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Review

Comprehensive Review and Perspectives of CO_2 Hydrate Storage in Subseafloor Saline Sediments: Formation, Stability, and Optimization Strategies

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Cite This: https://doi.org/10.1021/acs.energyfuels.3c05036

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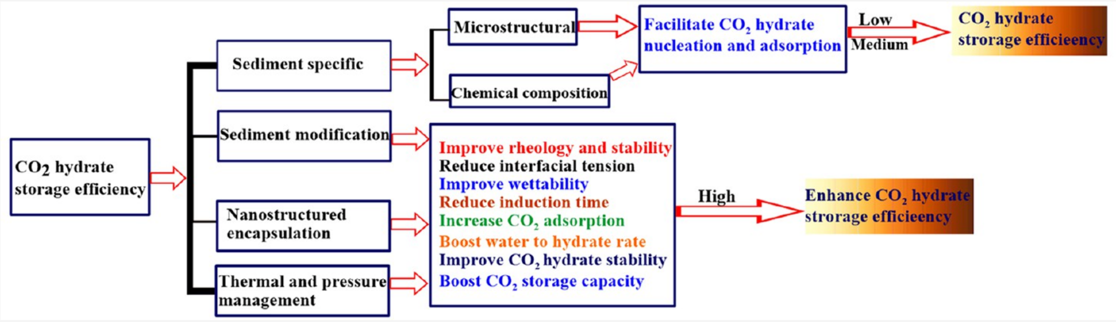

ABSTRACT: Exploring various strategies for CO_2 hydrate storage in subseafloor saline sediments reveals a promising yet challenging path toward mitigating anthropogenic CO_2 emissions and advancing clean energy development. Research has revealed the efficacy of sediment-specific modifications, including the use of inorganic emulsifiers, L-leucine (an amino acid), and nanoparticle coatings, in enhancing CO_2 hydrate formation stability and storage capacity. These modifications aid in overcoming the challenges posed by the harsh environmental conditions of salinity and sediment heterogeneity, providing increased stability, enhanced CO_2 adsorption efficiency, and reduced induction time. Furthermore, advancements in nanomaterials have introduced nanostructured encapsulation systems capable of confining and stabilizing CO_2 within a solid matrix under fluctuating pressure, temperature, and salinity conditions. Incorporating nanoparticles into polymers and surfactants yields a nanofluid that exhibits increased stability, improved wettability, interfacial tension (IFT) reduction, and elevated CO_2 hydrate storage efficiency, with the synergistic effects of these components playing a critical role. Moreover, innovative thermal and pressure manipulation strategies, alongside the integration of kinetic promoters, have shown significant potential in optimizing CO_2 hydrate formation kinetics and enhancing long-term stability. These strategies involve novel electrical heating systems, pressure management techniques, and chemical additives that collectively contribute to increased hydrate formation rates and gas storage capacities. Despite these promising developments, the field faces several challenges, including optimizing encapsulation materials to match geological characteristics, the long-term stability of CO_2 hydrates under extreme conditions, and scaling laboratory experiments to field applications. Addressing these issues necessitates a multifaceted approach, incorporating empirical data and theoretical insights to design, screen, and formulate effective CO_2 hydrate storage solutions in subseafloor saline sediments.

1. INTRODUCTION

Pursuing viable solutions to mitigate greenhouse gas emissions has propelled scientific inquiry into innovative carbon capture and storage (CCS) methods. Among these, the formation and storage of CO_2 hydrates within subseafloor saline sediments have emerged as a promising possibility for long-term carbon sequestration.[1] This approach evolved through a rich historical context steeped in scientific exploration and technological advancements. The inception of CO_2 hydrate storage research can be traced back to the mid-20th century when the concept of gas hydrates, crystalline compounds formed by water and guest molecules under specific pressure and temperature conditions, began captivating scientific curiosity.[2,3] Initially regarded as a geological curiosity, the understanding of gas hydrates matured gradually, laying the groundwork for exploring their potential applications in CO_2 capture and storage.[2,4] The turn of the 21st century marked an essential era for climate change discussions, propelling intensified efforts

Received: December 19, 2023
Revised: April 13, 2024
Accepted: April 16, 2024

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toward mitigating CO_2 emissions.[5] Researchers and policymakers alike sought innovative methods to sequester CO_2, leading to a surge in studies exploring the feasibility of storing CO_2 within gas hydrates, particularly in subseafloor environments. Numerous investigation studies have revealed that CO_2 sequestration in subseafloor environments involves various forms and methodologies to capture and store CO_2 to mitigate climate change. One such form is under the seabed, where CO_2 can be stored as a lake with a CO_2 hydrate cap, providing enhanced safety and increased storage capacity by preventing CO_2 leakage and allowing for a larger amount of CO_2 to be sequestered beneath the hydrate cap.[6] Another method involves CO_2 hydrate sediments, where CO_2 is injected into marine sediments, resulting in the formation of CO_2 hydrates, thus leveraging the kinetics and morphology of hydrate formation for sequestration,[7] as illustrated in Figure 1.

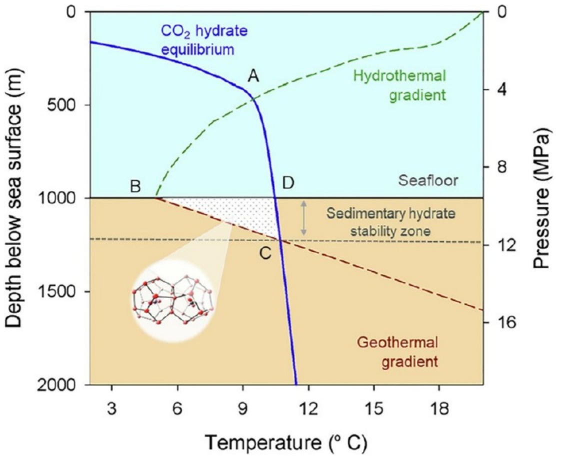

Figure 1. Conceptual representation of the CO_2 hydrate stability zone in a marine setting, assuming a seafloor depth of 1000 m. Reproduced with permission from ref 16. Copyright 2022, Elsevier.

Additionally, CO_2 replacement with natural gas hydrates (NGH) presents an environmental advantage, as it can exploit the trapped methane for energy while simultaneously storing CO_2.[8,9] These processes not only store carbon but also stabilize methane hydrate formations,[9] providing an innovative dual benefit of potent greenhouse gas management and energy recovery. In addition, permafrost regions, which underlie about 25% of the Northern Hemisphere land surface, are significant carbon stores.[10] Currently, these areas are experiencing rapid thawing due to climate warming, posing risks of releasing stored carbon into the atmosphere. Research indicates that aerobic conditions in thawing permafrost ecosystems could contribute more to the permafrost carbon feedback mechanism than anaerobic ones due to higher CO_2 emissions in aerobic conditions.[10] Additionally, the concept of storing CO_2 in gas hydrates within permafrost offers a novel approach to sequestering carbon, potentially allowing for the simultaneous extraction of methane, contributing to energy production while securing CO_2 storage.[11] Each of these CO_2 sequestration forms plays a crucial role in the broader spectrum of carbon capture and storage technologies aimed at reducing atmospheric CO_2 levels and combatting global warming. Early studies primarily focused on fundamental aspects, such as the thermodynamics and kinetics governing CO_2 hydrate formation and stability.[12] Experimental investigations, coupled with theoretical modeling, aimed to decipher the complex interplay between sediment properties, saline water composition, and the dynamics of CO_2 hydrate formation.[13] As the field progressed, researchers increasingly delved into the intricacies of sediment properties, recognizing their crucial role in influencing the storage potential of CO_2 within hydrate structures, as described in Figure 2. From grain size distribution and pore structure to mineral composition and organic content, sediment properties emerged as crucial determinants shaping the efficacy and longevity of CO_2 hydrate storage.[14,15]

Recent advancements have introduced nanostructured encapsulation as an essential strategy, enhancing the formation, stability, and storage efficiency of CO_2 hydrates in subseafloor environments,[17,18] as illustrated by Figure 3. This approach leverages nanotechnology to optimize CO_2 storage within saline sediments, addressing challenges of mass transfer, material compatibility, and environmental impact, thereby ensuring the long-term integrity and viability of CO_2 storage solutions.[17,18] Despite these innovations, the field faces challenges encompassing the scalability of laboratory findings, understanding molecular mechanisms, and assessing environmental implications.[19,20] Addressing these challenges necessitates an integrated approach combining experimental investigations, simulation studies, and comprehensive evaluations of nanoparticle-assisted surfactant and polymer formulations. Moreover, thermal and pressure management strategies are vital in optimizing CO_2 hydrate formation and stability in subseafloor saline sediments. 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.[14] Thermal management involves

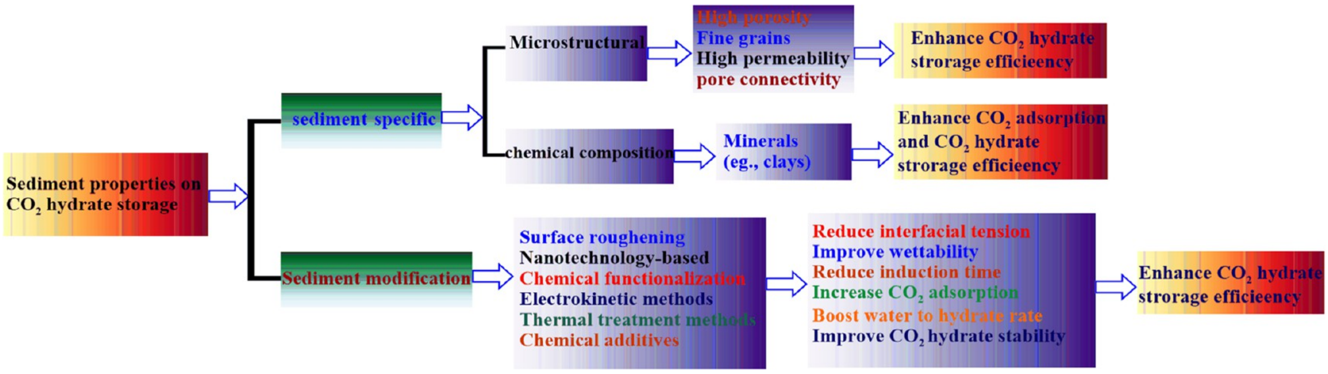

Figure 2. Influence of sediment properties on CO_2 hydrate storage potential.

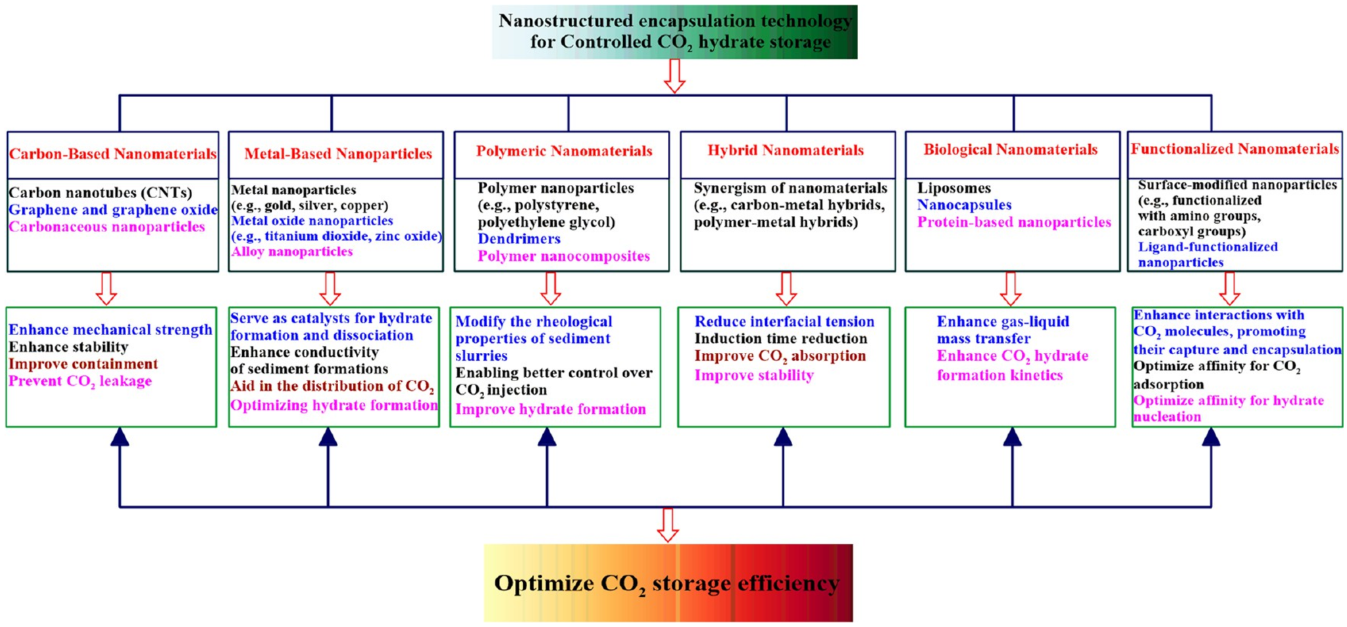

Figure 3. Nanostructured encapsulation technology for controlled CO_2 hydrate storage in subseabed saline sediments.

