.00	3.00	274.15	20.27
8		75.00	3.00	274.15	20.26
9		150.00	3.00	274.15	20.43
10	3 wt% NaCl	0.00	3.50	274.15	26.00
11		75.00	3.50	274.15	25.95
12		150.00	3.50	274.15	25.64

Fig. 13. Influence of electrostatic field on CO_2 hydrate formation in saltwater system, Illustration of the arrangement of ions in the salt solution system when subjected to an electrostatic field [64].
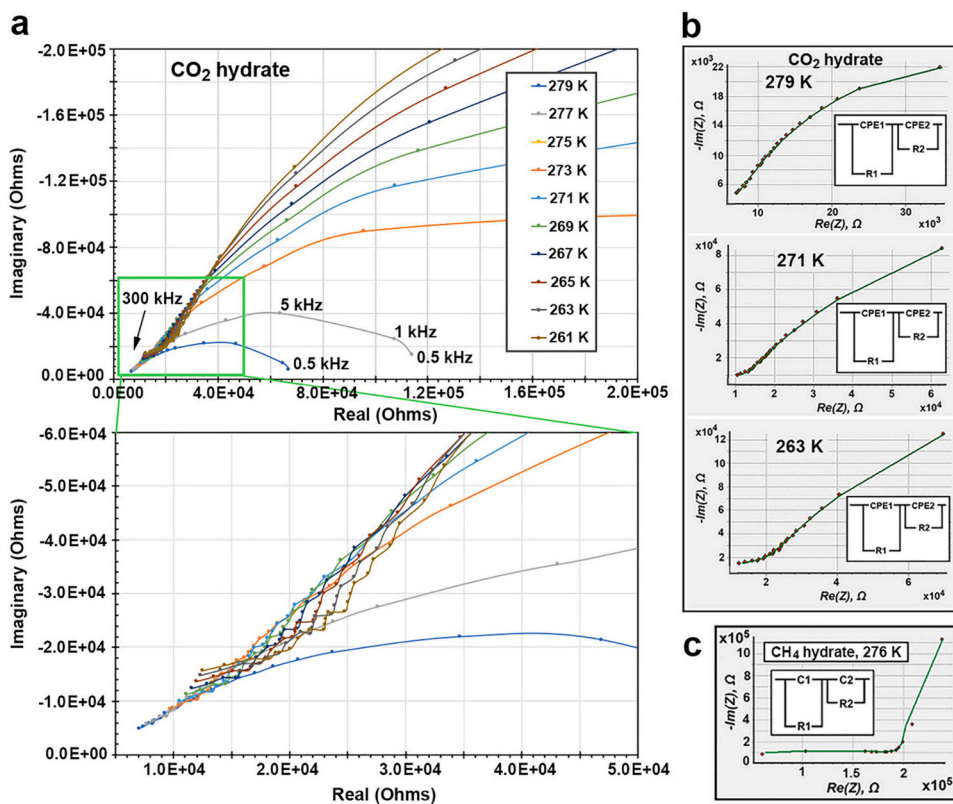

Fig. 14. Electrical impedance characteristics of CO_2 hydrate during synthesis cycles. (a) Comparison of real/actual impedance (ReZ) and imaginary impedance (ImZ) for pure CO_2 hydrate across multiple frequencies (0.5–300 kHz) as a function of temperature (K). Each data point in the temperature curve corresponds to a specific frequency, with the highest frequency depicted on the left side of the x-axis and the lowest on the right. (b) Illustration of real versus imaginary impedance (Z) at three temperatures for CO_2 hydrate, covering the step-dwell thermal range. Embedded are insets showing Equivalent Circuit Model (ECM) fits. The frequency range for these fits is 10–300 kHz, representing the simplest ECMs required for acceptable fits with less than 5 % error in the fitted resistance values. (c) Presented example of complex impedance (Z) and ECM fit for pure CH_4 hydrate for comparative analysis. The frequency range for this comparison is 1–30 kHz. This comparison aids in understanding the differences in impedance behavior between pure CO_2 hydrate and CH_4 hydrate, offering insights into their respective electrical characteristics [71].

during synthesis cycles [35,71,78]. By monitoring these electrical characteristics, researchers can better understand the physical and chemical processes within the hydrate structure. Second, the observed differences compared to CH_4 hydrate highlight the specificity of electrical responses associated with CO_2 hydrate. This specificity can be leveraged for developing tailored optimization strategies. For instance, adjustments in synthesis conditions, such as temperature, pressure, or reactant concentrations, can be fine-tuned based on the unique electrical signatures of CO_2 hydrate. Optimization may involve manipulating these synthesis parameters to enhance the efficiency and stability of CO_2 hydrate formation.

Further, Stern et al. [71] reported that the electrical conductivity of CO_2 hydrate is notably higher than that of pure CH_4 hydrate, particularly across the temperature range of 260–281 K, as illustrated in Fig. 15.
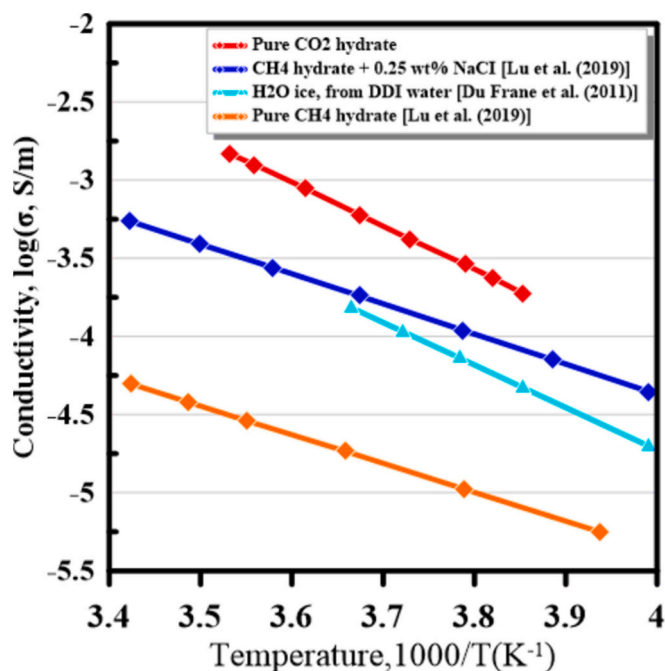
Fig. 15. Electrical conductivity comparison between pure CO_2 hydrates along with pure CH_4 hydrate [79], CH_4 hydrate +0.25 % NaCl [79], and H_2O ice [80]. Adapted from ref. [71].

This can be attributed to the distinct properties of the guest molecules. CO_2, with a larger quadrupole moment and greater volumetric expansion during hydrate formation, likely induces structural changes and facilitates the creation of additional charge carriers, contributing to increased conductivity. Differences in lattice structure and defects, along with the temperature dependence of electrical properties, further influence the observed variations in conductivity between CO_2 and CH_4 hydrates. Thus, the composition of the guest molecule (CO_2) could play a crucial role in determining the electrical conductivity of CO_2 hydrates. The higher electrical conductivity of CO_2 hydrates may indicate enhanced stability and formation efficiency. It could be advantageous for monitoring and controlling CO_2 hydrate formations, especially in scenarios where electrical properties play a role, such as in electromagnetic (EM) methods, particularly in remote settings within the gas hydrate stability zone.

4.2. Novel approaches for optimizing temperature conditions

Exploring innovative strategies to enhance temperature conditions for the formation and stability of CO_2 hydrates in sub-seafloor saline sediments involves tapping into the capabilities of smart materials and phase change materials (PCMs). Smart materials, such as shape memory alloys and polymers, can respond to external stimuli, enabling precise control over the release of stored thermal energy [81,82]. Strategically integrating these materials within the sediment layers makes regulating the temperature environment and facilitating the targeted formation and maintenance of CO_2 hydrates possible [82]. Additionally, phase change materials, such as paraffin wax, fatty acids, and salt hydrates, are known for storing and releasing large amounts of energy during phase transitions, presenting an innovative avenue for managing temperature conditions [83]. By leveraging the latent heat associated with phase changes, these materials can achieve controlled heating within the sub-seafloor sediments, contributing to the optimization of CO_2 hydrate formation and stability. Table 2 illustrates the significant research findings on the effectiveness of employing smart materials and phase change materials (PCMs) in optimizing temperature conditions to enhance CO_2 hydrate formation and stability.

Furthermore, innovations in heat transfer mechanisms for sediment layers are being pursued to enhance temperature management in sub-seafloor environments. Advanced thermal conductivity enhancement techniques, such as nanofluids or thermally conductive additives, such as graphite, carbon nanotubes, metallic particles (such as copper or aluminum), and various types of ceramics, offer promising ways to improve heat transfer within the sediment matrix [44,86]. By incorporating these innovative heat transfer mechanisms, it becomes feasible to distribute and regulate thermal energy more effectively within the sub-seafloor saline sediments, thereby influencing the conditions conducive to CO_2 hydrate formation and stability. Table 3 evaluates different advanced thermal conductivity enhancement techniques and their effects on CO_2 hydrate formation and stability. Additionally, novel heat transfer enhancement designs, such as structured interfaces or engineered porous media, are being explored to optimize the thermal profile within the sediment layers [35,87]. These innovations can potentially refine the temperature conditions necessary to promote CO_2 hydrate formation and ensure stability in sub-seafloor saline sediments.

5. Pressure management strategies for optimizing CO_2 hydrate formation

The influence of subsurface pressure is fundamental in the formation and storage of CO_2 hydrate, as it determines the phase of CO_2—whether it will be in liquid or gaseous form [94,95]. Pressures exceeding 800 m depth are typically high enough to maintain CO_2 in a condensed state, which is ideal for maximizing storage capacity [94]. Controlled pressure level conditions during CO_2 injection, pressure cycling techniques, such as cyclic injection and withdrawal of fluids to induce pressure variations, as well as controlled oscillations in pressure levels to optimize the conditions for CO_2 hydrate formation in sub-seafloor saline sediments, have been identified as crucial factors in promoting efficient CO_2 hydrate formation and ensuring long-term stability [96,97]. The interplay between pressure and temperature also plays a critical role [17,98].

When injecting CO_2, pressure increases within a structural closure must be carefully monitored. Appropriate management of this pressure

Table 2

Efficacy of smart materials and phase change materials (PCMs) in enhancing CO_2 hydrate formation temperature stability.

Smart Material/PCM	Impact on Temperature Regulation	CO_2 Hydrate Formation Enhancement	Potential Applications	Observations/ Comments	Reference
Encapsulated PCMs.	Smartly regulate drilling fluid temperatures.	Inhibits hydrate decomposition.	Drilling fluids for gas hydrate reservoirs.	Tetradecane core with melamine-urea-formaldehyde resin shell	[84]
Graphene oxide-modified hydrogels.	Tailored phase transition behaviors.	Allows regulation of salt PCM phase transitions.	Modified hydrate salt hydrogels.	GO provides interaction with PAAAM and hydrate salt.	[85]
GO and SDS accelerators.	Enhanced formation kinetics.	Reduces the time and gas consumption for hydrate formation.	Kinetic promoters for CO_2 hydrates.	The addition of accelerators significantly improves the rate of formation.	[45]
PCM microcapsules	Intelligent temperature control of mediums.	Prevents unwanted decomposition of gas hydrates.	Smart regulation systems.	Emphasizes the key role in maintaining desired operational temperatures.	[84]
TBAB and CP systemic promoters	Enhances hydrate formation	Increased CO_2 capture by hydrate formation	CO_2 capture and storage	Demonstrates that certain promoters can improve hydrate creation processes.	[42]

Table 3
Comparative analysis of advanced thermal conductivity enhancement techniques for optimal CO_2 hydrate stability.

Enhancement Technique	Concentration & Conditions	Impact on Hydrate Formation	Observations and Insights	Reference
Nanofluids	0.1–0.5 wt%	Reduced induction time, Increased kinetics.	Nanofluids at optimal concentrations can significantly decrease the induction time of CO_2 hydrate formation, implying a kinetic enhancement.	[88,89]
Graphite Nanoparticles	0.4 wt% under 3.5 MPa and 277.15 K	Increased maximum CO_2 consumption.	The addition of graphite nanoparticles has been observed to decrease induction time by 80.8 % and increase CO_2 consumption by 12.8 % compared to pure water.	[90]
Carbon Nanotubes (CNTs)	0.01–0.05 wt% mixed with surfactants.	High initial formation rate & gas uptake	Functionally adding carbon nanotubes with surfactants led to the highest initial hydrate formation rate and gas uptake without affecting equilibrium conditions.	[91]
Metallic Particles (Copper and Aluminum)	1.57×10^{-2} M - 1.57×10^{-1} M	Lower average induction time.	Copper particles at higher concentrations were more effective, lowering the average induction time for forming CO_2 hydrate.	[92]
Ceramics	Varied (Specific studies required)	Improvement in the heat transfer process	Ceramics and other conductive additives can potentially enhance heat transfer, improving hydrate reservoirs' gas productivity.	[93]

is crucial for the integrity of the CO_2 formation and storage and maximizing the useable space within the reservoir [99]. Further, the controlled oscillations in pressure levels via the pressure cycling technique help to stabilize the CO_2 front and prevent the segregation of less dense CO_2-rich streams within the storage formation [100]. In addition, temperature and pressure have a synergistic relationship during the formation of CO_2 hydrates. The pressure and temperature conditions can significantly influence this process's kinetics and the hydrates' subsequent stability [17]. CO_2 hydrates form more readily and are more stable at high pressures and low temperatures [17,98]. These conditions can also influence the hydrate formation rate and dissociation [98]. Therefore, pressure control is key in mitigating the risks associated with CO_2 hydrate dissociation [101,102], emphasizing the importance of integrating pressure management strategies into comprehensive risk assessment and mitigation frameworks for sub-seafloor CO_2 storage projects.

High-pressure reactor systems, including autoclaves, pressure vessels, and custom-designed high-pressure cells, play a vital role in simulating the conditions required for CO_2 hydrate formation. These systems are designed to withstand and control high pressures, typically ranging from hundreds to thousands of psi (pounds per square inch), allowing researchers to simulate the extreme pressure conditions encountered in deep-sea environments. Autoclaves, for example, are commonly used in laboratory settings to subject CO_2 and water mixtures to high pressures, enabling the investigation of CO_2 hydrate formation kinetics and thermodynamics [21]. Pressure vessels and custom-designed high-pressure cells are also employed to replicate specific pressure conditions and study the behavior of CO_2 hydrates under varying pressure regimes to optimize the process [103]. These high-pressure reactor systems are instrumental in advancing CO_2 hydrate formation and developing pressure management strategies for carbon capture and storage applications [98,103].

5.1. The role of pore pressure in CO_2 hydrate formation

Pore size distribution and particle surface area significantly influence the formation kinetics of CO_2 hydrates. The surface area of pores can impact gas consumption during hydrate formation by affecting the rate at which CO_2 molecules are adsorbed onto the hydrate-forming particles [104]. The growth kinetics of gas hydrates is proposed to be dependent on several factors including the chemical potential difference of water in hydrate versus aqueous phase neighboring porous particles [104]. Numerous research investigations have shed light on the crucial role of pore pressure variations in CO_2 hydrate formation and stability. These studies have revealed that changes in pore pressure can significantly influence the conditions under which CO_2 hydrates form and remain stable within porous media. The findings indicate that higher pore pressures generally promote the formation of CO_2 hydrates by providing the necessary thermodynamic conditions for their stabilization [105]. Conversely, lower pore pressures can destabilize and dissociate CO_2

hydrates, impacting their stability [52,105]. Moreover, higher pore pressures have been observed to accelerate the rate of CO_2 hydrate nucleation and growth, leading to more rapid formation within the porous medium [105]. Conversely, lower pore pressures may result in slower kinetics, affecting the overall efficiency of CO_2 hydrate formation processes [105,106]. These insights significantly affect the development of effective pressure management strategies to optimize CO_2 hydrate formation. Furthermore, studies have highlighted the impact of pore pressure variations on the morphology and distribution of CO_2 hydrates within porous media. Higher pore pressures have been associated with the formation of more extensive and interconnected CO_2 hydrate structures, which can influence the permeability and mechanical properties of the host medium [105,107]. On the other hand, lower pore pressures may lead to the formation of less interconnected and more dispersed CO_2 hydrate phases, affecting their overall distribution and stability [107]. Table 4 concisely presents the collective insights from diverse research efforts with different experimental conditions concerning how pore pressure variations can affect the formation and stability of CO_2 hydrates.

5.2. Innovations in pressure control methods

One key area of innovation lies in the development of adaptive pressure control algorithms such as model predictive control (MPC) and proportional-integral-derivative (PID) controllers, which have emerged as practical tools for continuous monitoring and adjustment of pressure conditions for CO_2 hydrate formation and stability in sub-seafloor saline sediments [111,112]. The adaptive nature of MPC algorithms incorporates real-time data and a receding horizon approach to control the system dynamically, fortifying the formation and maintenance of CO_2 hydrates. The robustness and adaptability of MPC, backed by its computational and predictive strength, make it particularly effective for managing the complex dynamics involved in the process of CO_2 hydrates within sub-seafloor saline sediments [113–115]. Conversely, PID controllers operate based on feedback mechanisms that compare a reference value with a measured variable to determine the necessary adjustments. Though tuning can be challenging, especially for non-linear or time-varying systems, PID controllers are widely utilized in industry due to their simplicity and reliability. They ensure stable operations through continuous modulation of the control variables [111,112,116]. Adaptive pressure control algorithms employ empirical formulas, phase equilibrium calculations, statistical thermodynamic models, and graphical methods to predict changes in temperature-pressure and other parameters critical to hydrate formation [45]. These predictive tools allow the control systems to adjust to environmental changes and maintain optimal CO_2 hydrate formation and stability conditions [45]. By leveraging advanced control strategies, adaptive pressure control algorithms can dynamically regulate the injection or extraction of fluids, maintaining optimal pressure levels critical for CO_2 hydrate formation and stability under the fluctuating conditions of the subsurface

Table 4

Comprehensive synthesis of pore pressure variability impacts on CO_2 hydrate formation and stability across multiple studies.

Research Focus	Experimental Conditions	Key Findings	Influence of Pore Pressure	Reference
Stability of CO_2 Hydrates	High-pressure reactor system	CO_2 hydrates formed in laboratory-scale high-pressure reactors mimicking oceanic sediment conditions were stable for at least a month.	Stable pore pressure maintains CO_2 hydrate stability.	[52]
Kinetics of Formation	Laboratory conditions with kinetic promoter	The water-to-hydrate conversion rate was enhanced. However, reduced the formation process time with the use of a green kinetic promoter.	Pore pressure variations can impact the rate of hydrate formation.	[107]
Hydrate Phase Equilibrium	Silica gel porous media	Porous media affects the phase equilibrium of hydrate formation due to competition water activity and large specific surface areas.	Pore pressure impacts the phase equilibrium and formation rate.	[108]
Hydrate Formation in Sub-Freezing Conditions	Porous media below the freezing point	CO_2 hydrate formation studied in porous media below freezing point revealed the stochastic nature of formation behaviors.	Variations in pore pressure alter formation behaviors significantly.	[109]
Impact of Liquefaction	Porous media with varying degrees of CO_2 liquefaction	CO_2 liquefaction promoted the hydrate formation process, and the amount was critical in affecting the process in porous media.	Pore pressure adjustment can enhance the effects of CO_2 liquefaction on hydrate formation.	[105]
Clay Suspensions Influence	Presence of clay suspensions in porous media.	NMR kinetics studies showed the presence of clay affects hydrate formation and dissociation in porous media.	Pore pressure changes alongside clay content can impact the kinetics of hydrate formation and dissociation.	[110]

environment [98,117]. Table 5 captures a concise research overview of adaptive pressure control algorithms to improve the kinetics and stability of CO_2 hydrates.

Moreover, using hydraulic fracturing or depressurization techniques represents another innovative approach to pressure control in sub-seafloor saline sediments. These techniques depart from traditional static pressure management, introducing dynamic interventions influencing CO_2 hydrate behavior. Hydraulic fracturing, for instance, involves the injection of high-pressure fluids to create fractures in the sediment, facilitating the release and transport of CO_2 [120,121]. This fracturing process needs to be well understood as it can significantly increase fracture pressure and influence crack propagation patterns, where the presence of hydrates and ice crystals in sediments can alter the dynamics [120–122]. On the other hand, depressurization techniques focus on controlled pressure reduction to induce phase transitions and optimize hydrate dissociation [123–125]. The key is to implement these strategies cautiously, as the interaction between the fractures and the propagation of pressure waves plays a vital role in managing CO_2 hydrate stability [125]. Both hydraulic fracturing and depressurization, individually or combined, have shown promise in improving gas production efficiency from marine hydrate reservoirs [126]. The intricate behavior of CO_2 hydrates under these dynamic pressure management techniques suggests a need for careful calibration and understanding environmental conditions to achieve optimal stability and production [127]. The findings from various research investigations, as described in Table 6, underline the complexity of using hydraulic fracturing or depressurization techniques in pressure control for CO_2 hydrate formation and stability. Each technique has specific implications for how CO_2 hydrates behave and remain stable under different conditions. Implementing CO_2 in fracturing not only aids in

optimizing hydrate management but also presents an opportunity for eco-friendly exploitative methods in unconventional reservoirs. It offers a dual benefit of enhancing gas recovery while contributing to CO_2 sequestration efforts [128]. The advancements in these innovative pressure control methods underline a significant shift toward more responsive and effective CO_2 hydrate management strategies in marine settings [129].