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.[21] Understanding and implementing these strategies are vital for harnessing the full potential of CO_2 hydrate-based storage solutions in subseafloor saline sediments

Integrating recent sedimentology developments and CO_2 hydrate storage research has elucidated the crucial role of subseabed sediment-specific characteristics and modification techniques in enhancing CO_2 hydrate storage efficiency. This comprehensive review reveals a novel relationship between sediment qualities, such as heterogeneity, particle size, mineralogy, and porosity, and the effectiveness of CO_2 sequestration as a clathrate hydrate in saline sediments beneath the seafloor. It advances understanding by merging geological data with the dynamics of CO_2 hydrate formation, offering fresh insights into the impact of sediment attributes on hydrate stability and long-term storage potential. Furthermore, it evaluates sediment interaction with CO_2 hydrates to propose a predictive framework that could significantly bolster the understanding of subsurface CO_2 hydrate storage feasibility and effectiveness. In addition, this review ventures into the realm of nanotechnology, highlighting its potential in improving CO_2 hydrate storage through nanostructured encapsulation and nanoparticle-assisted surfactant−polymer formulations. It offers an in-depth analysis of nanostructured materials and catalyst formulations, examining molecular interactions, rheological properties, and the response to varying sediment interactions and temperature fluctuations. Despite its promise, the review reveals the technological and economic hurdles facing the field application of these nanoenabled strategies. Moreover, exploring thermal and pressure management strategies unveils their potential in optimizing CO_2 hydrate formation and stability within the challenging environment of subseafloor saline sediments. It underscores the need for further investigation into the specific mechanisms at play, considering sediment heterogeneity, temperature, and pressure, to develop effective strategies for large-scale application. The comparison of several experimental and simulation findings related to sediment-specific and sediment modification, nanotechnologies like nanoparticle-assisted surfactant−polymer, and thermal/pressure management strategies reveals both successes and limitations. Identified research gaps in current CO_2 hydrate formation, stability, storage, and optimization strategies are addressed, and potential interventions are proposed. 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. INFLUENCE OF SEDIMENT PROPERTIES ON CO_2 HYDRATE STORAGE

2.1. Sediment-Specific CO_2 Hydrate Formation Mechanisms. *2.1.1. Microstructural Analysis of Sediments in CO_2 Hydrate formation.* The formation of CO_2 hydrates within subseafloor saline sediments is a process that heavily hinges upon the microstructural characteristics of the sediment itself, as described in Table 1. These sediments have diverse properties that play a crucial role in dictating the mechanisms through which CO_2 hydrates are formed. One key factor influencing CO_2 hydrate formation is the porosity and permeability of the sediment matrix.[22,23] Sediments with high porosity provide ample space for the migration and accumulation of CO_2 molecules, facilitating their interaction with water molecules to form hydrates.[22,23] Permeability, conversely, determines the ease of movement of fluids within the sediment. Sediments with higher permeability may encourage faster CO_2 infiltration and subsequent hydrate formation due to enhanced fluid movement.[24] Moreover, the grain size distribution within sediments significantly impacts CO_2 hydrate formation mechanisms. Fine-grained sediments possess a larger surface area per unit volume, enabling more extensive contact between CO_2 and water molecules and expediting the nucleation and growth of hydrate crystals.[25] Conversely, coarser sediments might exhibit slower formation kinetics due to reduced interfacial contact between CO_2 and water molecules.[26,27] The presence and distribution of clay minerals within sediments also notably influence CO_2 hydrate

Table 1. Microstructural Characteristics of Saline Sediments and Their Influence on CO_2 Hydrate Formation within Porous Media

Microstructural Characteristic	Porous Media	Influence on CO_2 Hydrate Formation	Remarks	Refs
Porosity	Sandstone, siltstone, clay	Higher porosity facilitates increased surface area for CO_2 interaction and hydrate nucleation.	Sediments with higher porosity show enhanced CO_2 uptake potential, suggesting potential for efficient hydrate formation. Assess sediments with optimal porosity for targeted hydrate storage.	22, 23
Pore Size Distribution	Various sediment types	Variation in pore sizes affects gas diffusion and hydrate growth. Smaller pores favor faster gas hydrate formation.	Understanding pore size distribution aids in predicting preferential regions for CO_2 hydrate formation. Fine-tuning pore size distribution might enhance hydrate formation rates.	26, 27
Pore Connectivity	Sandstone, shale	Enhanced connectivity enables efficient gas migration and hydrate growth throughout the sediment matrix.	Assess sediments with higher connectivity for favorable CO_2 hydrate distribution and formation.	25
Mineral Composition	Various sediment types	Different minerals act as nucleation sites for hydrate formation. Minerals with higher surface energies tend to facilitate nucleation.	Identify and evaluate sediment compositions favoring CO_2 hydrate nucleation. Optimize mineral compositions for efficient hydrate formation.	29
Grain Size Distribution	Sand, clay	Varied grain sizes influence pore structure and gas diffusion rates. Fine-grained sediments often exhibit increased surface area for hydrate formation.	Identify sediments with diverse grain sizes for optimized CO_2 hydrate storage. Fine-grained sediments offer superior hydrate formation potential.	25
Interfacial Properties	Sandstone, mudstone	Interactions at interfaces between water, gas, and sediment grains significantly influence hydrate growth and distribution.	Evaluate interfacial properties for a precise understanding of CO_2 hydrate characteristics. Alter the properties at the interface to provide specific conditions for the growth of hydrates.	30

formation. With their high surface area and ion exchange capacities, clays can act as nucleation sites for hydrate formation.[28] Additionally, they may influence the movement and distribution of CO_2 and water molecules, potentially altering the kinetics and stability of formed hydrates.[29]

Abbasi et al.[31] examined the microstructural analysis of sediments in forming CO_2 hydrates, emphasizing the profound impact of sediment properties on CO_2 hydrate storage. Using advanced microcomputed tomography (μCT) setups, including synchrotron-based and lab-based configurations, the research explored the detailed visualization of sediments' internal structures at resolutions ranging from submicron to nanoscale. The experimental design demonstrated the potential of μCT in capturing high-resolution images of sediments, allowing for 3D visualization and quantitative analysis of various sediment properties. Techniques such as coherent diffractive imaging facilitated the examination of pore geometry, mineral composition, pore-size distribution, fracture-aperture distribution, and porosity within sediments. The findings revealed sediments' complex and diverse characteristics, offering crucial data for assessing their appropriateness for different purposes, such as evaluating reservoir capacities, comprehending fluid flow dynamics, and predicting mechanical behaviors in scenarios like gas hydrate formation or storage assessments. Using μCT imaging for gas hydrate characterization revealed a multifaceted landscape within sedimentary structures. It uncovered complex growth patterns of gas hydrates within pore spaces and along surfaces, offering insights into their diverse behaviors. The observed modes of hydrate growth, such as the floating model, displayed the propensity of hydrates to develop in pore spaces without direct contact with the pore surface, allowing for advancement in multiple directions. Inhomogeneous distributions of hydrates within the pore space further emphasized the complexity of their occurrence, showing variations in their spatial arrangements and concentrations. Additionally, the emergence of various growth shapes, like bridge formations, surface growth, and spike-shaped configurations, highlighted the diverse morphologies adopted by gas hydrates within these structures, as shown in Figure 4. These findings enhance the understanding of gas hydrate formation mechanisms and emphasize the importance of pore-scale behaviors in influencing the overall characteristics and distribution of gas hydrates within sedimentary systems. Moreover, the study highlighted the influence of sediment properties on the mechanical behavior and saturation phases of gas hydrates. It explored how different hydrate saturation levels impact sediment strength, considering factors such as hydrate-free sediments, low and high hydrate saturation phases, and their implications on pore-scale mechanisms and strength evolution. Varying hydrate saturation levels, from hydrate-free sediments to low and high hydrate saturation phases, showed distinct pore-scale mechanisms and their impact on sediment strength, as shown in Figure 5. In hydrate-free sediments, the absence of gas hydrates allowed for more flexible pore structures and higher sediment deformability. Low hydrate saturation phases revealed a coexistence of hydrate and free gas, fostering localized concentration points and potential pore-scale damage due to localized stress concentrations. In contrasting, high hydrate saturation levels significantly altered sediment behavior by forming a connected hydrate network, reinforcing sediment matrix and increasing strength. The strength evolution across these phases underscored the critical role of hydrate saturation in dictating

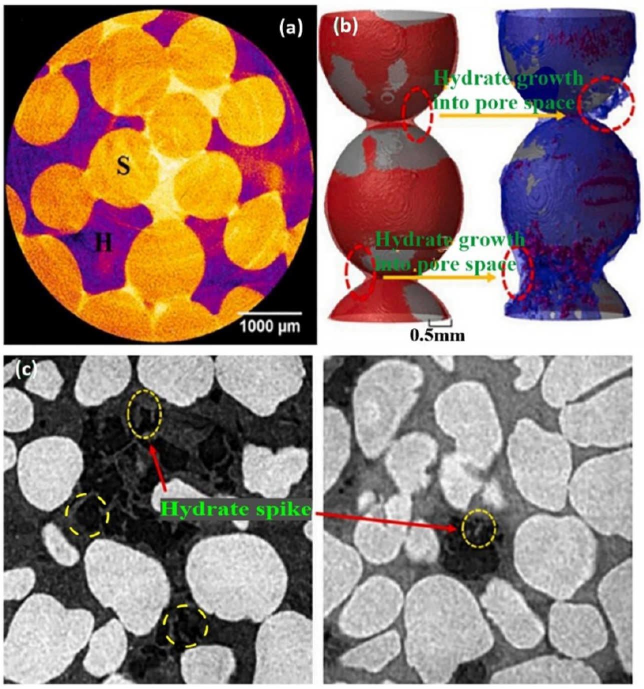

Figure 4. Microcomputed tomography shows the gas hydrate growth pattern in porous media: (a) the hydrate bridge, (b) surface hydrate growth, and (c) the hydrate spike. Adapted with permission from ref 31. Copyright 2022, Elsevier.

pore-scale mechanisms—ranging from localized damage in low saturation to enhanced strength in highly saturated sediments. Understanding these pore-scale mechanisms becomes essential for comprehending gas hydrate reservoir stability, geomechanical behavior, and potential implications for energy extraction or geological stability assessments.

Further, studies using μCT imaging to explore seepage characteristics and permeability within hydrate-bearing sediments unveiled critical findings regarding the behavior of gases and fluids within these environments. Observations revealed the direct correlation between hydrate saturation levels and water and gas flow pathways. Variations in hydrate saturation significantly influenced the flow paths, demonstrating distinctive behaviors in relative permeability. As hydrate saturation increased, a notable impact on water and gas flow paths emerged, indicating alterations in percolation behavior. Higher hydrate saturation levels tended to obstruct water flow paths due to the predominance of gas hydrates occupying a significant portion of the pore space. Consequently, this reduced the relative permeability of the gas phase. Conversely, lower hydrate saturation levels showed a more pronounced ability for water and gas to permeate through the sediments due to less obstruction by gas hydrates, resulting in relatively higher relative permeabilities. These findings shed light on the complex interaction between hydrate saturation and fluid flow behavior, offering comprehensive insights into percolation dynamics and relative permeability variations within hydrate-bearing sediments. Additionally, the study briefly touched upon the use of various other techniques such as Raman spectroscopy, X-ray diffraction (XRD), nuclear magnetic resonance (NMR), magnetic resonance imaging (MRI), neutron scattering, high-pressure differential scanning calorimetry (DSC), and high-pressure reactors, uncovered multifaceted insights into gas hydrate properties, phase equilibrium, structure, and formation/dissociation kinetics. Raman spectroscopy emerged as a critical tool, revealing the molecular composition, structure type, and existence of gas hydrates. XRD and NMR provided crucial information on crystal structure, lattice parameters, and dynamics of gas molecules within hydrates, aiding in understanding formation/dissociation kinetics. MRI proved instrumental in visualizing hydrate formation/dissociation, offering quantifiable data on porosity, fluid distribution, and saturation within pore spaces. Neutron scattering is particularly valuable at high gas pressures, quantified hydrate formation/dissociation, and essential for unconventional fuel recovery hypotheses. High-pressure DSC and reactors facilitated precise measurements of phase

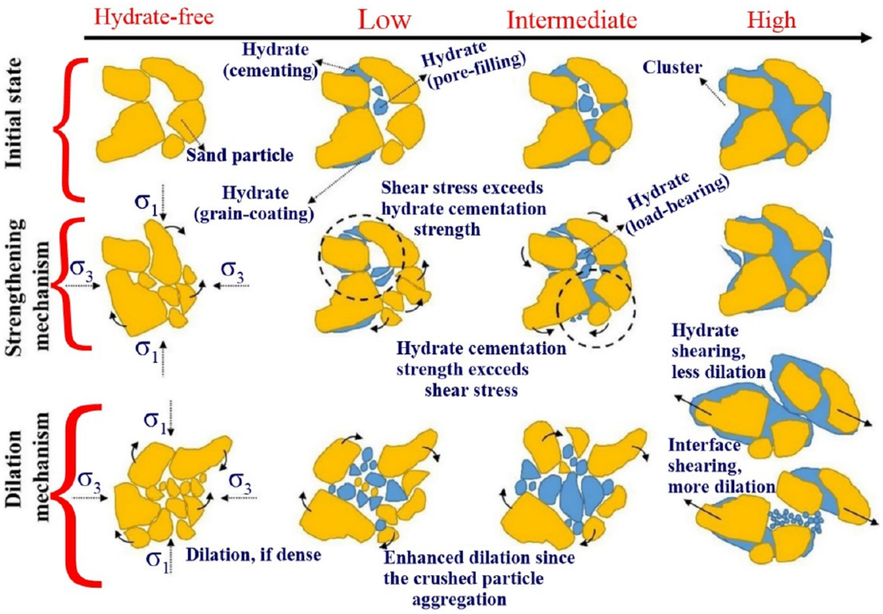

Figure 5. Influence of hydrate saturation on pore-scale mechanisms and sediment strength evolution. Adapted with permission from ref 31. Copyright 2022, Elsevier.

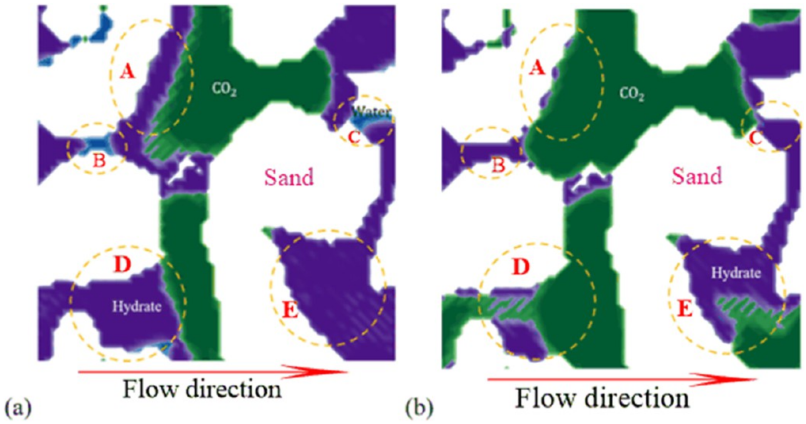

Figure 6. Impact of hydrate growth patterns on pore morphology and permeability in CO_2-water two-phase flow simulation: (a) at 274 K and (b) at 280 K. Adapted with permission from ref 24. Copyright 2022, Elsevier.

equilibrium, thermal properties, and heat flux during phase change, offering insights into hydrate stability under varying conditions. These techniques collectively advanced the comprehension of gas hydrate behavior, providing detailed structural, kinetic, and thermodynamic information crucial for optimizing gas hydrate recovery strategies, understanding geological stability, and exploring gas hydrates as a potential energy resource.