6. Integrated approaches for enhanced CO_2 hydrate formation

Integrating various methodologies for optimizing CO_2 hydrate formation is essential for advancing carbon capture and storage (CCS) technologies. This section delves into the synergistic effects of combined thermal and pressure management and innovative strategies that enhance the stability and efficiency of CO_2 hydrates. By understanding the interplay between temperature, pressure, and the use of additives, researchers can develop more effective approaches to facilitate the formation and long-term stability of CO_2 hydrates in sub-seafloor environments.

6.1. Synergistic effects of combined thermal and pressure management

Controlled manipulation of temperature parameters is integral in the formation of CO_2 hydrates. It has been demonstrated that by thermodynamic promotion, CO_2 molecules can efficiently occupy the hydrate cages under moderate temperature conditions [135,136]. Proper temperature settings aid in surpassing phase equilibrium constraints, potentially resulting in the solidification of CO_2 within water molecular frameworks [136]. Studies have observed phenomena such as supercooling, thermal hysteresis, and hydrate reformation pertinent to the

Table 5

Summary of research on adaptive pressure control algorithms for optimizing CO_2 hydrate formation and stability.

Study Focus	Adaptive Control Algorithm Details	Investigated Conditions	Key Findings	Potential Impact on CO_2 Hydrate Stability	References
CO_2 Hydrate Formation Kinetics.	Implementation of advanced algorithms in lab-scale reactors.	High-pressure conditions	Improved conversion efficiency and reduced formation process time.	Enhanced CO_2 hydrate formation and stability	[107]
Hydrate-Stability Modeling.	Framework development for pressure predictions.	Varied thermodynamic states.	Accurate prediction of hydrate stability under varying conditions.	More predictable CO_2 hydrate formation and preservation.	[118]
Replacement Kinetics.	Control of CO_2 replacement in CH_4 hydrate environments.	High-pressure, low temperature environment.	Insights on structure and morphology changes during replacement.	Optimized CO_2 injection strategies for stability.	[119]
CO_2 Hydrate Morphology.	Control algorithms to manage formation and dissociation kinetics.	Elevated pressure and low temperature conditions.	Enhanced hydrate formation and blockage prevention.	Improved safety and efficiency in transport pipelines.	[103,107]

Table 6

Overview of hydraulic fracturing and depressurization techniques as pressure control methods in CO_2 hydrate formation and stability: implications and interactions.

Research Focus	Key Findings	Technique Employed	Implications for CO_2 Hydrate Stability	Reference
Fracture Propagation.	Hydraulic fractures tend to propagate along interfaces in sediment matrix and massive hydrate. The fracturing pressure can significantly increase if hydrates or ice crystals are present.	Hydraulic fracturing with discrete fracture models.	Suggests a nuanced approach to fracturing in varied sediment and hydrate structures could enhance stability.	[120,130]
Pressure Wave Propagation.	Resonance in pressure wave propagation can influence bottom-hole pressure, thus affecting CO_2 hydrate stability.	Advanced hydraulic fracturing techniques to analyze pressure propagation.	Indicates that pressure monitoring is crucial for maintaining stability during hydraulic fracturing.	[131]
Depressurization Methods.	Depressurization assists in CO_2-CH_4 replacement in hydrate structures, affecting hydrate stability. CO_2 injection is considered efficient for potential storage and stability.	Depressurization-assisted development and gas extraction methods.	Shows depressurization as a viable strategy for managing pressure and enhancing the stability of CO_2 hydrate.	[123,132,133]
CO_2 Fracturing Technology.	The phase change in CO_2 fracturing introduces technical feasibility for reducing CO_2 emissions and has broad application prospects in unconventional reservoirs.	CO_2 fracturing to create fractures, phase-field simulation to understand fracturing dynamics.	Demonstrates the potential of CO_2 fracturing as a method for sustainable pressure control and hydrate stability.	[128,134]

thermodynamics of CO_2 hydrates and their kinetics in cold thermal energy applications [20,136]. In complement to temperature, pressure is a crucial factor influencing the formation and stability of CO_2 hydrates. Elevated pore pressures have been linked to the acceleration of the nucleation and growth rate of CO_2 hydrates, indicating optimized formation within porous media when combined with low temperatures [137,138]. Such conditions can lead to extensive and interconnected hydrate structures, affecting the host medium's stability, permeability, and mechanical properties [24,138].

The synergistic interactive effects of temperature and pressure management have been fundamental in the evolution of CO_2 hydrate studies, as described in Table 7. Fig. 16 outlined the CO_2 hydrate kinetic and thermodynamic evaluations under the synergic effect of pressure and temperature alongside the promoters' role in altering CO_2 hydrate's kinetic properties and thermodynamic stability under synergic varying pressure and temperature conditions from different study investigations [7,13,139–146]. The additives facilitating CO_2 hydrate formation could fall into three categories: single, mixed, and gas additives, each offering tailored applications within specific temperature and pressure ranges, as described in Fig. 16. The extent of equilibrium shift varies based on additive composition. Notably, adding additives to the system shifts the equilibrium curve toward higher temperatures and lower pressures, facilitating the formation and stability of CO_2 hydrate. As shown in Fig. 16, low pressure below 2 MPa with high temperatures of 280 to 293 K is optimal for CO_2 hydrate formation, ensuring CO_2 hydrate stability and long-term storage potential. Therefore, simultaneously optimizing temperature and pressure parameters alongside additives presents a promising strategy for enhancing CO_2 hydrate formation and stability. By fine-tuning these variables, researchers can identify optimal conditions across various operational scenarios, broadening the applicability of CO_2 hydrate technology. The categorization of additives allows for
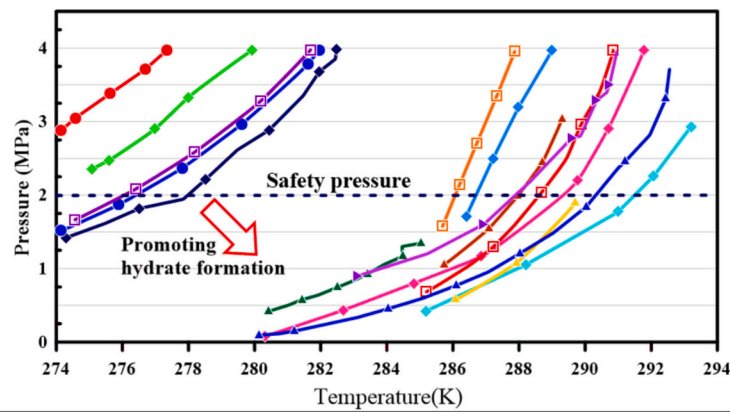
tailored solutions, while the observed equilibrium shift toward higher temperatures and lower pressures with additive inclusion highlights the potential to overcome thermodynamic barriers. Overall, this approach offers opportunities for improved carbon capture and storage technologies with enhanced efficiency and adaptability. In addition, the study by Zhou et al. [147] reported multiscale analyses that provide insight into the kinetic performance of CO_2 molecules during hydrate growth, emphasizing the importance of optimizing both parameters simultaneously for enhanced CO_2 capture. Recent advanced research investigations suggest effective CO_2 hydrate formation requires meticulous coordination between temperature and pressure controls [101,148]. This can be engineered through real-time monitoring systems and adaptive control algorithms that incorporate empirical formulas, phase equilibrium calculations, and graphical methods, which are instrumental in predicting and adjusting the parameters for hydrate formation [9,101,148].

6.1.1. Computational models predicting optimal conditions for CO_2 hydrate formation

The synergistic effects of combined thermal and pressure management are critical for optimizing the formation of CO_2 hydrates—a technology with implications for carbon capture, storage, and energy transportation. Through various computational models and experimental investigations, researchers have honed in on the synergistic effects of these variables to optimize conditions for CO_2 hydrate formation. Table 8 presents recent research findings from various computational models that predicted the optimal conditions for CO_2 hydrate formation. These models are instrumental in forecasting the behavior of this complex system under varying environmental parameters and have profound utility in scientific inquiry and applied engineering. They serve as a virtual testing ground for hypotheses, enabling

Table 7

Summary of different research investigation findings on synergistic effects of combined thermal and pressure management for optimizing CO_2 hydrate formation.

Research Investigation	Thermal Management Approach	Pressure Management Approach	Synergistic Effects	Implications for CO_2 Hydrate Formation	Reference
Monoethylene Glycol and Glycine Mixture.	Utilization of thermodynamic inhibitors to adjust low temperatures.	Controlled pressure ranges from 2.0 to 4.0 MPa.	Higher inhibition effect at 15 wt% mixture, with the synergistic impact more significant at 10 wt%.	Enhanced CO_2 hydrate phase boundary prevention compared to individual components.	[149]
High-Pressure Liquid CO_2.	CO_2 is compressed to mimic natural geological conditions.	CO_2 storage in deep oceanic sediments under high-pressure environments.	Saline water may impair hydrate formation or dissociation kinetics.	Potentially offers a method for CO_2 sequestration but with considerations for saline environments.	[98]
CO_2 Hydrate Thermodynamics	Investigation of phase equilibrium, supercooling, and thermal hysteresis.	Focus on the effects of pressure changes on CO_2 hydrate formation.	Improved understanding of CO_2 hydrate behavior under varied thermodynamic conditions.	Insights into how to optimize conditions for hydrate formation for cold energy applications	[135]
Mixed Gas Hydrate Formation.	Thermal management to address gas composition.	Addressing pressure behaviors in multiphase pipelines with high CO_2 content.	Synergistic effects were noted in the stabilization of mixed gas hydrates.	Application in optimizing pipeline management to prevent hydrate formation blockages.	[150]

Fig. 16. Synergistic effects of temperature and pressure alongside different additives on CO_2 hydrate formation and stability: Illustration of equilibrium shift with parameters variation [148].

Table 8
Based on recent research findings, comparative analysis of computational models for optimizing CO_2 hydrate formation conditions.