Lu et al.[24] investigated the complex process of CO_2 hydrate formation within microscopic sand pores, aiming to understand its influence on permeability. The research uses the phase field method and lattice Boltzmann method to examine the relationship between two-phase flow dynamics, hydrate formation rates, and resultant changes in porous structure. The material specifications involve meticulously recreating sand grains using scanned images and growth methodologies to achieve the desired porosity. Notably, the study acknowledges the limitation of a relatively small computational domain compared to the representative element volume (REV) in natural porous media. Despite this, the sand sediments studied are remarkably homogeneous. The methodology includes comprehensive simulations of two-phase flow involving CO_2 and water, considering factors like initial phase distributions, pressure gradients, and temperature variations. The nuanced observations reveal that the hydrate formation rate significantly influences pore morphology. Slower formation rates tend to lead to a pore-filling type of hydrate, impacting solid-phase surface area and pore size, thereby reducing effective permeability. The findings offer insights into the relationship between hydrate morphology, flow dynamics, and resultant permeability changes. The visual representations illustrate how different hydrate growth patterns—grain coating or pore filling—impact the solid-surface area and pore spaces, as shown in Figure 6(a,b). Notably, slower formation rates facilitate more extensive pore-filling, resulting in smaller pore spaces and larger solid-phase surface areas, consequently reducing effective permeability. At position A in Figure 6(a), hydrate occurs by covering the surface of sand grains. A thin hydrate coating can also be noticed in place D (b). In (a), the gaps at locations D and E are filled with large hydrate clumps; in (b), injected CO_2 is present at the same positions. In addition, the hydrate masses in locations B and C in (a) capture water patches, but in (b), the same voids at locations B and C are filled with hydrate. These findings suggest that a higher rate of hydrate formation in certain areas prevents some residual water patches from contacting CO_2 and ceasing to convert it into hydrate. In scenario (b), where hydrates are formed slower, the injected CO_2 displaces water and remains in the pathway as CO_2. Since CO_2 cannot transform into hydrates without water, this leads to a discrepancy in the normalized effective permeability across the solid phase surface area and the pore size.

The study raises intriguing correlations between hydrate formation rates, flow speed, and resulting pore morphology, shedding light on potential mechanisms behind the observed permeability changes. It suggests that the varying rates of hydrate formation under different flow conditions significantly affect the hydrate morphology, ultimately influencing permeability changes within the porous medium, with slower formation rates predominantly leading to a pore-filling type of hydrate growth. This distinction in growth patterns significantly influenced the solid-phase surface area and pore size within the medium, as shown by Figure 7, consequently

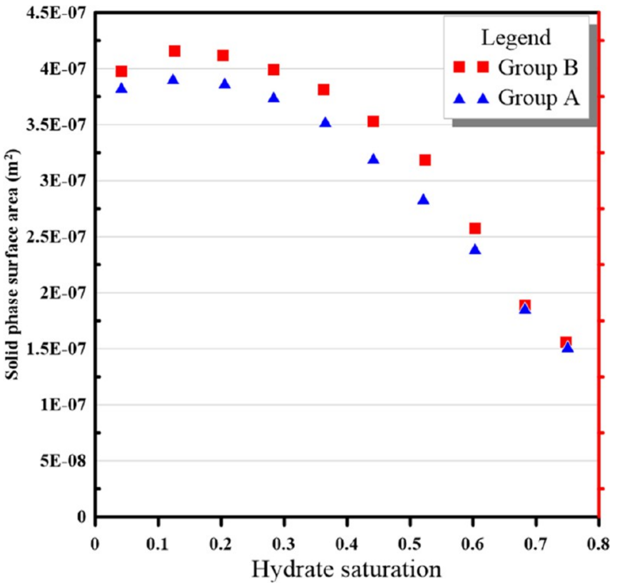

Figure 7. Correlation of hydrate formation kinetics with pore morphology: insights into permeability changes in porous media. Group A hydrates with a more grain-coating morphology, and Group B hydrates with a more pore-filling morphology. Redrawn with permission from ref 24. Copyright 2022, Elsevier.

driving notable changes in effective permeability. The observed correlation between hydrate formation kinetics and resultant pore morphology shed crucial light on the mechanisms underpinning alterations in permeability within these complex systems. Additionally, the research indicates that while these factors impact permeability, the differences observed might not be substantial enough to disregard existing mathematical models. Even amidst the complexities of two-phase flows during hydrate formation, established models for normalized effective permeability could still hold relevance for reservoir-scale simulations.

Also, Sadeq et al.[32] studied the complex behaviors of CO_2 hydrate formation in subseafloor sediments using advanced imaging techniques and accurate experimental settings. The investigations involved small cylindrical Bentheimer sandstone plugs, recognized for their homogeneity and high porosity, primarily consisting of quartz. The plugs conducted a controlled experiment using high-pressure vessels, precise pumps injecting fluid, and a powerful μCT scanner for high-resolution 3D imaging. The experimental procedure commenced with saturating the sample with a sodium iodine brine solution before injecting CO_2 gas at specific pressure and flow rates to create a partially saturated porous medium. Subsequent temperature reduction induced CO_2 hydrate formation, observed and tracked using μCT imaging techniques. The resulting images unveiled vital insights into the distribution, morphology, and interface interactions of various components within the sandstone pores, such as grains, brine, CO_2 gas, and hydrate. The μCT imaging highlighted a distinctive distribution pattern of CO_2 hydrate within the pore space, primarily residing at the interface between brine and gas yet notably avoiding direct contact with the grain surface, as shown in Figure 8. This behavior resonated with established models, indicating a layer of free brine coating the grain surface, suggesting the brine as the wetting phase and inhibiting direct hydrate contact with the grain. This observed preferential hydrate nucleation at the water−gas interface is crucial, impacting the sealing capacity of the sediment, limiting CO_2 flux and potentially affecting methane recovery rates.

Moreover, the study explored the changes in P-wave velocities before and after hydrate formation, clarifying a 7−8% increase posthydrate formation, remarkably increasing from 2880 to 3100 m/s under a confining pressure of 8 MPa, as shown in Figure 9. This aligns with Waite et al.[33] concept of free-floating hydrates, attributing the velocity changes merely to modifications in pore fluid bulk modulus rather than the sediment matrix stiffness. During the initial phase, the velocity remained constant. It did not show any substantial variation until the formation of CO_2 hydrate nuclei commenced, illustrated by Figure 10. The progressive velocity increase provided evidence of hydrate formation within the pore space. The process of hydrate formation reached completion after the velocities became stable.

Statistical analysis of CO_2 hydrate and gas clusters provided crucial insights into their size distributions and surface area−volume relationships. These patterns revealed the presence and spatial arrangement of various-sized clusters within the sediment's pore network, as shown in Figure 11. Notably, the prevalence of different-sized clusters, particularly smaller versus larger clusters, offered valuable insights into how gas molecules were trapped within the hydrate structures. Moreover, the assessment of surface area−volume ratios proved to be a critical factor in understanding the dissociation rates during gas exchange processes, particularly CO_2−CH_4 exchange.[34] The lower surface area-volume ratios inferred from the analysis implied that the relationship between the exposed surface area of the clusters and their volumes was relatively smaller. This revelation holds profound implications: it suggested that gas dissociation, a crucial aspect of gas recovery, would occur slower due to the reduced exposed surface area. Consequently, these findings directly affect hydrate-rich sediments' production rates and storage capacities. Lower dissociation rates during gas exchange processes, as indicated by the lower surface area-volume ratios, imply a slower release of gases, impacting the efficiency of gas recovery mechanisms. Additionally, this phenomenon might decrease the overall storage capacity of sediments for gases like carbon dioxide, a crucial consideration for industries involved in carbon capture and storage endeavors. Therefore, the findings underline the significance of understanding cluster distributions and their surface area-volume relationships in devising efficient gas recovery strategies and evaluating the feasibility of storing gases within hydrate-bearing sediments. The slower dissociation rates indicated by these characteristics highlight the need

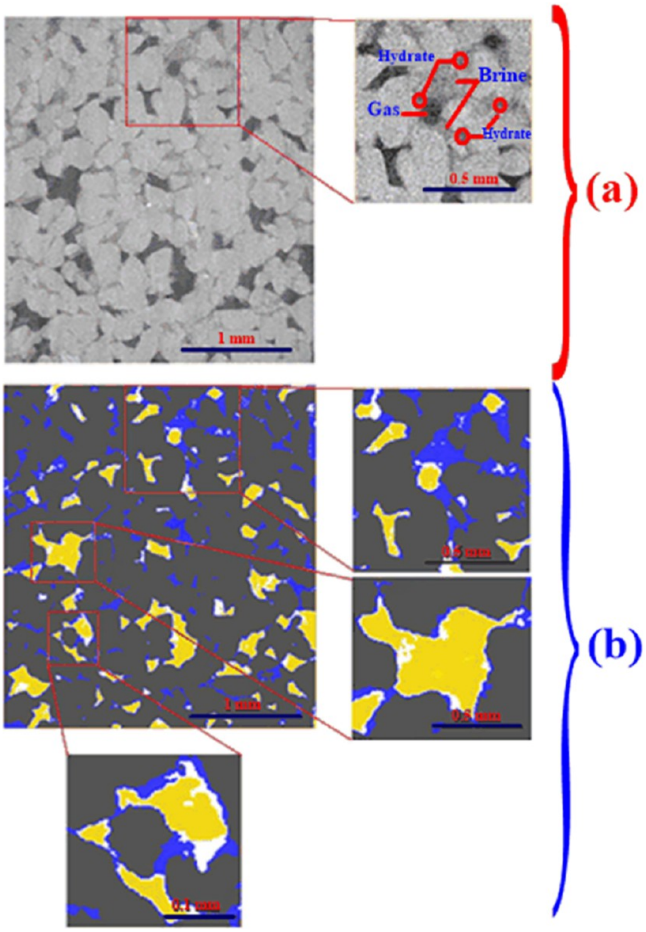

Figure 8. μCT 2D slices imaging reveals unique CO_2 hydrate distribution: insights into pore space behavior and impact on sediment sealing and gas flux: (a) raw images and (b) cemented images. Within the raw images, CO_2 appears black, whereas hydrate is depicted as dark gray. Brine is slightly lighter in color, and a light gray hue represents sandstone. The segmented images show grain particles as dark gray, hydrates as white, brine as blue, and CO_2 gas as yellow. Adapted with permission from ref 32. Copyright 2018, Elsevier.

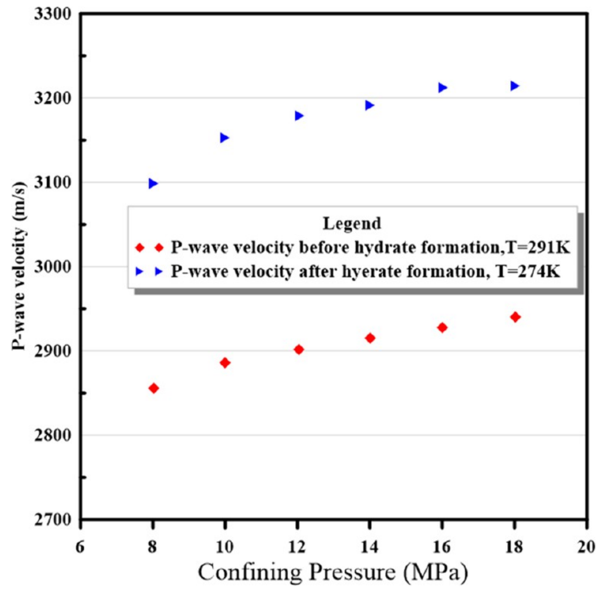

Figure 9. Effect of hydrate formation at pore pressure of 3 MPa on Bentheimer sandstone P-wave velocities: insight into bulk modulus influence. Redrawn with permission from ref 32. Copyright 2018, Elsevier.

for nuanced approaches to maximize gas recovery and optimize storage capacities in such geological.

References 24, 31, and 32 collectively highlight the necessity of understanding the complex interaction between sediment properties, hydrate morphology, and flow dynamics within pore-scale environments for informed decision-making regarding CO_2 hydrate storage strategies.

2.1.2. Sediment's Chemical Composition Influence on CO_2 Hydrate Nucleation and Growth. The formation mechanisms of CO_2 hydrates in subseafloor saline sediments are influenced by various sediment properties, particularly the sediment's chemical composition, as described in Table 2. The chemical composition of sediments alters the surface properties, affecting CO_2 molecule adsorption and creating favorable conditions for hydrate formation.[35] Variations in composition influence nucleation kinetics and crystal growth rates, impacting CO_2 hydrate formation and stability.[36]

Sediments rich in clay minerals, such as illite and smectite, possess unique properties influencing CO_2 hydrate formation.[42,43] These clays often reveal a high specific surface area and abundant interlayer spaces capable of adsorbing CO_2 molecules.[42] Consequently, the presence of clay minerals facilitates the initial adsorption of CO_2 onto sediment surfaces, serving as nucleation sites for hydrate formation. Moreover, the mineralogical composition plays an essential role in determining the availability of pore space within sediments. For instance, sediments composed of predominantly quartz or carbonate minerals may have relatively lower specific surface areas than clay-rich sediments.[44] However, the interconnected pore networks within these sediments can still provide sites for CO_2 molecules to accumulate and initiate hydrate formation through mechanisms distinct from those in clay-rich sediments.[45] In addition, variations in grain size and sediment porosity influence CO_2 hydrate formation mechanisms. Fine-grained sediments offer larger surface areas per unit volume, potentially enhancing CO_2 adsorption and facilitating nucleation.[46] Conversely, coarser sediments might provide fewer nucleation sites but could foster longer-term stability for formed hydrates due to reduced diffusion rates.[16,36] The interplay between sediment properties and CO_2 hydrate formation is complex. The affinity of sediments to adsorb CO_2, the availability of nucleation sites, and the pore structure collectively dictate the kinetics and stability of hydrate formation.[15,43,47] Thus, understanding these mechanisms is crucial for predicting and optimizing CO_2 storage potential. Zhang et al.[36] investigated the impact of sediment properties, particularly particle size, on forming gas hydrates—a crucial area for exploring marine gas hydrate deposits. The investigation involved experiments using a high-pressure visualized reactor, and six sediment samples labeled A through F varied in particle size distributions—ranging from clay to silt and sand-dominated compositions from the Shenhu Sea area in the South China Sea. Medium A consists of 39% clay, 51.5% silt, and 10.02% sand, with a medium particle radius of 8.68 μm. Medium B exhibits 42.33% clay, 50% silt, and 8.04% sand, with a slightly smaller radius of 7.64 μm. Medium C has a significantly higher clay content at 76.8%, with 21.53% silt, 2% sand, and the smallest particle radius of 0.357 μm among the mediums discussed. Medium D consists of 62.8% clay, 36% silt, and 1.3% sand, with a particle radius of 1.45 μm. Medium E has 48.3% clay, 50.7% silt, 1.03% sand, and a medium particle radius of 4.03 μm. Lastly, Medium F comprises 36.5% clay, 60% silt, 4% sand, and a particle radius of 6.72 μm. The experiments revealed a distinctive pattern in the formation of

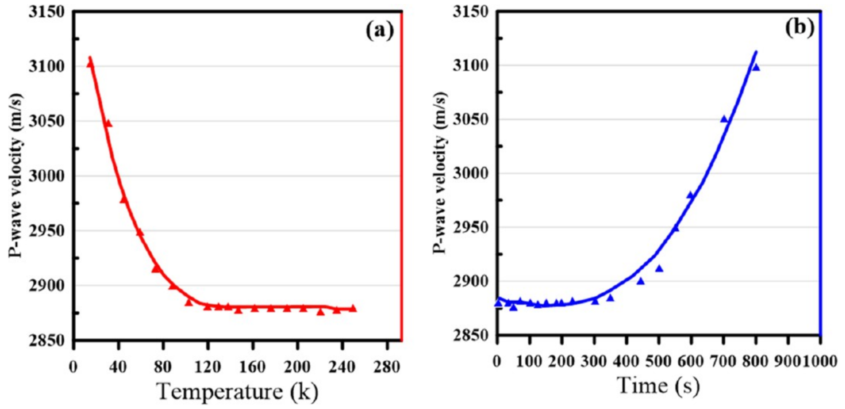

Figure 10. Velocity evolution during CO_2 hydrate formation: from stability to nucleation and completion at a confining pressure of 8 MPa as a function of (a) temperature (K) and (b) time (s). Redrawn with permission from ref 32. Copyright 2018, Elsevier.

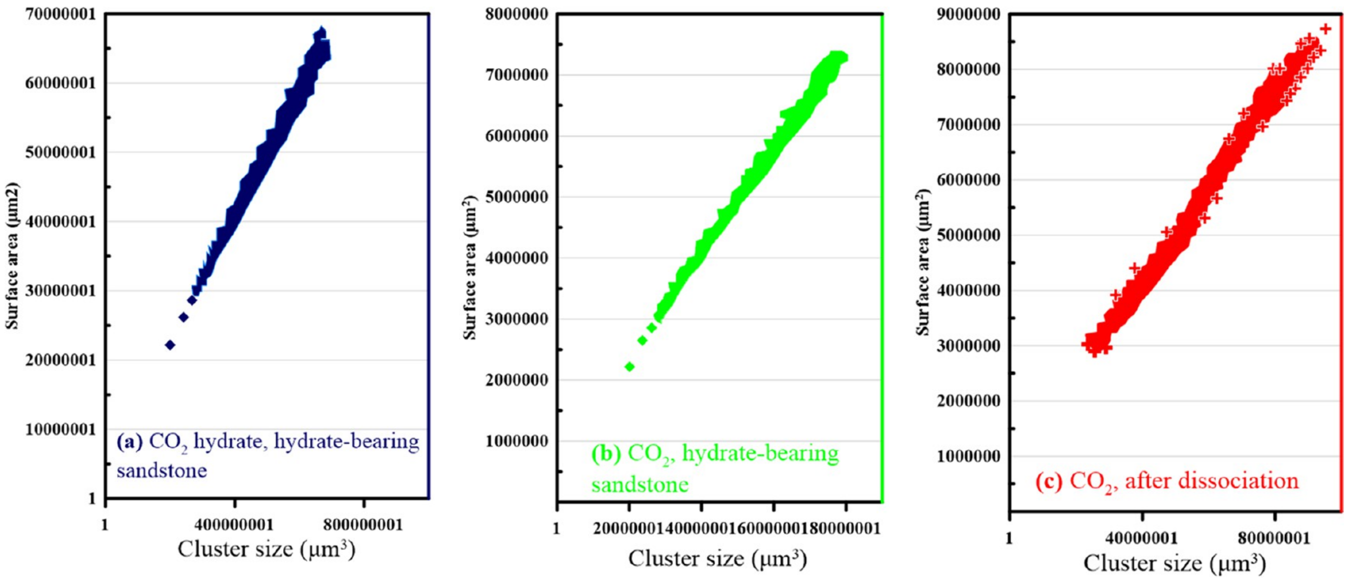

Figure 11. Insights into CO_2 hydrate and gas cluster distributions: implications for gas recovery and storage capacities in sedimentary environments. (a) The Bentheimer sample contains CO_2 hydrates, (b) clusters of CO_2 gas before hydrate dissociation, and (c) clusters of CO_2 gas following hydrate dissociation. Redrawn with permission from ref 32. Copyright 2018, Elsevier.

hydrates within sediment matrices. Hydrate generation showed a rapid initial phase within the sediment, spreading along its surfaces and rapidly expanding in volume, suggesting that specific components or characteristics within the sediment, beyond particle size alone, might play a catalytic role in facilitating the initiation and growth of hydrates. It implies that the sediment's chemical composition might contain elements or compounds that actively interact with the introduced CO_2 gases, promoting rapid and substantial CO_2 hydrate development. Observations indicated that sediment particle size was fundamental in dictating the nucleation induction time required for hydrate formation initiation. Larger particle sizes facilitated quicker nucleation induction times, promoting more concentrated and predictable hydrate formation. Conversely, smaller particles led to more erratic and extended nucleation induction times, as described in Figure 12. This study offers valuable insights into understanding the complexities of hydrate formation within sedimentary environments. It emphasizes the role of sediment properties, particularly particle size, in governing the kinetics of CO_2 hydrate formation. The findings suggest that sediment particle size profoundly influences the ease and predictability of hydrate formation, providing crucial implications for assessing CO_2 hydrate storage potential and behavior within diverse geological settings.

2.1.3. Comparative Analysis of Sediment-Specific Influence on CO_2 Hydrate formation. Comparing the influence of microstructural characteristics (as shown in Table 1) and sediment chemical composition (Table 2) on CO_2 hydrate formation in subseafloor saline sediments, several deductions can be drawn as follows: (1) Microstructural analysis: High porosity and fine grains enhance the potential for CO_2 hydrate nucleation because of the greater surface area. However, permeability, pore connectivity, and mineralogical components also play significant roles in determining the rate and distribution of hydrate formation. (2) Chemical composition: Sediment composition is a key in CO_2 molecule adsorption, impacting nucleation kinetics and growth rates. Minerals such as clays facilitate CO_2 adsorption due to their high surface area and serve as prospective nucleation sites, while salinity affects CO_2 solubility and hydrate formation rates.

2.2. Sediment Modification Techniques for Enhanced CO_2 Hydrate Storage.

Sediment surface modification techniques offer various possibilities to modify sediment properties for optimized CO_2 hydrate storage systems, such as surface roughening, chemical functionalization, electrokinetic methods, nanotechnology-based modifications and thermal treatment methods. By strategically altering surface characteristics, enhancing nucleation sites, and improving interaction potentials, these methods hold promise in advancing the feasibility and efficacy of subseafloor CO_2 hydrate storage as a viable carbon capture and storage (CCS) solution.

2.2.1. Surface Roughening (SR). SR increases the available surface area for hydrate formation.[48,49] By introducing controlled roughness to the sediment surface, such as mechanical abrasion or chemical treatments, the contact area for CO_2 molecules and water can be significantly expanded.[49] This modification facilitates nucleation sites for hydrate formation, promoting higher storage capacities and quicker formation kinetics. Rao et al.[49] investigated the intricate dynamics of CO_2 hydrate growth in confined spaces, demonstrating the critical influence of surface properties, especially interfacial tension, on the spreading behavior of CO_2 hydrates on solid substrates. The study investigates CO_2 hydrate formation within restricted spaces created by parallel silicon wafers. These spaces, designed to mimic natural sediment conditions, allowed observation of CO_2 hydrate growth and spreading on solid surfaces. The materials used included original silicon wafers and those pretreated using different methods like PFDTES solution, crude oil, and piranha solution to alter their surface properties. Findings revealed distinctive behaviors in CO_2 hydrate growth: initial appearance at the gas−liquid interface followed by spreading across the solid surface, as shown in Figure 13. The spreading phenomenon suggested a continuous formation mechanism at the advancing edge, indicating a potential water transport channel facilitating ongoing hydrate generation. Surface

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Table 2. Summary of Synthesis of Research Findings on Impact of Sedimentary Chemical Composition on CO_2 Hydrate Nucleation and Growth Dynamics

Factor	Influence on Nucleation	Influence on Growth	Detailed Findings	Refs
Clay Content	High clay content can inhibit nucleation due to reduced pore water activity and the internal energy of confined crystals.	Clay content impacts the kinetics of CO_2 hydrate formation and storage capability.	Hydrate growth is inhibited in fine-grained sediments due to hydrophilic mineral surfaces and small crystal confinement.	37
Salinity	Salinity can affect the hydration shells around CO_2 molecules, essential for nucleation.	Alters the structural stability of CO_2 hydrates.	Salinity significantly reduces the hydrate formation kinetics; however, presence of promoters like amino acids, such as L-tryptophan or L-leucine, can offset the salinity inhibitory effect and enhance the rate.	37, 38
Sediment Particle Size	Smaller grain sizes can lead to a faster nucleation rate of CO_2 hydrate.	Larger grains may hinder rapid hydrate growth.	Small grain size leads to faster and more abundant formation of hydrates, while fine sediment can hinder replacement due to higher stability of hydrates.	39
Water Saturation	Adequate water supply is crucial for nucleation, and nucleation is critical in freshwater environments.	Water saturation affects the spreading of hydrates.	With an adequate supply of mixed gas, nucleation can prompt rapid hydrate growth and spread.	40
Presence of Minerals	Certain minerals like montmorillonite can facilitate CO_2 hydrate nucleation.	Mineral surfaces may influence the morphology of hydrates.	Heterogeneous nucleation on the surfaces of clay minerals like montmorillonite is significant for CO_2 storage in marine sediments.	41

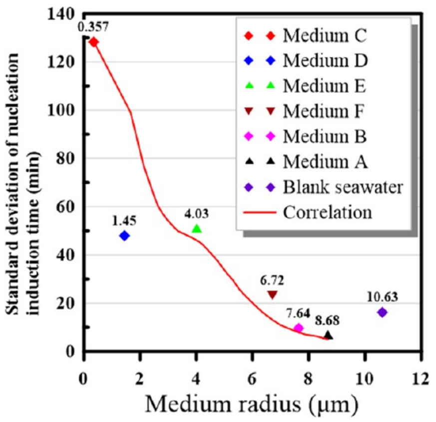

Figure 12. Effect of sediment particle size on hydrate nucleation: impact on formation initiation. Data retrieved from ref 36. Copyright 2018, Elsevier.

property modifications influenced hydrate formation significantly. Hydrophobic surfaces resulting from PFDTES solution or crude oil pretreatment hindered hydrate spreading, while hydrophilic surfaces induced by piranha solution supported hydrate film expansion.

Interfacial tension plays a crucial role in the behavior of CO_2 hydrate formation on solid surfaces. Traditionally, factors like pressure and temperature are considered primary influencers in chemical reactions, but in Rao et al.[49] study, the interfacial tension between the hydrate and silicon wafer emerged as a critical determinant in the growth dynamics of CO_2 hydrates. Unlike the more conventional variables, interfacial tension significantly influenced the rate of hydrate spreading and the resulting film thickness, as shown in Figure 14. This emphasizes its unique and dominant role in shaping the behavior of CO_2 hydrate formation on solid surfaces. In this context, the interfacial tension acted as a regulatory force governing how rapidly the hydrate spread and how thick the resulting film became on the solid substrate. This effect was especially pronounced compared to the variations in pressure and temperature typically associated with influencing chemical reactions. The findings suggest that modifications in the interfacial tension between the hydrate and the solid surface significantly impacted the spreading rate and thickness of the formed CO_2 hydrate film.

Also, Asadi et al.[48] examined the impact of modified surfaces, specifically hydrophilic and hydrophobic, on the kinetics of tetrahydrofuran (THF) hydrate formation for CO_2 storage. The materials used included 304 stainless steel plates obtained from a Taiwanese company and THF purchased from Merck Company with a purity of 99.5%. The experimental setup involved laser surface texturing to create specific surface characteristics, ultrasonic treatment to remove surface contaminants, and an apparatus equipped with various sensors to record temperature, volume changes, and other parameters during hydrate formation at ambient pressure. The experiment focused on elucidating the modified surfaces' wetting behavior, surface morphology, and roughness. Wetting behavior analysis revealed changes in contact angles, demonstrating the intermediate model for the surfaces' behavior. Surface characterization through scanning electron microscopy (SEM) and atomic force microscopy (AFM) highlighted changes in surface morphology and roughness, influencing the hydrophobicity or hydrophilicity of the surfaces. The results

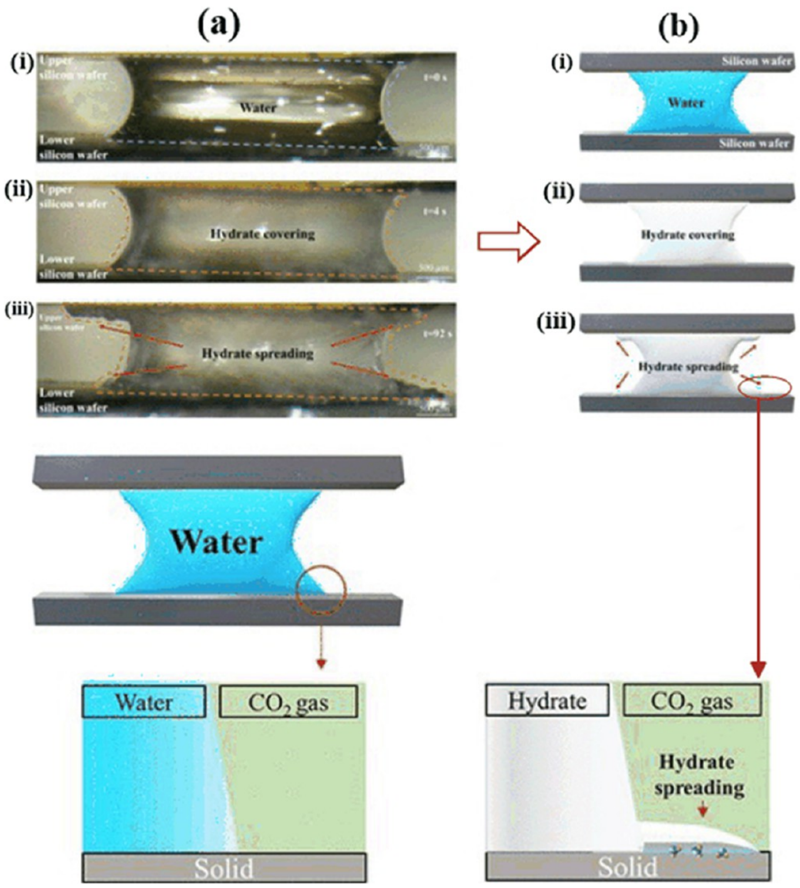

Figure 13. CO_2 hydrate growth dynamics: unveiling behavior patterns and potential formation mechanisms. (a) A sequence of consecutive images illustrating the process of CO_2 hydrate formation using a water droplet (i) confined between two silicon wafers: the hydrate film initially forms on the boundary between the gas and liquid phases (ii) and subsequently expands over the solid surface (iii). The blue dashed lines represent the water region, while the orange dashed lines indicate the hydrate profile. (b) The concept model illustrates the process of hydrate growth in a confined area, as deduced from panel (a): initial stage before hydrate formation (i), formation of a hydrate film covering (ii), and spreading of the hydration film (iii). Adapted with permission from ref 49. Copyright 2023, American Chemical Society.