Model Type	Conditions Studied	Promoters/Inhibitors	Key Findings	Reference
Molecular Dynamics (MD) Simulation.	Different systems and initial conditions.	Metal particles (Cu, Fe, Ag) and varying mass fractions	Adding metal particles can influence the growth kinetics of CO_2 hydrate systems. Optimal mass fractions range from 0.2 wt% to 1.3 wt% for enhanced growth.	[77]
Chemical Affinity Model.	Inhibitory compound systems.	Glucose and attapulgite	An optimal system of 15 mg/ml glucose and 1.00 mg/ml attapulgite was found, extending the induction time by ~122 % and reducing gas consumption by 23.72 %.	[151]
Artificial Neural Networks (ANN).	Multiphase systems, including crude oil.	Not specified	ANN models were developed to predict hydrate formation rate in pure and multiphase systems, achieving high accuracy with R^2 values close to 1.	[152]
Integrated Model for Sub-seabed CO_2 Storage.	Sand sediment morphologies.	Not specified	This model classifies hydrate formation in three locations within sand sediment, assisting the design of sub-seabed CO_2 storage systems.	[137]
Experimental Observations and Growth Models.	Various conditions of hydrate formation.	Green kinetic promoter	Experimental results indicated promoters could significantly enhance water to hydrate conversion, indicating a path to efficient formation processes.	[107]

researchers and engineers to identify the most efficient pathways to enhance CO_2 hydrate formation rates and stability. The table encapsulates the essence of this sophisticated work, offering a comprehensive look at the parameters involved, the interactions considered, and the outcomes predicted by these advanced computational tools.

6.2. Optimizing conditions for maximum CO_2 hydrate stability

The stabilization of CO_2 hydrates is a critical area of research with significant implications for CO_2 sequestration, gas storage, and energy applications. Enhancing CO_2 hydrate formation and stability can offer a viable carbon capture and storage strategy and provide potential

solutions for energy challenges such as cold storage and natural gas transport. Researchers and engineers are developing various innovative methods to optimize the conditions for maximum CO_2 hydrate stability in this context. Two noteworthy advancements are hybrid methodologies that combine thermal and pressure management and multi-stage approaches that boost CO_2 hydrate formation efficiency. Table 9 provides a comparative analysis of the relevance and efficiency of these two techniques from various research investigations.

6.2.1. Hybrid methodologies merging thermal and pressure management

Hybrid methods that strategically merge thermal and pressure management play an essential role in enhancing CO_2 hydrate formation

Table 9

Comparative analysis of CO_2 hydrate formation techniques: Hybrid methodologies and multi-stage approaches.

Research Investigation	Hybrid Methodology (Thermal and Pressure)	Multi-Stage Approach	Key Findings	Relevance and Efficiency	Reference
Formation Kinetics and Observations.	No	Yes (Stages 1, 2, 3)	Three distinct stages of hydrate formation were identified; adding tryptophan as a kinetic promoter affects formation rates.	Progressive stages led to effectively effective CO_2 hydrate formation.	[107]
Gas Hydrate-Based CO_2 Capture.	Yes	No	State-of-the-art developments in hydrate-based reactors suggest advancements in both thermal and pressure management.	Integration of such hybrid systems can lead to more stable CO_2 hydrate structures.	[159]
ANN Modeling on CO2 Hydrate Kinetics.	Yes	No	Use of ANN models to predict hydrate formation in pure and multiphase systems. Outlines the importance of temperature and pressure control in kinetics.	Indicates that a combined thermal-pressure management strategy can be beneficial for predicting and enhancing hydrate formation.	[152]
Phase Equilibrium Conditions.	Yes (Pressure Range 1.38–3.95 MPa)	Yes (Temperature Control)	Conditions required for phase equilibrium provided insights into the necessary temperature and pressure for stable hydrate formation.	Demonstrates the importance of meticulously controlled thermobaric conditions for hydrate stability.	[101]
Multi-layered Sediments Kinetics.	No	Yes (Layered Conversion Efficacy)	The conversion rate in sediments depends on layer structure, potentially requiring staged or stepped methodologies for optimization.	A multi-stage approach considering sediment layering could enhance overall CO_2 hydrate formation efficiency.	[160]
CO_2 Hydrate Morphology and Stability.	Yes (Strategies for Stability)	No	Explores challenges in hydrate stability and suggests integrating methods to improve CO_2 hydrate formation kinetics and understanding of stability dynamics.	Hybrid methodologies are implied to overcome the challenges of slow formation rates and uncertain stability in CO_2 hydrates.	[21]
Hydrate Nuclei Activity.	Yes	No	Suggests small molecules like CO_2 are more active in hydrate nuclei formation, implying that pressure changes could enhance activity.	This supports hybrid methodologies where pressure management is crucial for stable hydrate formation.	[147]
Dendrite Growth Rate.	Yes (Temperature Control)	No	Growth rate studies show that controlling temperature can lead to three orders of magnitude higher growth rates for CO_2 hydrates.	Reinforces that thermal management is a crucial aspect of hybrid methodologies for enhanced hydrate formation.	[161]
Synthesis and Dissociation Behavior.	Yes	No	Developing reliable and efficient CO_2 hydrate synthesis methods and investigating the material's properties and behavior.	Focuses on understanding how thermal dynamics and pressure conditions affect CO_2 hydrate synthesis and dissociation, pointing toward hybrid methodology benefits.	[162]

and ensuring the stability of the hydrates. A hybrid thermal management system employs heat transfer methods to maintain the ideal temperature conditions conducive to hydrate formation [153]. For instance, a well-designed system might incorporate varied techniques, ranging from liquid cooling, which is highly efficient in removing excess heat due to its higher heat capacity, to air cooling, which is more straightforward and cost-effective for specific scenarios. Additionally, phase change materials (PCMs) are integrated due to their capacity to absorb and release substantial energy during the phase change, helping to stabilize the operating temperature within the system [154]. Such systems can be customized to manage the temperature conditions precisely, ensuring they remain within the target range that promotes the stable growth of CO_2 hydrates. The synergy between these thermal management techniques, such as composite PCMs incorporating materials like materials like expanded graphite, enhances their performance within the thermal management system [154]. The performance can be further optimized by employing pressure oscillation techniques that can improve mass transfer rates and alleviate the limitations that obstruct the diffusion of CO_2 molecules into the water, contributing to more efficient and robust CO_2 hydrate formation. This dual-faceted approach of meticulous thermal and pressure regulation optimizes the environment for CO_2 hydrate formation, achieving maximum stability for the hydrates. Studies have further shown that water-based nanofluid particles can enhance the number of hydrate nucleation sites and promote heterogeneous nucleation [28,155]. This increases the rate of hydrate nucleation and shortens the induction time for hydrate formation [155]. Furthermore, the addition of kinetic accelerators or promoters, as mentioned in various studies, has proven beneficial in improving the efficiency of hydrate formation by optimizing the crystallization process [45,107,112].

6.2.2. Multi-stage approaches for enhanced formation efficiency

Multi-stage approaches aim to improve the efficiency of CO_2 hydrate formation by sequentially applying different techniques to promote nucleation and growth stages of hydrate formation. The first stage might involve rapidly mixing CO_2 with water under high-pressure conditions to instigate the nucleation process. Subsequently, a second stage can employ pressure or thermal cycling or the introduction of kinetic or thermodynamic promoters to encourage the hydrates to grow on a larger scale and at a faster rate [20,42,45,107,156]. By carefully managing these stages, achieving more rapid CO_2 absorption and reducing the system's overall energy consumption is possible, making the hydrate formation process more efficient and sustainable. Such staged methodologies can adapt to the dynamic processes and inherent random nucleation nature of hydrate formation, leading to a more controlled and effective CO_2 capture process [45,147,157,158].

7. Challenges, research gaps, future perspective and innovation

7.1. Challenges in optimizing CO_2 hydrate formation and stability

In carbon capture and storage (CCS), optimizing CO_2 hydrate formation and stability in sub-seafloor saline sediments through effective thermal and pressure management poses several challenges, including kinetic barriers and additive selection, sediment heterogeneity, permeability reduction, and impact of temperature and pressure variations. These challenges are critical to address to ensure the reliability and efficiency of CO_2 sequestration in marine environments. Addressing these challenges requires a multi-disciplinary approach, which includes a thorough understanding of sedimentology, fluid mechanics, thermodynamics, and environmental science. Continuous research and technological advancements are necessary to overcome these obstacles and develop efficient CO_2 hydrate formation and storage methods in sub-

seafloor saline sediments. This study outlines some of these critical challenges as follows:

One of the profound challenges is the sluggish kinetics of CO_2 hydrate formation in saline subsea environments. The slow formation rate can be a significant barrier to establishing CO_2 hydrates as a practical means of CO_2 storage. Furthermore, while various kinetic promoters can enhance the hydrate formation rate, many of these additives are not eco-friendly, raising environmental concerns [25].

Electrical heating systems enhance CO_2 hydrate formation and stability by controlling heating, accelerating kinetics, and optimizing stability conditions. However, the technical complexity of delivering and distributing heat within sediments poses a significant challenge, where uneven heating may cause heterogeneous hydrate formation, posing stability risks. Ensuring uniform heating is vital for consistent CO_2 hydrate formation, demanding advanced control systems and engineering solutions to monitor and manage temperature precisely. Furthermore, differences in thermal conductivity between CO_2 hydrate and other sediment components, like methane hydrate or saline pore water, add complexity to this task. Also, the high energy demand and cost-effectiveness of electrical heating systems are significant challenges, especially in remote overseas locations. This energy consumption can compromise the environmental benefits of CO_2 sequestration if derived from non-renewable sources. Effective thermal management is essential to enhance efficiency and minimize energy wastage during heating.

The characteristics of the porous medium, such as porosity, capillary pressure, permeability, water saturation, surface area, bed height, and particle size, are crucial in determining the thermodynamics and kinetics of CO_2 hydrate formation. These parameters, which vary widely in natural sediments, dictate the extent to which CO_2 hydrates can form and remain stable, making it challenging to design a universally applicable optimization strategy [106]. Moreover, the potential for CO_2 hydrate saturation to occupy the pore space of sand sediments results in significant permeability reductions [137]. This can cause blockage of gas flow, complicating the storage process and requiring careful management to prevent undesirable outcomes.

Thermal and pressure management are central to stabilizing CO_2 hydrates, with temperature significantly influencing hydrate stability. Properly maintaining conditions within the hydrate stability zone is essential. Overly high or low temperatures can detrimentally affect the formation kinetics and stability of CO_2 hydrates. Additionally, while pressure has comparably less impact, it must be carefully managed, especially considering the potential for hydrate dissociation during changes in seabed geothermal or geobaric conditions.

7.2. Research gaps, future perspective, and innovation

Studies have evidenced challenges regarding the slow kinetics of CO_2 hydrate formation and the subsequent efficiency of the process under sub-seafloor conditions [21]. Further research should focus on elucidating the underlying mechanisms governing CO_2 hydrate formation kinetics under sub-seafloor conditions, particularly in saline sediments. This entails investigating factors such as the influence of mineral composition, pore structure, and fluid properties on hydrate nucleation and growth rates. Additionally, exploring novel techniques for accelerating hydrate formation, such as developing tailored additives or applying external stimuli, could enhance the efficiency of CO_2 capture and storage processes in marine environments.