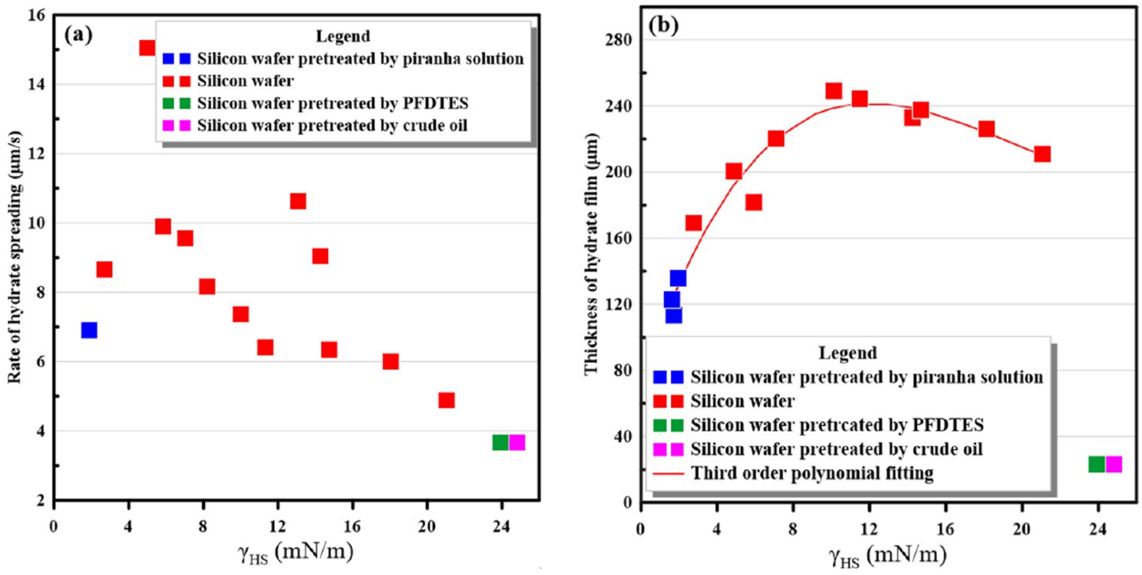

Figure 14. Interfacial tension's dominance: unveiling its vital role in CO_2 hydrate formation on solid surfaces. (a) Rate of hydrate spread and (b) thickness of hydrate film influenced by the interfacial tension between hydrate and silicon surfaces, observed on both untreated and pretreated silicon wafers. Redrawn with permission from ref 49. Copyright 2023, American Chemical Society.

indicated that modified surfaces significantly influenced the nucleation and growth of THF hydrate. Hydrophilic surfaces showed higher nucleation rates due to increased contact areas for water molecules, while hydrophobic surfaces showed

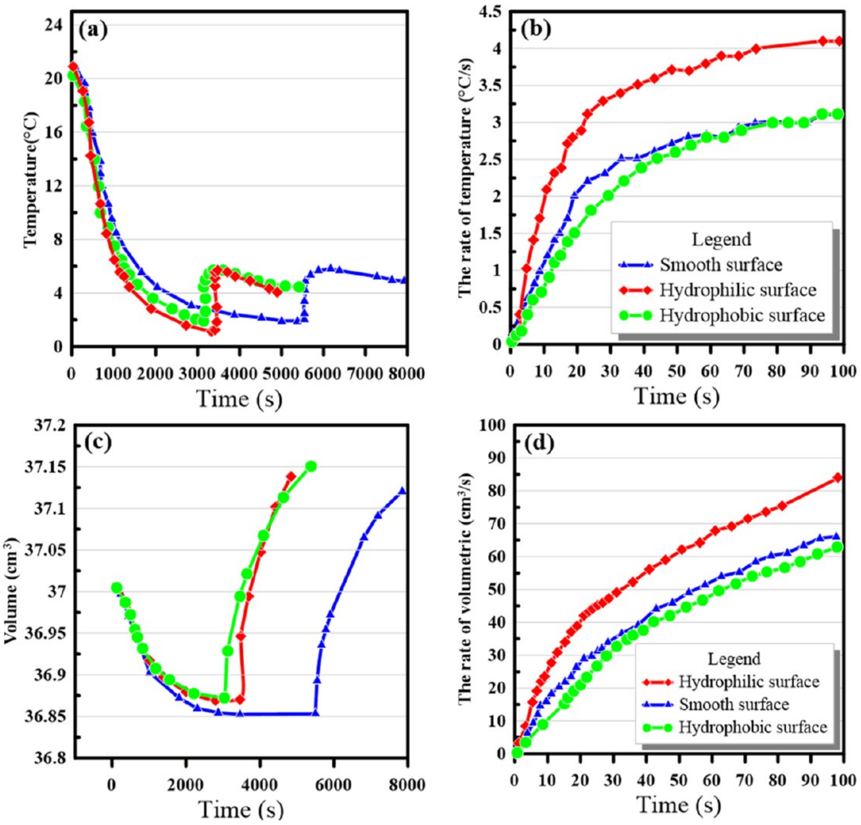

Figure 15. Surface modification effects on THF hydrate nucleation and growth: insights into hydrophilic and hydrophobic surface dynamics. (a) The overall temperature trend of the system, (b) temperature rate, (c) trend in volume changes of the H_2O-THF solution, and (d) volumetric rate. Redrawn with permission from ref 48. Copyright 2022, Elsevier.

contrasting behavior, as shown in Figure 15. Induction and relaxation times varied, indicating the stochastic nature of the process. Additionally, temperature and volumetric changes during hydrate formation revealed distinct trends for different surfaces, with hydrophilic surfaces displaying enhanced nucleation speed, as clarified in Figure 15. However, despite the observable impact of surface characteristics on hydrate formation kinetics, the relationship between surface roughness and induction/relaxation times appeared nonreproducible due to the stochastic nature of these parameters, as demonstrated in Figure 16. The study concluded that while surface modifications influence THF hydrate formation, the complex, stochastic nature of the process makes it challenging to establish direct correlations between surface properties and specific kinetic parameters.

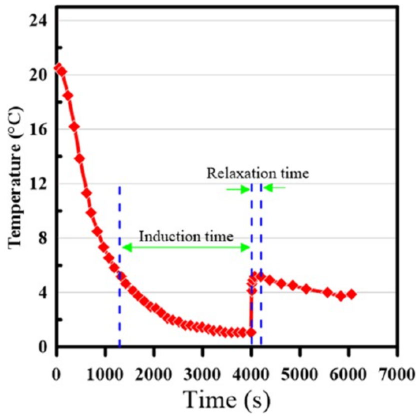

Figure 16. Surface influence on THF hydrate formation kinetics for a smooth surface. Redrawn with permission from ref 48. Copyright 2022, Elsevier.

The complex relationship between surface characteristics and hydrate formation rate is highlighted by both refs 49 and 48 investigations. Their findings emphasize the importance of fully understanding surface properties in regulating gas hydrate behavior, which could improve hydrate management, energy storage, and evaluations of geological stability. However, while these studies provide crucial insights, they also highlight the complexity and stochastic nature of the hydrate formation process, indicating the need for further research to elucidate comprehensive correlations between surface properties and specific kinetic parameters.

2.2.2. Chemical Functionalization. Chemical functionalization involves coating sediment surfaces with compounds that promote CO_2 adsorption and subsequent hydrate formation.[26,50,51] Materials like porous polymers, zeolites, or specific surfactants can be applied to modify sediment surfaces, as described in Table 3. These substances offer active sites for CO_2 molecules to adhere to, accelerating the hydrate formation and enhancing storage efficiency.

2.2.3. Chemical Additives for Sediment Modification and Enhanced CO_2 Hydrate Storage. Chemical additives play an essential role in sediment modification by manipulating sediment properties to enhance the stability of CO_2 hydrate formation, which is crucial for improved CO_2 hydrate storage. Research indicates that the use of chemical additives can markedly reduce induction time and elevate both the

Table 3. Summary of Materials for Chemical Functionalization Enhancing CO_2 Adsorption and Hydrate Formation on Sediment Surfaces

Material	Example	Description	Function	Benefits	Refs
Porous Polymers	Polymeric Foam	Porous polymers possess a high surface area with interconnected voids, providing ample active sites for CO_2 molecules to adsorb and initiate hydrate formation.	Offer a vast surface area conducive to CO_2 adsorption	Increased surface area enhances CO_2 adsorption and subsequent hydrate formation	52
Zeolites	Zeolite 13X	Zeolites are crystalline, microporous aluminosilicates with well-defined pore structures. Their uniform pore sizes facilitate CO_2 adsorption and enable efficient nucleation of gas hydrates.	Provide uniform pore structures conducive to CO_2 adsorption	Controlled pore sizes enhance CO_2 adsorption and hydrate formation	53
Specific Surfactants	Fluorinated Surfactants	These surfactants modifysediment surfaces by reducing surface tension, facilitating CO_2 molecule interactions and aiding in forming stable hydrate structures at the interface.	Reduce surface tension, promoting CO_2 molecule interactions	Improved stability of formed hydrates at the sediment interface	54

formation rate and gas storage capacity of CO_2 hydrates, leading to a more industrially viable storage solution for CO_2 emissions and global warming mitigation efforts.[55] Specifically, the nucleation and growth of CO_2 hydrates are enhanced by strengthening the hydrogen-bonding network among water molecules or creating mass transfer pathways for accelerated movement of water and CO_2 molecules to the growth site.[47] Thermodynamic promoters have been shown to induce a three-stage hydrate formation process: the creation of promoter hydrates, the adjustment of crystal size, and the induction of CO_2 hydrate formation.[56] Nanoparticles such as silica (SiO_2) have been found to enhance CO_2 storage efficiency by promoting these mechanisms.[20] Furthermore, altering the water chemistry has significant consequences on the microfabric and micromechanical properties of sediments, influencing their capacity to support hydrate formation.[57]

Using chemical additives offers a range of strategies for modifying sediment properties to maximize CO_2 storage efficiency. One innovative method involves using surfactants or surface-active agents as chemical additives. Surfactants possess unique properties that can alter interfacial tensions between CO_2, water, and sediment grains, influencing the nucleation and growth of CO_2 hydrates.[58] By selectively adsorbing onto sediment surfaces, surfactants can facilitate the formation of a stable hydrate phase, effectively enhancing CO_2 storage capacity within the sediment matrix. Moreover, certain surfactants can modify sediment wettability, promoting CO_2 infiltration and hydrate formation in specific sediment types.[58,59] Another approach involves polymers as chemical additives to modify sediment properties for optimized CO_2 hydrate storage. Polymers can alter sediment permeability and porosity, influencing CO_2 transport and hydrate formation.[58] By selectively modifying the pore network within sediments, polymers can enhance CO_2 diffusion and adsorption, facilitating the nucleation and growth of CO_2 hydrates.[60,61] Additionally, polymers can aid in stabilizing the formed hydrate phase, mitigating dissociation and ensuring prolonged storage stability.[62] Also, introducing mineral-based additives, such as zeolites, specific metal oxides, and clays like montmorillonite and kaolinite, represents a novel possibility for sediment modification in CO_2 hydrate storage systems.[51] Minerals with particular surface properties can act as nucleation sites for CO_2 hydrate formation, accelerating the process and enhancing storage efficiency. Additionally, these minerals may possess adsorption capacities for CO_2 molecules, contributing to increased CO_2 uptake and subsequent hydrate formation.[51,63] Such mineral additives offer the potential to modify sediment properties, promoting favorable conditions for robust CO_2 hydrate storage. On top of that, nanoparticles offer an innovative approach to enhancing the efficiency of CO_2 hydrate storage in subseabed saline sediment formations by manipulating sediment properties at the micro level. Silicon dioxide (SiO_2) nanoparticles, for instance, have been shown to improve CO_2 storage efficiency by providing a framework that supports a better gas-to-hydrate conversion rate.[20,64] The enhancement can be attributed to several key factors, such as the potential to facilitate mass transfer, which plays a crucial role during hydrate formation by moving CO_2 from the gas phase to the water phase more efficiently.[64] This is particularly important as the nucleation process begins and continues to promote the growth of CO_2 hydrates.[64] Additives like graphite nanoparticles not only help shorten the induction time for hydrate formation but also provide continuous support for the