Two significant research gaps emerge when optimizing CO_2 hydrate formation and stability using electrical heating systems. First, there is a lack of comprehensive understanding of the electrical properties of CO_2 hydrates and how these properties change under varying sub-seafloor conditions. The available data on the electrical conductivity of CO_2 hydrate suggests that it is higher than methane hydrate at geologically relevant temperatures [71]. However, how this affects the formation and stability when using electrical heating systems needs further examination. Elucidating these properties could improve monitoring and

management strategies for CO_2 in gas hydrate stability zones. Secondly, while electrical heating may provide a targeted and controlled means to manage the thermal environment for CO_2 hydrate formation, substantial knowledge exists concerning such systems' long-term sustainability and efficiency. It is crucial to analyze the energy consumption versus the stability and capacity of the formed hydrates, considering the environmental impact and economic viability. The induction time, stochastic nucleation, and memory effect are aspects of CO_2 hydrate formation kinetics that are dominant in this context. Research is required to optimize these systems, ensuring maximal energy efficiency while maintaining the stability of CO_2 hydrates.

Moreover, there is a notable lack of comprehensive understanding concerning the stability dynamics of CO_2 hydrates in sub-seafloor environments. Experimental work has often been limited to short-term evaluations, and more prolonged observations are required to fully grasp the longevity and resilience of the CO_2 hydrate stability over extended periods.

The impact of varying sediment compositions, especially the role of clay and organic content in the sediments, has not been extensively studied. Organic matters present due to marine environments potentially impact the kinetics of hydrate formation, [163,164], though this effect needs to be researched in more depth.

In addition to improving the management of CO_2 hydrate formation in sand sediments, the current models for predicting CO_2 hydrate formation and morphology within sand sediments require further refinement and validation for several reasons. Firstly, sand sediments exhibit complex heterogeneity in grain size distribution, pore geometry, and mineral composition, which can significantly influence CO_2 hydrate formation kinetics and morphology. Therefore, models need to account better for these heterogeneous conditions to predict CO_2 hydrate behavior accurately. Secondly, experimental validation of these models is essential to ensure their reliability across various environmental conditions. CO_2 hydrate formation is influenced by temperature, pressure, salinity, and gas composition, which necessitates validation under varied scenarios to enhance model robustness. Accurate modeling of CO_2 hydrate structures is crucial for optimizing formation and management strategies, as it identifies optimal conditions for CO_2 hydrate stability and storage capacity within sand sediments.

8. Conclusion

This work presents a detailed thermal and pressure management review on enhancing CO_2 hydrate formation and stability in marine saline sediments. The precise interaction of thermal and pressure management influences was observed to improve hydrate formation kinetics and stability, reduce nucleation times, enhance hydrate growth rates, increase water-to-hydrate conversion rate, and boost CO_2 storage capacity. The following conclusions were made from this study:

1. Marine sediment salinity variations, particularly NaCl, significantly impact CO_2 hydrate formation and stability, with higher salinity levels impeding formation, suggesting that low-salinity areas are better for CO_2 formation and storage. Managing this involves precise thermal and pressure controls to counter salt ions' destabilizing effect. Maintaining conditions matching the CO_2 hydrate stability window, typically at deep ocean exceeding 800 m depth with low temperatures and high pressures, ensures secure stability and storage. Adding kinetic promoters and surfactants can boost formation, indicating chemical interventions can optimize CO_2 hydrate storage.

2. The electrical heating systems boost CO_2 hydrate formation and stability by regulating heating, accelerating kinetics, and optimizing stability conditions. Their ability to provide precise thermal management, coupled with their excellent efficiency and sustainability credentials, positions them as a key technology in the advancement of carbon capture and sequestration methods necessary for achieving

net-zero carbon emissions and adhering to international climate goals.

3. Overly high or low temperatures can detrimentally affect the formation kinetics and stability of CO_2 hydrates. Molecular dynamics simulation studies indicate that the linear growth rate of new hydrate cages decreases sharply as the temperature drops, highlighting the importance of maintaining specific thermal conditions to promote the formation of CO_2 hydrates. While studies indicate pressure has a comparatively minimal effect on CO_2 hydrate formation as temperature, other studies show that varying pressures, temperatures, and flow rates still contribute to the growth period of hydrate formation, with higher pressures generally favoring the stability of CO_2 hydrates, suggesting that high pressure primarily enhance the formation of hydrate nuclei rather than individual crystal growth, highlighting the system's complexity.

4. Sediment heterogeneity can impede CO_2 migration, providing numerous nucleation sites for a more stable hydrate formation. In contrast, the sediment's chemical composition directly affects phase equilibrium and hydrate morphology, which are decisive for the formation and stability of CO_2 hydrates. Thermal conductivity variation within gas-saturated sediments exposed to changing hydrate formation conditions can signal the degree of heterogeneity, implying a need for strategic thermal management to optimize conditions conducive to hydrate stability. By implementing a holistic approach that considers sedimentary characteristics and applied thermal and pressure management, significant improvements can be realized in the sustainable formation and stability of CO_2 hydrates as potential carbon storage solutions.

5. The synergistic effects of thermal and pressure modifications, as evidenced by enhanced kinetic and thermodynamic performance when using combined promoters and adjusted environmental parameters, significantly boost the water-to-hydrate conversion rate and hydrate formation kinetics. Additionally, tailored thermal management, such as introducing temperature oscillations during gas exchange processes, has facilitated optimized CO_2 replacement in hydrate formations. The entwined pressure and thermal input modality is a promising frontier for the field's evolution. Furthermore, integrating multi-stage and hybrid methodologies, including kinetic promoters, offers additional leverage to maximize formation rates and gas storage capacities.

6. Applying thermal and pressure manipulation strategies for optimizing CO_2 hydrate formation faces challenges like kinetic barriers (sluggish kinetics), additive selection, sediment heterogeneity, and energy consumption. Addressing these challenges requires further research on underlying intermolecular mechanisms of CO_2 hydrate coupled with sedimentology interaction, fluid mechanics, thermodynamics, additive assessments, and refining the current predictive models. Despite promising laboratory and simulation findings, hurdles such as high project costs and a lack of broad field trials impede real-world applications of techniques like electrical heating systems.

CRediT authorship contribution statement

Erasto E. Kasala: Writing – original draft, Formal analysis, Data curation, Conceptualization. **Jinjie Wang:** Writing – review & editing, Supervision, Formal analysis. **Wakeel Hussain:** Writing – review & editing, Visualization, Investigation. **Asia Majid:** Validation, Visualization, Investigation. **Edwin E. Nyakilla:** Investigation, Validation.

Declaration of competing interest

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

Data availability

The data that has been used is confidential.

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References

[1] Pandey G, Poothia T, Kumar A. Hydrate based carbon capture and sequestration (HBCCS): an innovative approach towards decarbonization. Appl Energy 2022; 326:119900.

[2] Zheng J, Chong ZR, Qureshi MF, Linga P. Carbon dioxide sequestration via gas hydrates: a potential pathway toward decarbonization. Energy Fuel 2020;34: 10529–46.

[3] Nagashima HD, Miyagi T, Yasuda K, Ohmura R. Clathrate hydrates at temperatures below the freezing point of water: a review. Fluid Phase Equilib 2020;517:112610.

[4] Kumar Y, Sangwai JS. Environmentally sustainable large-scale CO_2 sequestration through hydrates in offshore basins: ab initio comprehensive analysis of subsea parameters and economic perspective. Energy Fuel 2023;37(13):8739–64.

[5] Luo J, Xie Y, Hou MZ, Xiong Y, Wu X, Lüddeke CT, et al. Advances in subsea carbon dioxide utilization and storage. Energy Reviews 2023;2:100016.

[6] Castellani B. Potential pathway for reliable Long-term CO2 storage as clathrate hydrates in marine environments. Energies 2023;16:2856.

[7] Wang X, Zhang F, Lipiński W. Research progress and challenges in hydrate-based carbon dioxide capture applications. Appl Energy 2020;269:114928.

[8] Hassanpouryouzband A, Joonaki E, Vasheghani Farahani M, Takeya S, Ruppel C, Yang J, et al. Gas hydrates in sustainable chemistry. Chem Soc Rev 2020;49: 5225–309.

[9] Lee Y, Kim H, Lee W, Kang DW, Lee JW, Ahn Y-H. Thermodynamic and kinetic properties of CO2 hydrates and their applications in CO2 capture and separation. J Environ Chem Eng 2023;11:110933.

[10] Sinehbaghizadeh S, Saptoro A, Mohammadi AH. CO2 hydrate properties and applications: a state of the art. Prog Energy Combust Sci 2022;93:101026.

[11] Liu J, Fu R, Lin Y, Shi Q, Liu Y, Li T, et al. Mechanical destabilization and cage transformations in water vacancy-contained CO2 hydrates. ACS Sustain Chem Eng 2022;10:10339–50.

[12] He Z, Mi F, Ning F. Molecular insights into CO2 hydrate formation in the presence of hydrophilic and hydrophobic solid surfaces. Energy 2021;234:121260.

[13] Bavoh CB, Lal B, Osei H, Sabil KM, Mukhtar H. A review on the role of amino acids in gas hydrate inhibition, CO2 capture and sequestration, and natural gas storage. J Nat Gas Sci Eng 2019;64:52–71.

[14] Zhang X, Yang H, Huang T, Li J, Li P, Wu Q, et al. Research progress of molecular dynamics simulation on the formation-decomposition mechanism and stability of CO2 hydrate in porous media: a review. Renew Sust Energ Rev 2022;167:112820.

[15] Mwakipunda GC, Abelly EN, Mgimba MM, Ngata MR, Nyakilla EE, Yu L. Critical review on carbon dioxide sequestration potentiality in methane hydrate reservoirs via CO2–CH4 exchange: experiments, simulations, and pilot test applications. Energy Fuel 2023;37:10843–68.

[16] Thoutam P, Rezaei Gomari S, Chapoy A, Ahmad F, Islam M. Study on CO2 hydrate formation kinetics in saline water in the presence of low concentrations of CH4. ACS omega 2019;4:18210–8.

[17] Liu F-P, Li A-R, Qing S-L, Luo Z-D, Ma Y-L. Formation kinetics, mechanism of CO2 hydrate and its applications. Renew Sust Energ Rev 2022;159:112221.

[18] Rehman AN, Pendyala R, Lal B. Effect of brine on the kinetics of carbon dioxide hydrate formation and dissociation in porous media. Materials Today: Proceedings 2021;47:1366–70.

[19] Cao X, Wang H, Yang K, Wu S, Chen Q, Bian J. Hydrate-based CO2 sequestration technology: feasibilities, mechanisms, influencing factors, and applications. J Pet Sci Eng 2022;219:111121.

[20] Liu C, Zhou X, Liang D. Molecular insight into carbon dioxide hydrate formation from saline solution. RSC Adv 2021;11:31583–9.

[21] Dhamu V, Qureshi MF, Barckholtz TA, Mhadeshwar AB, Linga P. Evaluating liquid CO2 hydrate formation kinetics, morphology, and stability in oceanic sediments on a lab scale using top injection. Chem Eng J 2023;478:147200.

[22] Wang P, Teng Y, Zhao Y, Zhu J. Experimental studies on gas hydrate-based CO2 storage: state-of-the-art and future research directions. Energ Technol 2021;9: 2100004.

[23] Zadeh AH, Kim I, Kim S. Characteristics of formation and dissociation of CO2 hydrates at different CO2-water ratios in a bulk condition. J Pet Sci Eng 2021; 196:108027.

[24] Yang M, Song Y, Jiang L, Zhu N, Liu Y, Zhao Y, et al. CO2 hydrate formation and dissociation in cooled porous media: a potential technology for CO2 capture and storage. Environ Sci Technol 2013;47:9739–46.

[25] Gautam R, Kumar S, Kumar A. Intensified carbon dioxide hydrate formation kinetics in a simulated subsea sediment: application in carbon capture and sequestration. Energy Fuel 2022;36:9194–202.

[26] Husebø J, Ersland G, Graue A, Kvamme B. Effects of salinity on hydrate stability and implications for storage of CO2 in natural gas hydrate reservoirs. Energy Procedia 2009;1:3731–8.

[27] Zarghami S, Boukadi F, Al-Wahaibi Y. Diffusion of carbon dioxide in formation water as a result of CO 2 enhanced oil recovery and CO 2 sequestration. J Pet Explor Prod Technol 2017;7:161–8.

[28] Pahlavanzadeh H, Khanlarkhani M, Rezaei S, Mohammadi AH. Experimental and modelling studies on the effects of nanofluids (SiO2, Al2O3, and CuO) and surfactants (SDS and CTAB) on CH4 and CO2 clathrate hydrates formation. Fuel 2019;253:1392–405.

[29] Zhao J, Liu Y, Yang L, Zhang L, Song Y. Organics-coated nanoclays further promote hydrate formation kinetics. The Journal of Physical Chemistry Letters 2021;12:3464–7.

[30] Zhao Y, Zeng F, Zhao D, Lin L, Zhang Z. Molecular study on carbon dioxide hydrate formation in salty water. Cryst Growth Des 2023;23:8361–9.

[31] Kumar A, Palodkar AV, Gautam R, Choudhary N, Veluswamy HP, Kumar S. Role of salinity in clathrate hydrate based processes. J Nat Gas Sci Eng 2022;108: 104811.

[32] Omrani S, Ghasemi M, Mahmoodpour S, Shafiei A, Rostami B. Insights from molecular dynamics on CO2 diffusion coefficient in saline water over a wide range of temperatures, pressures, and salinity: CO2 geological storage implications. J Mol Liq 2022;345:117868.

[33] Li Y, Han S, Zhang B, Tang H, Han J, Kang H, et al. Nucleation and dissociation of carbon dioxide hydrate in the inter-and intra-particle pores of dioctahedral smectite: mechanistic insights from molecular dynamics simulations. Appl Clay Sci 2022;216:106344.

[34] Lichtschlag A, Haeckel M, Olierook D, Peel K, Flohr A, Pearce CR, et al. Impact of CO2 leakage from sub-seabed carbon dioxide storage on sediment and porewater geochemistry. International Journal of Greenhouse Gas Control 2021;109: 103352.

[35] Song Y, Wang S, Cheng Z, Huang M, Zhang Y, Zheng J, et al. Dependence of the hydrate-based CO2 storage process on the hydrate reservoir environment in high-efficiency storage methods. Chem Eng J 2021;415:128937.

[36] Kou X, Li X-S, Wang Y, Liu J-W, Chen Z-Y. Heterogeneity of hydrate-bearing sediments: definition and effects on fluid flow properties. Energy 2021;229: 120736.

[37] Ndlovu P, Babaee S, Naidoo P. Review on CH4-CO2 replacement for CO2 sequestration and CH4/CO2 hydrate formation in porous media. Fuel 2022;320: 123795.

[38] Mok J, Choi W, Kim S, Lee J, Seo Y. NaCl-induced enhancement of thermodynamic and kinetic CO2 selectivity in CO2+ N2 hydrate formation and its significance for CO2 sequestration. Chem Eng J 2023;451:138633.

[39] Gurjar P, Dubey S, Kumar S, Palodkar AV, Kumar A. Carbon dioxide sequestration as hydrates in clayey-sandy sediments: experiments and modeling approach. Chem Eng J 2023;475:146455.

[40] Sahu C, Sircar A, Sangwai JS, Kumar R. Effect of sodium tripolyphosphate (STPP) and tetrasodium pyrophosphate (TSPP) on the formation kinetics of CO2 hydrate in bulk and porous media in the presence of pure water and seawater relevant for CO2 sequestration. International Journal of Greenhouse Gas Control 2022;114: 103564.

[41] Wei Y, Maeda N. Kinetic promotion of gas hydrate formations using dispersions. Chem Eng Sci 2023;286:119673.

[42] Liu N, Huang J, Meng F, Yang L. Experimental study on the mechanism of enhanced CO2 hydrate generation by thermodynamic promoters. ACS Sustain Chem Eng 2023;11:5367–75.

[43] He Y, Sun M-T, Chen C, Zhang G-D, Chao K, Lin Y, et al. Surfactant-based promotion to gas hydrate formation for energy storage. J Mater Chem A 2019;7: 21634–61.

[44] Yan S, Dai W, Wang S, Rao Y, Zhou S. Graphene oxide: an effective promoter for CO2 hydrate formation 2018;11:1756.

[45] Li L, Zhao S, Wang S, Rao Y. CO 2 hydrate formation kinetics based on a chemical affinity model in the presence of GO and SDS. RSC Adv 2020;10:12451–9.

[46] Srivastava S, Kollemparembil AM, Zettel V, Claßen T, Gatternig B, Delgado A, et al. Experimental investigation of CO2 uptake in CO2 hydrates formation with amino acids as kinetic promoters and its dissociation at high temperature. Sci Rep 2022;12:8359.

[47] Phan A, Striolo A. Chemical promoter performance for CO2 hydrate growth: a molecular perspective. Energy Fuel 2023;37:6002–11.

[48] Farhang F, Nguyen AV, Hampton MA. Influence of sodium halides on the kinetics of CO2 hydrate formation. Energy Fuel 2014;28:1220–9.

[49] Tanikawa W, Hirose T, Hamada Y, Gupta LP, Ahagon N, Masaki Y, et al. Porosity, permeability, and grain size of sediment cores from gas-hydrate-bearing sites and their implication for overpressure in shallow argillaceous formations: results from the national gas hydrate program expedition 02, Krishna-Godavari Basin. India Marine and Petroleum Geology 2019;108:332–47.

[50] Ren J, Zeng S, Chen D, Yang M, Linga P, Yin Z. Roles of montmorillonite clay on the kinetics and morphology of CO2 hydrate in hydrate-based CO2 sequestration. Appl Energy 2023;340:120997.

[51] Li Y, Liu W, Xing F, Wang S, Tang L, Lin S, et al. Carbonation of the synthetic calcium silicate hydrate (CSH) under different concentrations of CO2: chemical phases analysis and kinetics. Journal of CO2 Utilization 2020;35:303–13.

[52] Qureshi MF, Zheng J, Khandelwal H, Venkataraman P, Usadi A, Barckholtz TA, et al. Laboratory demonstration of the stability of CO2 hydrates in deep-oceanic sediments. Chem Eng J 2022;432:134290.

[53] Holzammer C, Finckenstein A, Will S, Braeuer AS. How sodium chloride salt inhibits the formation of CO2 gas hydrates. J Phys Chem B 2016;120:2452–9.

[54] Falahieh MM, Bonyadi M, Lashanizadegan A. Effect of different salts on the kinetic parameters of the carbon dioxide hydrate formation. J Nat Gas Sci Eng 2022;100:104461.

[55] Sun Y, Jiang S, Li S, Wang X, Peng S. Hydrate formation from clay bound water for CO2 storage. Chem Eng J 2021;406:126872.

[56] Chang J, Hou C, Wan D, Zhang X, Xu B, Tian H, et al. Enhanced CO2 adsorption capacity of bi-amine CO-tethered flue gas desulfurization gypsum with water of hydration. Journal of CO2 Utilization 2020;35:115–25.

[57] Liu X, Feng P, Cai Y, Yu X, Yu C, Ran Q. Carbonation behavior of calcium silicate hydrate (CSH): its potential for CO2 capture. Chem Eng J 2022;431:134243.

[58] Yu Y-S, Zhang X, Liu J-W, Lee Y, Li X-S. Natural gas hydrate resources and hydrate technologies: a review and analysis of the associated energy and global warming challenges. Energy Environ Sci 2021;14:5611–68.

[59] Yu Y, X-w ZHANG, Liu J-W, Lee Y, Li X. Natural gas hydrate resources and hydrate technologies: a review and analysis of the associated energy and global warming challenges. Energy Environmental Science Technology 2021; 14: 5611-5668..

[60] Liu L, Sun Z, Zhang L, Wu N, Yichao Q, Jiang Z, et al. Progress in global gas hydrate development and production as a new energy resource. Acta Geologica Sinica-English Edition 2019;93:731–55.

[61] Zhang X, Li P, Yuan Q, Li J, Shan T, Wu Q, et al. A comprehensive review of the influence of particle size and pore distribution on the kinetics of CO2 hydrate formation in porous media. Greenhouse Gases: Science and Technology; 2023.

[62] Kvamme B, Aromada SA, Saeidi N. Heterogeneous and homogeneous hydrate nucleation in CO2/water systems. J Cryst Growth 2019;522:160–74.

[63] Hong W-L, Pape T, Schmidt C, Yao H, Wallmann K, Plaza-Faverola A, et al. Interactions between deep formation fluid and gas hydrate dynamics inferred from pore fluid geochemistry at active pockmarks of the Vestnesa ridge, West Svalbard margin. Mar Pet Geol 2021;127:104957.

[64] Zhao Q, Chen Z-Y, Li X-S, Xia Z-M. Experimental study of CO2 hydrate formation under an electrostatic field. Energy 2023;272:127119.

[65] Meng Z, Xu J, Hao Y, Chen J, Wang B, Zhang X, et al. Molecular study on the behavior of CO2 hydrate growth promoted by the electric field. Geoenergy Science and Engineering 2023;221:111261.

[66] Wang B, Liu S, Wang P. Microwave-assisted high-efficient gas production of depressurization-induced methane hydrate exploitation. Energy 2022;247: 123353.