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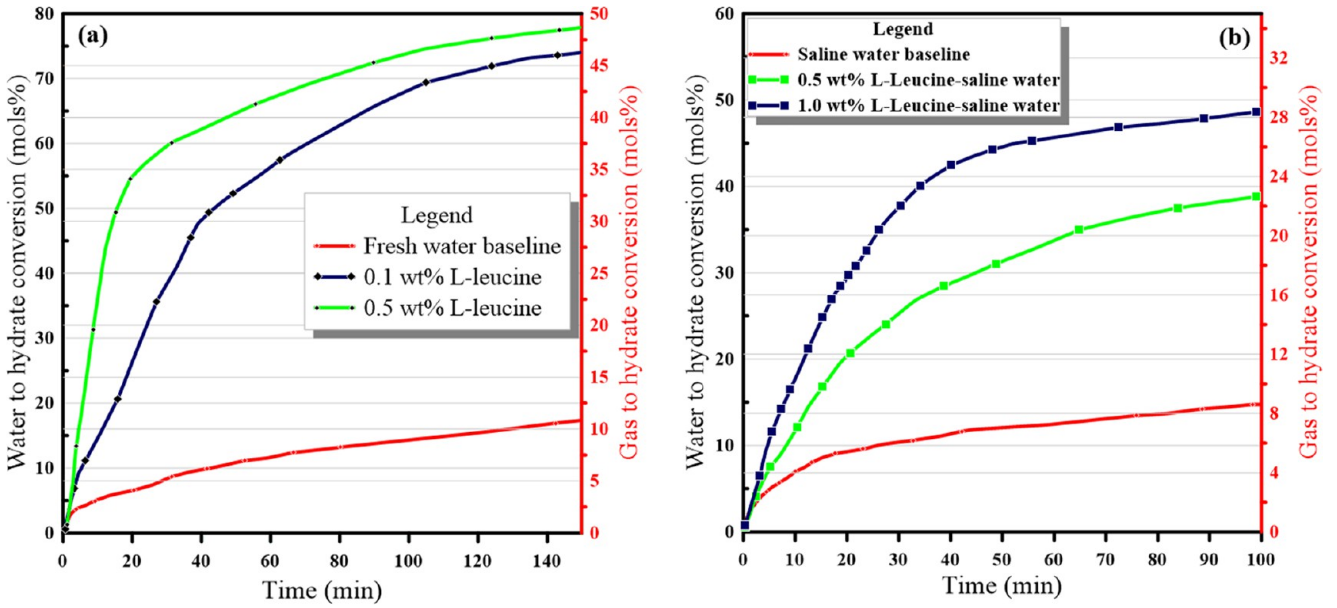

Figure 17. (a) The effects of L-leucine concentrations of 0.1 and 0.5 wt % on the hydrate formation rate in a nonsaline system. The first nucleation point occurs at time zero. (b) Illustration of water-to-hydrate and gas-to-hydrate conversion in a saline solution of 3.5 wt % NaCl with 0.5 and 1.0 wt % L-leucine. Also, the first nucleation point is at time zero. Redrawn with permission from ref 38. Copyright 2022, American Chemical Society.

hydrate structure to grow by creating an environment that enhances gas−liquid mass transfer.[17] Moreover, the presence of nanoparticles modifies the kinetic process by altering the local structure of water molecules, promoting the formation of a hydrogen-bonding network that is conducive to the rapid creation of CO_2 hydrates.[47] This microscopic structural support, alongside the factors mentioned above, maximizes CO_2 storage efficiency by ensuring the steadfast and ample formation of CO_2 hydrates within sedimentary matrices. Additionally, specific interaction properties of the nanoparticles with both hydrates and sediment components can lead to an improvement in the structural stability of the hydrate−sand-nanoparticle systems,[65] which is crucial for the long-term storage and stability of CO_2 hydrates.

Song et al.[20] studied enhancing CO_2 storage in marine hydrates through various sediment modification techniques. The study used the nuclear magnetic resonance (NMR) technique to analyze hydrate distribution and phase transition processes. The materials used include CO_2, seawater with a 1% salinity, silicon dioxide (SiO_2) nanoparticles, sodium dodecyl sulfate (SDS), and specific sand types to create uniform marine sediments. The experimental setup involves a 12-MHz proton NMR system, a high-pressure vessel, and ISCO pumps for injecting CO_2 and seawater. Findings revealed that high initial water saturation and suitable temperatures and pressures in marine sediments facilitate efficient CO_2 storage. Chemical additives, such as SiO_2 nanoparticles and SDS, influenced pore water distribution but minimally affected bound water in small pores. SiO_2 nanoparticles at 0.15 wt % improved water conversion percentage and CO_2 storage efficiency by 49.2% and 4.17%, respectively, compared to pure seawater in 8-h tests. The study further explored the impact of sediment moisture content, storage pressure, and temperature on CO_2 formation. High initial water saturation enhanced CO_2 storage, while higher pressures and suitable temperatures improved storage capacity. SiO_2 nanoparticles accelerated water conversion and increased CO_2 storage efficiency, indicating that proper sediment conditions and additives fundamentally enhance CO_2 storage in marine hydrates. These insights contribute to potential applications of kinetic additives for efficient CO_2 storage.

Gautam et al.[38] investigated the complex mechanisms of CO_2 hydrate formation and growth, analyzing the impact of several conditions on this phenomenon. The study used a meticulously designed setup with specific materials—an ultrapure CO_2 gas cylinder, sodium chloride (NaCl), L-leucine, and silica sand of particular dimensions—combined with deionized water. This experimental apparatus, a high-pressure packed bed reactor, facilitated precise pressure and temperature control, which is essential for studying hydrate formation. The experiments followed a systematic procedure: mixing liquid samples with silica sand in the reactor, pressurizing it with CO_2, monitoring pressure and temperature changes, and subsequently dissociating the hydrates. Calculations involved determining gas consumption, hydrate conversion, gas recovery, and hydrate formation rate, offering a comprehensive understanding of the process dynamics. The findings unfolded intriguing insights. Salinity was identified as a significant factor impeding hydrate conversion, with a 4-fold reduction observed in saline systems compared to freshwater. However, adding L-leucine, particularly in saline environments, remarkably intensifies hydrate formation rates, significantly enhancing water-to-hydrate and gas-to-hydrate conversions, as described in Figure 17. Figure 17(a) indicates that adding 0.1 wt % L-leucine to freshwater increased hydrate formation by six times. L-Leucine may have promoted hydrate formation initially as a kinetic promoter. The study also studied how salinity affects CO_2 hydrate formation, as shown in Figure 17(b). According to the study, saline water with 3.5 wt % NaCl affected formation kinetics. The hydrate conversion rate dropped to 28% of freshwater levels due to salinity. Despite this inhibitory effect, water salts assisted nucleation, lowering hydrate growth induction times. Induction time is the time until hydrate nuclei appear. This suggests that saline surroundings may boost hydrate nucleation. L-Leucine increased hydrate growth and water-to-hydrate conversion. With 0.1 wt % L-leucine, freshwater water-to-hydrate conversion was 73%. Approximately 73% of water molecules became hydrates. In a saline solution with 1.0 wt % L-leucine, water-to-hydrate conversion was 50%—the conversion process enhanced, suggesting L-leucine efficiently converted water molecules into hydrate structures. L-Leucine also altered gas-to-hydrate conversion in addition to water-to-hydrate conversion. CO_2 gas molecules become solid hydrates through gas-to-hydrate conversion. The researchers found that a gas-dominated reactor converted less gas to hydrate. Despite gas presence, L-leucine converted 45–48% of gas in freshwater and 30% in saline water with 1.0 wt %. L-Leucine boosted water-to-hydrate and gas-to-hydrate conversion rates, increasing CO_2 storage capacity. In the experimental procedures, adding 0.5 wt % L-leucine to freshwater increased CO_2 storage capacity to 250 mg/g of water, as described in Figure 18. This was around ten times higher than the baseline without L-leucine—saline water, with 1.0 wt % L-leucine stored 165 mg of CO_2 per gram of water.

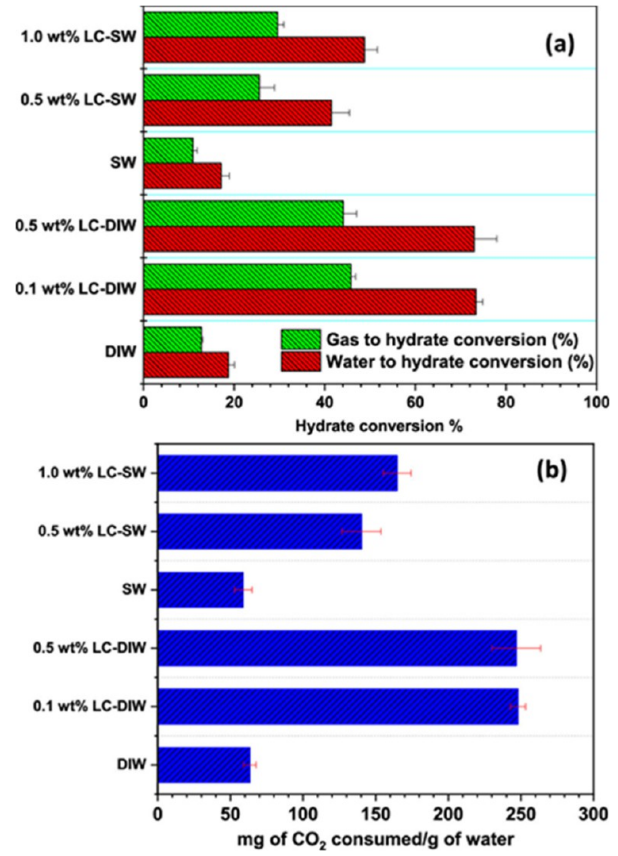

Figure 18. CO_2 uptake for hydrate formation: (a) converting water into hydrates or gas into hydrates and (b) the amount of CO_2 gas used relative to the amount of water used in the hydrate formation tests. DIW is deionized water. SW is seawater. and LC is L-leucine. Reproduced with permission from ref 38. Copyright 2022, American Chemical Society.

Moreover, Gautam et al.[38] examined how stable these hydrates were in different environments—saline (containing salt) versus nonsaline (without salt). The findings emphasized a crucial point: the amount of hydrates in the sediment played a key role in determining their stability during dissociation. Essentially, the more hydrates formed, the more stable the system was, impacting the subsequent temperature profiles during dissociation. When dissociation occurred, the temperature changes within the sediment were influenced by the amount of hydrates and their following breakdown, creating distinct temperature profiles, as shown in Figure 19. Regarding L-leucine, it is noteworthy for a few reasons. First, it is deemed environmentally friendly, implying that its use does not pose significant risks to the surrounding ecosystem, especially in subsea environments. Second, the study found that L-leucine had the remarkable ability to enhance the kinetics or speed of hydrate formation. This meant that when L-leucine was introduced into the system, the rate at which CO_2 hydrates formed was significantly accelerated. This augmentation of hydrate formation kinetics by L-leucine is crucial in subsea carbon capture and storage applications. By accelerating the formation of CO_2 hydrates, especially in saline environments where hydrate formation might otherwise be slower or less efficient, L-leucine could play a fundamental role. Faster formation of CO_2 hydrates translates to quicker and more effective carbon capture from the environment, facilitating the storage of CO_2 in a stable form.

The implications of these findings extend to practical applications, suggesting avenues for improving CO_2 hydrate formation rates and conversions, crucial for deploying hydrate-based carbon capture and storage (CCS) technologies at scale. The study's meticulous investigation offers promising prospects for leveraging additives like L-leucine to optimize the efficiency of hydrate-based CCS, an essential step toward sustainable carbon mitigation strategies.

Sahu et al.[66] investigated CO_2 hydrate formation kinetics using different inorganic emulsifiers, specifically sodium tripolyphosphate (STPP) and tetrasodium pyrophosphate (TSPP), in both stirred tank reactor (STR) and porous bed reactor (PBR) setups. The experimental setup involved reactors made of stainless steel designed to withstand high pressure, using water baths to maintain a consistent temperature throughout the experiments. The process involved purging, gas injection, and subsequent monitoring of temperature and pressure changes during CO_2 hydrate formation and dissociation. The findings revealed that the addition of STPP and TSPP significantly influenced the induction time and kinetics of CO_2 hydrate formation. These additives showed promising results in reducing the induction time for hydrate nucleation, particularly STPP in pure water (PW) and TSPP in seawater (SW), as shown in Figure 20. This finding suggests that using these emulsifiers promoted the rate of CO_2 hydrate growth, converting more water into hydrates, ultimately partially offsetting the inhibitive effect of salts prevalent in saltwater. The nucleation phenomenon differed between the STR and PBR setups, impacting the temperature profiles during formation. STR exhibited more simultaneous hydrate crystal nucleation than the more distributed phenomenon in the PBR. Gas consumption and water-to-hydrate conversion were higher in pure water experiments than in seawater, consistent with the inhibiting effect of salts present in seawater. However, both STPP and TSPP improved gas uptake and water-to-hydrate conversion in seawater experiments, possibly due to the formation of byproducts aiding hydrate growth and countering the inhibitory effect of salts.

The study further emphasized the role of these additives in enhancing CO_2 hydrate formation kinetics, particularly STPP, which acted as a chelating agent, aiding faster growth even in seawater, as illustrated in Figure 21. The porous bed experiments revealed the effectiveness of silica sand particles

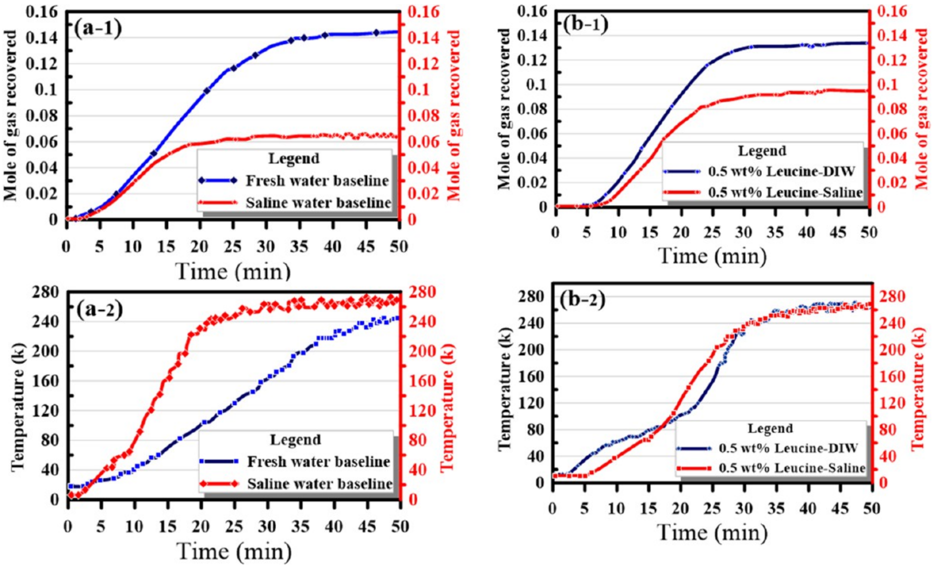

Figure 19. Number of gas moles attained during hydrate formation through thermal stimulation (a-1, b-1), attached with temperature profiles (a-2, b-2) reported during hydrate dissociation in saline and nonsaline systems. Redraw with permission from ref 38. Copyright 2022, American Chemical Society.

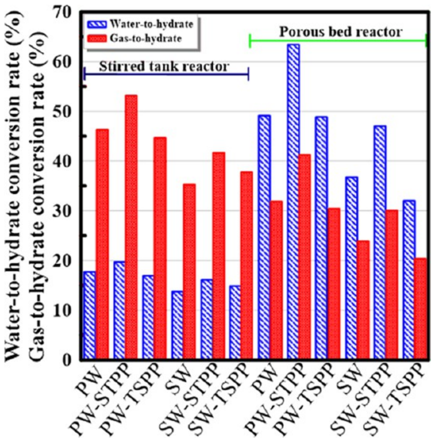

Figure 20. Conversion of water to hydrates and gas to hydrates in pure water (PW), seawater (SW), and synergic influence of integrated sodium tripolyphosphate (STPP) and tetrasodium pyrophosphate (TSPP) emulsifiers in PW and SW in both treated reservoir (STR) and porous bed reactor (PBR) systems. Redrawn with permission from ref 66. Copyright 2022, Elsevier.

in providing a larger surface area for better gas−liquid contact and subsequently facilitating hydrate formation. Thus, media porosity may affect hydrate formation. To boost CO_2 hydrate formation, the researchers advised combining STPP or TSPP with surfactants like sodium dodecyl sulfate (SDS). Surfactants modify gas−water contact to generate hydrates. In addition, the study discussed the potential application of these inorganic emulsifiers in sandstone reservoirs for CO_2 sequestration, proposing a conceptual injection well arrangement for efficient CO_2 sequestration through clathrate hydrates in subsea sediments, as illustrated in Figure 22. This proposed method aimed to establish continuous communication over a large distance within the reservoir to overcome heterogeneity issues. The proposed well arrangement involves using a pair of horizontal wells, which would provide the continuous injection of CO_2 gas and chemicals to enhance the formation of hydrates.

References 20, 38, and 66 underscored the potential of chemical additives and sediment modifications in optimizing CO_2 hydrate storage. The insights from these investigations pave the way for advancing hydrate-based carbon capture and storage (CCS) technologies, suggesting pathways for improving efficiency and addressing challenges associated with hydrate formation, stability, and subsequent gas release. The studies provide a foundation for further research and practical applications, offering promising possibilities for sustainable carbon mitigation strategies and efficient utilization of CO_2 hydrate storage in diverse geological settings.

2.2.4. Comparative Analysis of Sediment Modification Techniques for Enhanced CO_2 Hydrate Storage. Each sediment modification technique has its distinct mechanisms and benefits for enhancing CO_2 hydrate storage efficiency. Surface roughening increases the available surface area for nucleation, while chemical functionalization provides active sites for CO_2 adsorption. Additionally, chemical additives play a crucial role in altering sediment characteristics to support robust CO_2 hydrate formation. Collectively, these studies highlight the complexity of the hydrate formation process and the need for further research to develop optimized CO_2 hydrate storage solutions within subseafloor environments.

2.3. In Situ Monitoring and Assessment of Sediment−CO_2 Hydrate Interaction. The environmental impacts of CO_2 hydrate storage in deep-sea sediments necessitate rigorous assessment to safeguard oceanic water quality and ecosystem health against potential risks associated with CO_2 storage operations. Monitoring the geological storage of CO_2 through advanced methodologies, such as innovative rock physics models,[67] is essential for detecting any leakage early, ensuring the integrity and long-term stability of CO_2 storage.[67,68] New technologies and methodologies have allowed real-time monitoring of CO_2 hydrate formation and stability within varied sediment properties in recent years. These advancements have greatly enabled more accurate predictions of long-term storage potential and helped identify key factors influencing CO_2 hydrate storage efficiency in subseafloor saline sediments. One such technology is using

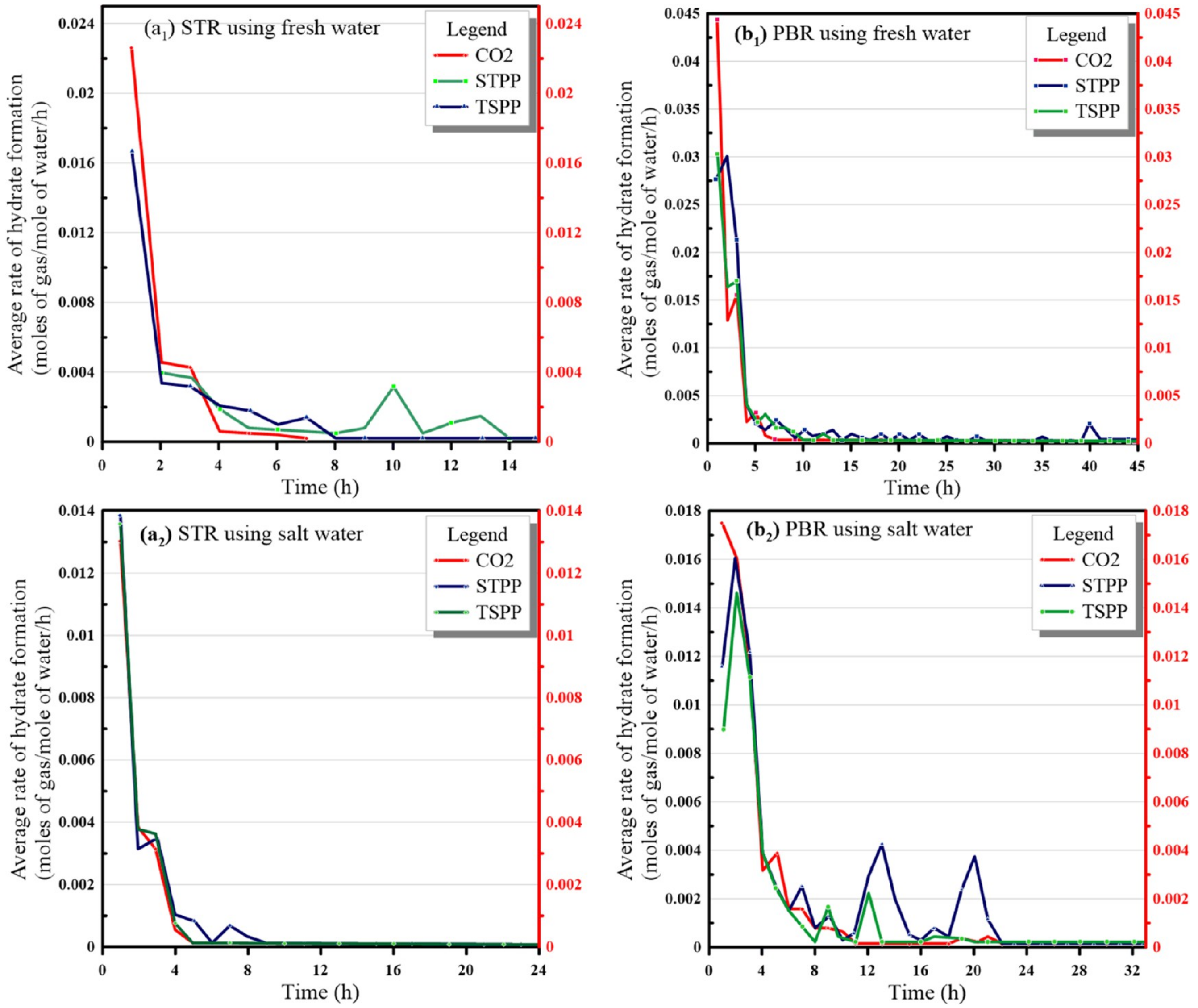

Figure 21. Hydrate formation rates in (a) stirred tank reactors (STR) using fresh and salt water. (b) Hydrate formation rates in porous bed reactors (PBR) using fresh and salt water. Redrawn with permission from ref 66. Copyright 2022, Elsevier.

fiber-optic distributed temperature sensing (DTS) systems. These systems can provide high-resolution temperature measurements along a single optical fiber, allowing real-time monitoring of temperature changes within sediment cores during CO_2 injection.[69,70] This technology has been used to study the effects of sediment permeability and water saturation on CO_2 hydrate formation and stability.[69] The results have shown that sediment permeability plays a critical role in hydrate formation and stability, with lower permeability sediments exhibiting higher hydrate saturation levels and longer-term stability. Another technology that has been used for in situ monitoring of CO_2 hydrate formation and stability is electrical resistivity tomography (ERT). ERT can provide high-resolution images of changes in electrical conductivity within sediment cores, which can be used to track the movement of fluids and the distribution of hydrate phases during CO_2 injection.[70,71] This technology has been used to study the effects of sediment heterogeneity on CO_2 hydrate formation and stability, showing that sediment heterogeneity can lead to preferential hydrate formation in certain regions of the sediment.[72] In addition to these technologies, acoustic measurements have been used for real-time CO_2 hydrate formation and stability monitoring.[73,74] Acoustic measurements can provide information on the elastic properties of the sediment and the presence of hydrate phases within the sediment.[74,75] This technology has been used to study the effects of sediment grain size and mineralogy on CO_2 hydrate formation and stability, with results showing that sediment grain size can significantly impact the distribution and stability of hydrate phases within the sediment.[76]

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 reveal frequency-dependent impedance during synthesis cycles, with distinct differences observed compared to CH_4 hydrate. This finding signifies a nuanced electrical behavior unique to CO_2

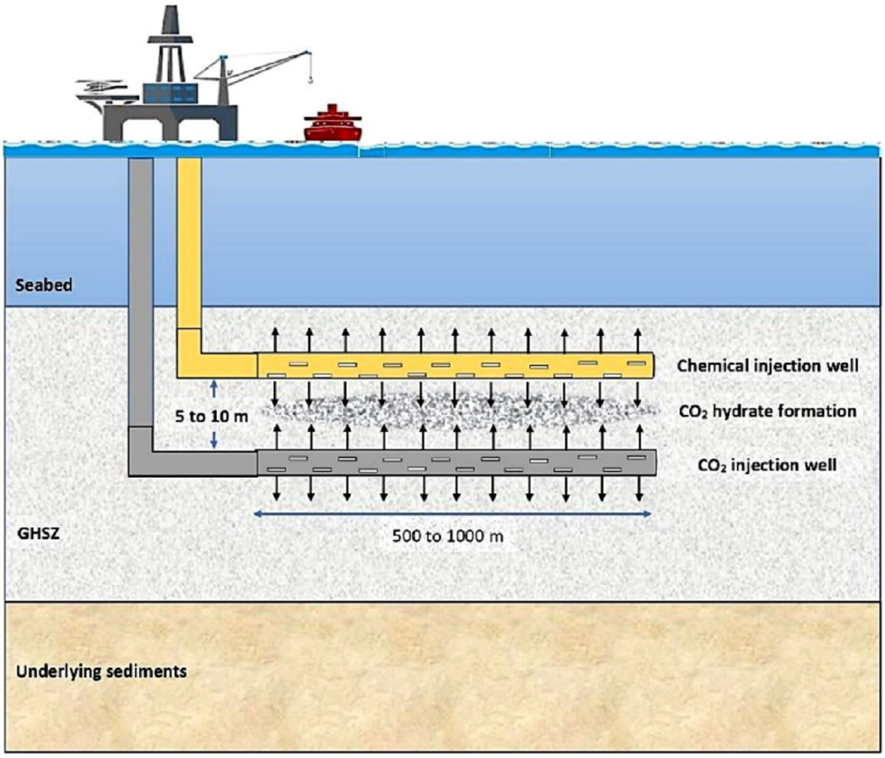

Figure 22. Profile of a subsea well configuration for effective CO_2 storage. Reproduced with permission from ref 66. Copyright 2022, Elsevier.

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 during synthesis cycles.[70,71] 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 Figure 23. 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.

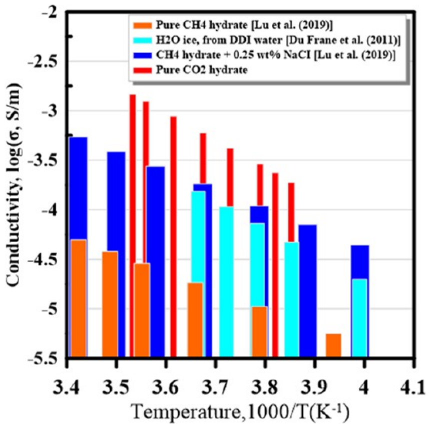

Figure 23. Electrical conductivity comparison between pure CO_2 hydrates along with pure CH_4 hydrate,[77] CH_4 hydrate + 0.25% NaCl,[77] and H_2O ice.[78] Data retrieved from ref 71. Copyright 2021, Wiley Online Library.

Table 4. Latest Developments in Nanomaterials for Tailored CO_2 Encapsulation in Hydrate Form

Nanomaterial	Study Focus	Key Findings	Refs
Carbon Nanotubes (CNTs)	Effects on nucleation and growth of CO_2 hydrate through molecular dynamics simulations.	Influence on nucleation and growth of CO_2 hydrate, insights from molecular dynamics simulations.	88
Nanoporous Silica Gels	CO_2 hydrate formation stability thermodynamics and kinetics in nanoporous silica gels.	Potential for CO_2 capture, thermodynamics, kinetics, and its role in enhancing the encapsulation process.	81
Graphite Nanoparticles	Effects on CO_2 hydrate formation process through experimental study.	Promotion of CO_2 hydrate formation, induction time, and gas consumption measurements.	89, 90
	Nanoabsorbents for CO_2 capture enhancement	The addition of 0.4% graphite nanomaterials led to improved dispersion stability in a hydrate formation reactor under specific conditions.	91
Graphene Oxide	Enhancing CO_2 capture via gas hydrate method	Insights into the development of new nanomaterial accelerators for CO_2 capture, improved kinetic behavior, and separation efficiency.	92
Composite Accelerators	Formation of CO_2 hydrate with composite accelerators, such as tetra-n-butylammonium bromide, sodium dodecyl sulfate, and nano graphite.	Effects on CO_2 hydrate formation, composite accelerators enhancement of formation rate.	93
Metal−Organic Frameworks	CO_2 adsorption	Metal−organic frameworks exhibit a remarkable ability to adsorb CO_2 due to large surface areas.	94
Mixed Gas Hydrates with H_2 + CO_2	Hydrate-based gas separation technology	Applicable to CO_2 capture and storage from synthetic gas mixtures generated through biomass gasification.	95
Red Blood Cell (RBC) Inspired Encapsulation	Enhancing gas−liquid mass transfer and CO_2 hydrate formation kinetics	143% higher gas uptake efficiency compared to traditional capsules.	96
		Optimized structure for maximizing CO_2 hydrate formation per surface area.	