[67] Liu Y, Hou J, Zhao H, Liu X, Xia Z. Numerical simulation of simultaneous exploitation of geothermal energy and natural gas hydrates by water injection into a geothermal heat exchange well. Renew Sust Energ Rev 2019;109:467–81.

[68] Mahmood MN, Guo B. A feasibility study of using geothermal energy to enhance natural gas production from offshore gas hydrate reservoirs by CO 2 swapping. Energy Engineering 2023;120.

[69] Pan L, Doughty C, Freifeld B. How to sustain a CO2-thermosiphon in a partially saturated geothermal reservoir: lessons learned from field experiment and numerical modeling. Geothermics 2018;71:274–93.

[70] Canbaz CH, Palabiyik Y, Ozyurtkan MH, Hosgor FB, Sari MM. Advanced materials for geothermal energy applications. Sustainable Materials for Transitional and Alternative Energy: Elsevier; 2021. p. 53–124.

[71] Stern LA, Constable S, Lu R, Du Frane WL, Roberts JJ. Electrical properties of carbon dioxide hydrate: implications for monitoring CO2 in the gas hydrate stability zone. Geophys Res Lett 2021;48:e2021GL093475.

[72] Shahbabaei M, Kim D. Assessment of hydrate formation, storage capacity, and transport properties of methane and carbon dioxide through functionalized carbon nanotube membranes. J Phys Chem C 2021;125:10011–26.

[73] Jing X, Chen L, Liu Y, Fu Z. Molecular dynamics simulation of CO2 hydrate growth and intermolecular weak interaction analysis. Chem Technol Fuels Oils 2022;58:410–21.

[74] Jing X, Luo Q, Cui X, Wang Q, Liu Y, Fu Z. Molecular dynamics simulation of CO2 hydrate growth in salt water. J Mol Liq 2022;366:120237.

[75] Fu Z, Jing X, Zhou L, Luo Q, Zhang P. Molecular simulation of imperfect structure I CO2 hydrate growth in brine. Acta Crystallographica Section C: Structural Chemistry; 2023. p. 79.

[76] Xu J, Du S, Hao Y, Yang X, Zhang J. Molecular simulation study of methane hydrate formation mechanism in NaCl solutions with different concentrations. Chem Phys 2021;551:111323.

[77] Liu N, Zhu H, Zhou J, Yang L, Liu D. Molecular dynamics simulations on formation of CO2 hydrate in the presence of metal particles. J Mol Liq 2021;331: 115793.

[78] Wang D, Li Y, Liu C, Zhan L, Lu H, Li C, et al. Study of hydrate occupancy, morphology and microstructure evolution with hydrate dissociation in sediment matrices using X-ray micro-CT. Mar Pet Geol 2020;113:104138.

[79] Lu R, Stern LA, Du Frane WL, Pinkston JC, Roberts J, Constable S. The effect of brine on the electrical properties of methane hydrate. J Geophys Res Solid Earth 2019;124:10877–92.

[80] Du Frane WL, Stern LA, Weitemeyer KA, Constable S, Pinkston JC, Roberts JJ. Electrical properties of polycrystalline methane hydrate. Geophys Res Lett 2011; 38.

[81] Wen Z, Yao Y, Luo W, Lei X. Memory effect of CO2-hydrate formation in porous media. Fuel 2021;299:120922.

[82] Hassan MHA, Sher F, Zarren G, Suleiman N, Tahir AA, Snape CE. Kinetic and thermodynamic evaluation of effective combined promoters for CO2 hydrate formation. J Nat Gas Sci Eng 2020;78:103313.

[83] Yin Z, Zheng J, Kim H, Seo Y, Linga P. Hydrates for cold energy storage and transport: a review. Advances in Applied Energy 2021;2:100022.

[84] Zhao X, Geng Q, Zhang Z, Qiu Z, Fang Q, Wang Z, et al. Phase change material microcapsules for smart temperature regulation of drilling fluids for gas hydrate reservoirs. Energy 2023;263:125715.

[85] Liu Y, Yang Y, Li S. Graphene oxide modified hydrate salt hydrogels: form-stable phase change materials for smart thermal management. J Mater Chem A 2016;4: 18134–43.

[86] Zhang W, Li H-Y, Xu C-G, Huang Z-Y, Li X-S. Research progress on the effects of nanoparticles on gas hydrate formation. RSC Adv 2022;12:20227–38.

[87] Phan A, Schlösser H, Striolo A. Molecular mechanisms by which tetrahydrofuran affects CO2 hydrate growth: implications for carbon storage. Chem Eng J 2021; 418:129423.

[88] Said S, Govindaraj V, Herri J-M, Ouabbas Y, Khodja M, Belloum M, et al. A study on the influence of nanofluids on gas hydrate formation kinetics and their potential: application to the CO2 capture process. J Nat Gas Sci Eng 2016;32: 95–108.

[89] Ansari AA, Ravesh R, Chakraborty S, Panigrahi PK, Das MK. CO2 hydrate formation kinetics in the presence of a layered double hydroxide Nanofluid. Chem Eng Technol 2023;46:1630–8.

[90] Zhou S-d, Yu Y-s, Zhao M-m, Wang S-l, Zhang G-Z. Effect of graphite nanoparticles on promoting CO2 hydrate formation. Energy Fuel 2014;28: 4694–8.

[91] Nashed O, Partoon B, Lal B, Sabil KM, Shariff AM. Investigation of functionalized carbon nanotubes' performance on carbon dioxide hydrate formation. Energy 2019;174:602–10.

[92] Nashed O, Partoon B, Lal B, Sabil KM, Yaqub S, Shariff AM. Methane and carbon dioxide hydrate formation in the presence of metal-based fluid. Materials 2022; 15:8670.

[93] Wei R, Shi K, Guo X, Wang T, Lv X, Li Q, et al. Evolving thermal conductivity upon formation and decomposition of hydrate in natural marine sediments. Fuel 2021;302:121141.

[94] Swarbrick R, Jenkins S, Scott D, Riddle G. The role of pressure in carbon capture and storage (CCS). Geological storage of carbon dioxide (CO2). Elsevier; 2013. p. 97–110e.

[95] Bian J, Wang H, Yang K, Chen J, Cao X. Spatial differences in pressure and heat transfer characteristics of CO2 hydrate with dissociation for geological CO2 storage. Energy 2022;240:122508.

[96] Klar A, Deerberg G, Janicki G, Schicks J, Riedel M, Fietzek P, et al. Marine gas hydrate technology: State of the art and future possibilities for Europe. 2019.

[97] Schicks J. From lab to field, from micro to macro–test of technologies for the production of hydrate bonded CH4 via CO2 sequestration in hydrates. ICGH 9-9th International Conference on Gas Hydrates. 2017.

[98] Dhamu V, Qureshi MF, Abubakar S, Usadi A, Barckholtz TA, Mhadeshwar AB, et al. Investigating high-pressure liquid CO2 hydrate formation, dissociation kinetics, and morphology in brine and freshwater static systems. Energy Fuel 2023;37(12):8406–20.

[99] Zhang K, Lau HC, Chen Z. Extension of CO2 storage life in the Sleipner CCS project by reservoir pressure management. J Nat Gas Sci Eng 2022;108:104814.

[100] Nazarian B, Held R, Høier L, Ringrose P. Reservoir management of CO2 injection: pressure control and capacity enhancement. Energy Procedia 2013;37:4533–43.

[101] Hu Q, Xiao X. Formation methods and applications of carbon dioxide hydrate: an overview. Carbon capture. For Sci Technol 2023;7:100113.

[102] Simmenes T., Hansen O.R., Eiken O., Teige G.M.G., Hermanrud C., Johansen S., et al. Importance of pressure management in CO2 storage. Offshore Technology Conference: OTC 2013. p. OTC-23961-MS: https://doi.org/10.4043/23961-MS.

[103] Liao S, Yuan B, Wang Y, Lv Z, Shang L, Zhou L, et al. Formation characteristics of carbon dioxide hydrate in a high-pressure flow loop. Energy Fuel 2023;37: 15657–70.

[104] Palodkar AV, Jana AK. Formulating formation mechanism of natural gas hydrates. Sci Rep 2017;7:6392.

[105] Zhang X, Wang J, Yang H, Li J, Li Y, Wu Q. Formation and storage characteristics of CO2 hydrate in porous media: effect of liquefaction amount on the formation rate, accumulation amount. Appl Therm Eng 2022;214:118747.

[106] Zadeh AH, Kim I, Kim S. Characteristics of CO2 hydrate formation and dissociation at different CO2-water ratios in a porous medium. International Journal of Greenhouse Gas Control 2023;125:103883.

[107] Qureshi MF, Dhamu V, Usadi A, Barckholtz TA, Mhadeshwar AB, Linga P. CO2 hydrate formation kinetics and morphology observations using high-pressure liquid CO2 applicable to sequestration. Energy Fuel 2022;36:10627–41.

[108] Wang L, Dou M, Wang Y, Xu Y, Li Y, Chen Y, et al. A review of the effect of porous media on gas hydrate formation. ACS omega 2022;7:33666–79.

[109] Zhang X, Yang H, Li J, Zhang M, Wang Y, Yao Z. Investigation of the formation behaviors of CO2 hydrate in porous media below the freezing point. Environ Prog Sustain Energy 2022;41:e13953.

[110] Feng Y, Zhao Y, Han Y, Liu Y, Zhang L, Zhao J, et al. Formation and dissociation of CO2 hydrates in porous media in the presence of clay suspensions. Chem Eng J 2023;465:142854.

[111] Schwenzer M, Ay M, Bergs T, Abel D. Review on model predictive control: an engineering perspective. Int J Adv Manuf Technol 2021;117:1327–49.

[112] Zhang P, Wu Q, Mu C, Chen X. Nucleation mechanisms of CO2 hydrate reflected by gas solubility. Sci Rep 2018;8:10441.

[113] Modekurti S, Bhattacharyya D, Zitney SE. Dynamic modeling and control studies of a two-stage bubbling fluidized bed adsorber-reactor for solid–sorbent CO2 capture. Ind Eng Chem Res 2013;52:10250–60.

[114] Mayne DQ, Rawlings JB, Rao CV, Scokaert PO. Constrained model predictive control: stability and optimality. Automatica 2000;36:789–814.

[115] Fang X, Chen W-H. Model predictive control with preview: recursive feasibility and stability. IEEE Control Systems Letters 2022;6:2647–52.

[116] Temel S, Yağli S, Gören S. P, pd, pi, pid controllers. Electrical and Electronics Engineering Department: Middle East Technical University; 2013.

[117] Rocoulet S, Lesage N, Jellema R, Tacnet J, Drouilly C. A new approach to manage CO2 hydrates during geological carbon sequestration. In: Offshore technology conference. Brasil: OTC; 2023. p. D021S5R05.

[118] Khan SH, Kumari A, Dixit G, Majumder CB, Arora A. Thermodynamic modeling and correlations of CH 4, C 2 H 6, CO 2, H 2 S, and N 2 hydrates with cage occupancies. J Pet Explor Prod Technol 2020;10:3689–70.

[119] Rossi A, Ciulla M, Canale V, Zannotti M, Minicucci M, Di Profio P, et al. Constant pressure CO2 replacement of CH4 in different hydrate environments: structure and morphology. Energy Fuel 2023;37:18968–76.

[120] Yang L, Shi F, Yang J. Experimental studies on hydraulic fracturing in hydrate sediment. Chem Technol Fuels Oils 2020;56:107–14.

[121] Zhang W, Shi X, Jiang S, Cao Q, Wang F, Wang Z, et al. Experimental study of hydraulic fracture initiation and propagation in highly saturated methane-hydrate-bearing sands. J Nat Gas Sci Eng 2020;79:103338.

[122] Sun X, Wang Z, Sun B, Wang W. Research on hydrate formation rules in the formations for liquid CO2 fracturing. J Nat Gas Sci Eng 2016;33:1390–401.

[123] Feyzi V, Mohebbi V. Depressurization assisted CO2-CH4 replacement in hydrate structure: molecular mechanism and kinetic modeling. J Mol Liq 2021;344: 117718.

[124] Zhang S, Ma Y, Xu Z, Zhang Y, Liu X, Zhong X, et al. Numerical Simulation Study of Natural Gas Hydrate Extraction by Depressurization Combined with Co2 Replacement. Available at SSRN 4680829. 2024.

[125] Ma Sholihah, Sean W-Y. Numerical simulation on the dissociation, formation, and recovery of gas hydrates on microscale approach. Molecules 2021;26:5021.

[126] Li S, Wu D, Wang X, Hao Y. Enhanced gas production from marine hydrate reservoirs by hydraulic fracturing assisted with sealing burdens. Energy 2021; 232:120889.

[127] Ju X, Liu F, Fu P, White MD, Settgast RR, Morris JP. Gas production from hot water circulation through hydraulic fractures in methane hydrate-bearing sediments: THC-coupled simulation of production mechanisms. Energy Fuel 2020;34:4448–65.

[128] Nianyin L, Jiajie Y, Chao W, Suiwang Z, Xiangke L, Jia K, et al. Fracturing technology with carbon dioxide: a review. J Pet Sci Eng 2021;205:108793.

[129] Li S, Zhang S, Ma X, Zou Y, Li N, Chen M, et al. Hydraulic fractures induced by water−/carbon dioxide-based fluids in tight sandstones. Rock Mech Rock Eng 2019;52:3323–40.

[130] Shi H, Zhao H, Zhou J, Yu Y. Experimental investigation on the propagation of hydraulic fractures in massive hydrate-bearing sediments. Eng Fract Mech 2023; 289:109425.

[131] He P, Lu Z, Deng Z, Huang Y, Qin D, Ouyang L, et al. An advanced hydraulic fracturing technique: pressure propagation and attenuation mechanism of step rectangular pulse hydraulic fracturing. Energy Sci Eng 2023;11:299–316.

[132] Gambelli AM. Analyses on CH4 and CO2 hydrate formation to define the optimal pressure for CO2 injection to maximize the replacement efficiency into natural gas hydrate in presence of a silica-based natural porous medium, via depressurization techniques. Chemical Engineering and Processing-Process Intensification 2021;167:108512.

[133] Shi K, Wei R, Guo X, Li Q, Lv X, Fan Q, et al. Enhancing gas production from hydrate-bearing reservoirs through depressurization-based approaches: knowledge from laboratory experiments. Energy Fuel 2021;35:6344–58.

[134] Feng Y, Haugen K, Firoozabadi A. Phase-field simulation of hydraulic fracturing by CO2, water and nitrogen in 2D and comparison with laboratory data. Journal of geophysical research. Solid Earth 2021;126:e2021JB022509.

[135] Wang X, Zhang F, Lipiński W. Carbon dioxide hydrates for cold thermal energy storage: a review. Sol Energy 2020;211:11–30.

[136] Aresta M, Dibenedetto A, Quaranta E, Aresta M, Dibenedetto A, Quaranta E. Thermodynamics and applications of CO 2 hydrates. Reaction Mechanisms in Carbon Dioxide Conversion 2016:373–402.

[137] Yu T, Sato T, Nakashima T, Inui M, Oyama H. An integrated model for CO2 hydrate formation in sand sediments for sub-seabed CO2 storage. International Journal of Greenhouse Gas Control 2016;52:250–69.

[138] Jiao L, Wang Z, Li J, Zhao P, Wan R. Stability and dissociation studies of CO2 hydrate under different systems using molecular dynamic simulations. J Mol Liq 2021;338:116788.

[139] Mooijer-Van Den Heuvel M, Witteman R, Peters C. Phase behaviour of gas hydrates of carbon dioxide in the presence of tetrahydropyran, cyclobutanone, cyclohexane and methylcyclohexane. Fluid Phase Equilib 2001;182:97–110.

[140] Kim S, Baek I-H, You J-K, Seo Y. Guest gas enclathration in tetra-n-butyl ammonium chloride (TBAC) semiclathrates: potential application to natural gas storage and CO2 capture. Appl Energy 2015;140:107–12.

[141] Rossi F, Gambelli AM. Thermodynamic phase equilibrium of single-guest hydrate and formation data of hydrate in presence of chemical additives: a review. Fluid Phase Equilib 2021;536:112958.

[142] Wang H, Wu Q, Zhang B. Influence of THF and THF/SDS on the kinetics of CO2 hydrate formation under stirring. Frontiers in Energy Research 2021;9:633929.

[143] Sato K, Tokutomi H, Ohmura R. Phase equilibrium of ionic semiclathrate hydrates formed with tetrabutylammonium bromide and tetrabutylammonium chloride. Fluid Phase Equilib 2013;337:115–8.

[144] Zhou S, Jiang K, Zhao Y, Chi Y, Wang S, Zhang G. Experimental investigation of CO2 hydrate formation in the water containing graphite nanoparticles and tetra-n-butyl ammonium bromide. J Chem Eng Data 2018;63:389–94.

[145] Gambelli AM, Presciutti A, Rossi F. Review on the characteristics and advantages related to the use of flue-gas as CO2/N2 mixture for gas hydrate production. Fluid Phase Equilib 2021;541:113077.

[146] Kang S-P, Lee H, Lee C-S, Sung W-M. Hydrate phase equilibria of the guest mixtures containing CO2, N2 and tetrahydrofuran. Fluid Phase Equilib 2001;185: 101–9.

[147] Zhou X, Zang X, Long Z, Liang D. Multiscale analysis of the hydrate based carbon capture from gas mixtures containing carbon dioxide. Sci Rep 2021;11:9197.

[148] Park JH, Park J, Lee JW, Kang YT. Progress in CO2 hydrate formation and feasibility analysis for cold thermal energy harvesting application. Renew Sust Energ Rev 2023;187:113783.

[149] Bharathi A, Nashed O, Lal B, Foo KS. Experimental and modeling studies on enhancing the thermodynamic hydrate inhibition performance of monoethylene glycol via synergistic green material. Sci Rep 2021;11:2396.

[150] Sayani JKS, Pedapati SR, Lal B. Phase behavior study on gas hydrates formation in gas dominant multiphase pipelines with crude oil and high CO2 mixed gas. Sci Rep 2020;10:14748.

[151] Rao Y, Wang S, Yang Y, Jia R, Zhou S, Zhao S, et al. Experimental study and chemical affinity model on the inhibition of CO2 gas hydrate formation. Chem Eng Sci 2023;281:119158.

[152] Shaik NB, Sayani JKS, Benjapolakul W, Asdornwised W, Chaitusaney S. Experimental investigation and ANN modelling on CO2 hydrate kinetics in multiphase pipeline systems. Sci Rep 2022;12:13642.

[153] Zhang L, Yang L, Wang J, Zhao J, Dong H, Yang M, et al. Enhanced CH4 recovery and CO2 storage via thermal stimulation in the CH4/CO2 replacement of methane hydrate. Chem Eng J 2017;308:40–9.

[154] Yang T, King WP, Miljkovic N. Phase change material-based thermal energy storage. Cell reports physical Science 2021:2.

[155] Lv X, Zhang J, Zuo J, Zhao D, Liu Y, Zhou S, et al. Study on the formation characteristics of CO2 hydrate and the rheological properties of slurry in a flow system containing surfactants. ACS omega 2022;7:2444–57.

[156] Abu Hassan MH, Sher F, Fareed B, Ali U, Zafar A, Bilal M, et al. Sustainable hydrates for enhanced carbon dioxide capture from an integrated gasification combined cycle in a fixed bed reactor. Ind Eng Chem Res 2021;60:11346–56.

[157] Li B, Sun Y, Jiang S, Shen Y, Qi Y, Zhang G. Investigating CO2–N2 phase behavior for enhanced hydrate-based CO2 sequestration. Energy 2023;289:129946.

[158] Li A, Wang J, Bao B. High-efficiency CO2 capture and separation based on hydrate technology: a review. Greenhouse gases: science and technology 2019;9: 175–93.

[159] Rehman Au, Lal B. Gas hydrate-based CO2 capture: a journey from batch to continuous. Energies 2022;15:8309.

[160] Dhamu V, Mengqi X, Qureshi MF, Yin Z, Jana AK, Linga P. Evaluating CO2 hydrate kinetics in multi-layered sediments using experimental and machine learning approach: applicable to CO2 sequestration. Energy 2024;290:129947.

[161] Tegze G, Pusztai T, Tóth G, Gránásy L, Svandal A, Buanes T, et al. Multiscale approach to CO2 hydrate formation in aqueous solution: phase field theory and molecular dynamics. Nucleation and growth. J Chem Phys 2006:124.

[162] Circone S, Stern LA, Kirby SH, Durham WB, Chakoumakos BC, Rawn CJ, et al. CO2 hydrate: synthesis, composition, structure, dissociation behavior, and a comparison to structure I CH4 hydrate. J Phys Chem B 2003;107:5529–39.

[163] Agrawal R, Kumar Y, Sarkhel R, Damdhar MS, Sangwai JS. Enhancing the CO2 sequestration potential in subsea terrain by hydrate formation from liquid CO2. Energy Fuel 2023;37:14961–76.

[164] Liu Y, Zhang L, Yang L, Dong H, Zhao J, Song Y. Behaviors of CO2 hydrate formation in the presence of acid-dissolvable organic matters. Environ Sci Technol 2021;55:6206–13.