3. NANOSTRUCTURED ENCAPSULATION FOR CONTROLLED CO_2 STORAGE

3.1. Fundamentals of Nanostructured Encapsulation of CO_2 Hydrate. Nanostructured encapsulation of CO_2 hydrate involves using nanomaterials such as porous metal−organic frameworks (MOFs),[79] graphene oxide,[80] or silica nanoparticles,[81] to confine and stabilize CO_2 within a solid matrix, offering a promising approach for controlled storage. Table 4 outlines the latest nanomaterial developments tailored specifically for CO_2 encapsulation in hydrate form. The principles underlying nanostructured encapsulation techniques for controlled CO_2 hydrate storage revolve around the ability of nanomaterials to provide a high surface area and tailored interactions with CO_2 molecules, leading to enhanced adsorption and confinement within the structure.[82−84] By leveraging the unique properties of nanomaterials, such as their high porosity and tunable surface chemistry, it becomes possible to encapsulate CO_2 hydrate in a controlled manner.[84] The mechanisms driving nanostructured encapsulation of CO_2 hydrate are multifaceted. First, the high surface area of nanomaterials facilitates increased contact with CO_2 molecules, promoting adsorption and confinement within the encapsulating structure.[85] Additionally, the tailored surface chemistry of nanomaterials enables selective interactions with CO_2, influencing its behavior and stability within the encapsulation matrix.[86] Furthermore, the confinement offered by nanostructures restricts the mobility of CO_2 molecules, contributing to enhanced storage stability and controlled release.[87] These mechanisms collectively enable nanostructured encapsulation to effectively address the challenges associated with CO_2 hydrate storage, offering a promising avenue for subseafloor saline sediment applications.

Nanostructured materials have revolutionized the storage of CO_2 hydrates by offering unique properties that enhance the efficiency and capacity of this process. The intricate architecture of these materials, with controlled particle size, structure, shape, and porosity, facilitates the rapid formation and stable containment of CO_2 hydrates. Some materials, such as silica (SiO_2) nanoparticles, have proven to improve CO_2 storage efficiency significantly.[20] However, particular challenges, such as nanoparticle agglomeration in solution, have been identified, emphasizing the need for further research in this area.[82,83] Nanoparticle agglomeration in solution can hinder CO_2 hydrate storage efficiency by reducing the surface area available for gas adsorption and altering the fluid dynamics required for effective hydrate formation. Additionally, the use of nanostructured catalysts can lead to the kinetic improvement of CO_2 hydrate formation, as demonstrated with graphene-carried $-SO_3-$ and Ag nanoparticles, which provide a considerable boost compared to conventional SDS promoters.[97] Ultimately, the tailored characteristics of nanostructured materials contribute to overcoming challenges associated with CO_2 capture, sequestration, and utilization, aligning with sustainable development goals for effective greenhouse gas reduction.[51] Nashed et al.[98] experimental investigations revealed that the incorporation of silver (Ag) nanoparticles, stabilized with sodium dodecyl sulfate (SDS), substantially enhances the stability and kinetics of CO_2 hydrate formation. Specifically, optimal stability was observed at a 0.08 wt % SDS concentration, resulting in the smallest nanoparticle size within the range of approximately 73.16 nm and improved distribution within the suspension. Moreover, adding Ag nanoparticles significantly reduced the induction time for gas hydrate formation and enhanced the initial rate of CO_2 consumption, particularly at lower concentrations, with the highest enhancement in gas consumption observed with a 0.1 wt % silver nanoparticle concentration. These findings signify the potential of nanostructured encapsulation techniques to facilitate controlled CO_2 hydrate storage, offering promising avenues for carbon capture and storage (CCS) initiatives in subseabed saline sediments. However, transitioning nanostructured encapsulation materials, stabilized with nanostructured catalysts, to field-scale CO_2 hydrate storage may face challenges in ensuring dispersion, addressing environmental impacts, and managing costs. Optimization of the stability under diverse conditions, assessing long-term effects and conducting thorough field testing to validate scalability and effectiveness in CCS initiatives is vital. Furthermore, the

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study by Nashed et al.[99] and Liu et al.[88] has reported that specific nanomaterials, particularly carbon nanotubes, can effectively promote the nucleation and growth of CO_2 hydrates, leading to increased formation rates and stability. The improvement is achieved through the construction of mass transfer channels that accelerate water and CO_2 molecules' reach to the growth site, thereby aiding in the formation of stable CO_2 hydrates. Giannakopoulou et al.[100] reported novel nanostructured encapsulation techniques for controlled CO_2 hydrate storage. The study employed a combination of synthetic procedures involving nanocarbon materials and ferrocene; the study achieved varied nanocarbon morphologies, including nanotubes, nanofibers, nanocubes, and nanospheres. The addition of ferrocene in the mixture with a magnesium reductant played a crucial role in controlling the morphology of the resulting nanocarbons, favoring the encapsulation growth of nanocubes or nanospheres over tubular nanostructures. These nanocarbons revealed good crystallinity, high specific surface areas, and total pore volumes, with ferrocene-containing samples showing enhanced properties. The findings suggest the potential of these nanostructured materials for applications in CO_2 adsorption and energy storage in subseabed saline sediments. While the revealed nanocarbon materials show promise for field-scale applications, applying nanocarbon materials for CO_2 hydrate storage at a field scale may face challenges in scaling up production, ensuring stability and durability, assessing cost effectiveness, compatibility with infrastructure, and evaluating long-term environmental impacts. To enhance their effectiveness, further investigations could optimize synthesis methods for scalability and cost effectiveness, conduct comprehensive characterization studies under field conditions, integrate nanocarbon materials with existing CO_2 capture and storage systems, enhance porosity and surface area, and implement long-term monitoring programs to assess environmental impacts. Addressing these challenges by conducting further investigations could facilitate the successful application of nanocarbon materials for CO_2 hydrate storage at a field scale.

3.1.1. Nanostructures Developing CO_2 Storage in Subseafloor Sediments. Various nanostructures enhance the controlled storage of CO_2 in subseafloor saline sediments. These nanostructures include porous nanoparticles,[101] nanotubes,[102] nanocapsules (NP),[103] and dendrimers.[104] Porous nanoparticles, such as mesoporous silica nanoparticles (MSNs) and metal−organic frameworks (MOFs), offer a high surface area for CO_2 adsorption and can be tailored to have specific pore sizes and surface chemistries, allowing for efficient encapsulation of CO_2 within the hydrate structure.[101,105] According to a study in nature, encapsulated MOF nanoparticles have shown high electric conductivity, contributing to improved stability and controlled CO_2 electroreduction processes.[101] Nanotubes, such as carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs), with their cylindrical nanostructures, provide a confined environment for CO_2 molecules, promoting controlled storage within the hydrated matrix.[102] Further, Nanocapsules, such as polymeric nanocapsules and lipid-based nanocapsules, consisting of a shell surrounding a CO_2-containing core, enable precise control over the release of CO_2, thereby contributing to the controlled storage and release of CO_2 hydrates.[103] In addition, dendrimers, such as poly(amidoamine) (PAMAM) and poly(propylene imine) (PPI) dendrimers, with their highly branched and well-defined structures, offer opportunities for designing specific CO_2-binding sites, facilitating the encapsulation of CO_2 within the nanostructured framework.[104] Various studies have revealed the influence of various nanomaterials with varied nanostructures on CO_2 hydrate formation, stability, and storage potential. According to the study by Li et al.,[106] different materials were used for nanoparticle suspension preparation. The primary reagents used included deionized water, CO_2 with defined purity percentages, sodium dodecyl sulfate (SDS), silicon dioxide (SiO_2), titanium dioxide (TiO_2), and multilayer carbon nanotubes (MWNTs). The nanoparticles' properties were characterized, including density, thermal conductivity, specific heat capacity, and specific surface area. The findings revealed that the addition of 0.5 g/L SDS to water significantly reduces surface tension from 72.10 to 37.00 mN/m and increases zeta potential from 3.550 to 56.07 mV, resulting in a shorter induction time from 50.000 to 35.00 min for CO_2 hydrate formation, with slightly enhanced gas consumption from 0.248 to 0.251 mol and storage capacity of 92.70 V/VH from 89.620 V/VH. Introducing 0.005 wt % SiO_2 to the SDS−water mixture increases induction time to 15.700 min, while maintaining a comparable surface tension and zeta potential, with a slight decrease in gas consumed to 0.241 mol and storage capacity to 89.07 V/VH. Similarly, incorporating 0.005 wt % TiO_2 or MWNTs maintains surface tension and zeta potential within a close range, with induction times of 21.00 and 12.50 min, respectively, a consistent gas consumption of 0.241 and 0.247 mol, respectively, alongside the storage capacity of 89.070 V/VH and 91 V/VH, respectively. Therefore, SiO_2 nanoparticles significantly reduced the induction time of CO_2 hydrate formation, indicated no significant effect on gas consumption, and showed a consistent final gas storage capacity of approximately 90.0 V/VH. TiO_2 nanoparticles, on the other hand, revealed longer induction times, minimal impact on final gas consumption, and consistent gas storage capacity, similar to SiO_2 nanoparticles. MWNT nanoparticles showed the most favorable effect, significantly reducing the induction time, providing consistent final gas consumption, and indicating improved gas storage capacity. These findings suggest a promising avenue for tailoring nanoparticle suspensions to enhance CO_2 hydrate storage efficiency and tailor release kinetics, contributing to the development of more effective carbon capture and storage technologies. The reduced induction time means faster CO_2 hydrate formation, improving the overall CO_2 storage efficiency. The observed increase in zeta potential implies a greater repulsion between nanoparticles, leading to improved dispersion stability and reduced aggregation. This increase indicates enhanced electrostatic repulsion forces within the suspension, indicating the stability and effectiveness of CO_2 hydrate formation. Moreover, the increased stability of CO_2 hydrate indicates enhanced CO_2 storage stability.

Cao[65] investigated the nanostructured encapsulation of CO_2 hydrate and its implications for controlled CO_2 hydrate storage in marine sediments. The study used water, CO_2, Silicon dioxide (SiO_2)-nanocapsules (NP), and sand nanoparticles, with specific dimensions and force fields employed for simulation. Molecular dynamics (MD) simulations were conducted using the LAMMPS software package to observe the evolutions of the structural stability of the gas hydrate−sand nanoparticle systems at 243.15K under the constant number of particles, volume, and temperature (NVT) ensemble. The study revealed potential energy changes and

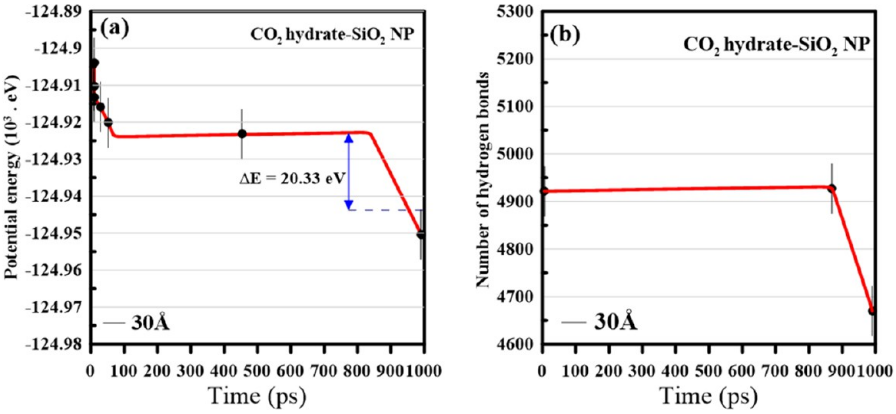

Figure 24. Molecular interaction and structural stability evolution in CO_2 hydrate−sand nanoparticle systems with a radius of ∼30 Å: insights from MD simulations. (a) The energy potential within the CO_2 hydrate−sand nanoparticle system. (b) The hydrogen bonds attained in the CO_2 hydrate−sand nanoparticle structure. Data retrieved from ref 65. Copyright 2023, Elsevier.

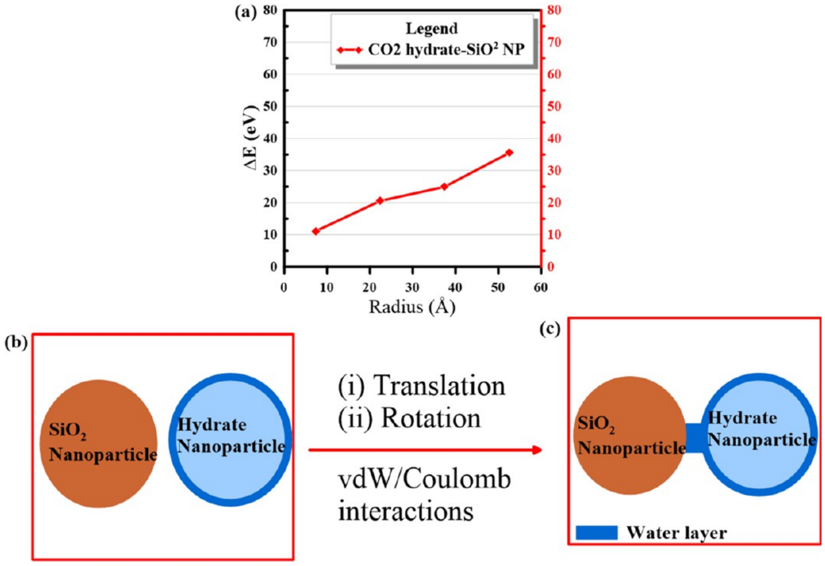

Figure 25. Influence of particle radii on potential energy in hydrate−sand nanoparticle systems. (a) The potential energy (Δ*E* (eV)) increases within the hydrate−sand nanoparticle systems. (b, c) Diagrammatical illustration of the movements of hydrate and sand particles. Redrawn with permission from ref 65. Copyright 2023, Elsevier.

the number of hydrogen bonds in the hydrate−sand nanoparticle systems with increasing MD simulation interaction time, indicating structural stability and molecular interaction changes, as shown in Figure 24. The decrease in the number of hydrogen bonds in CO_2 hydrate−sand nanoparticle structures indicates a rearrangement of the molecular structure, possibly due to the interaction between the hydrate and the sand nanoparticles. This drop in hydrogen bonds suggests a reorganization of the system, leading to a new equilibrium state, as evidenced by achieving an average value in the late period of the first evolution stage. These dynamics are crucial for optimizing CO_2 hydrate storage processes, suggesting the possibility of enhancing storage efficiency and stability by manipulating the interaction between hydrates and nanoparticle surfaces. The insights into the structural stabilities and interactions within CO_2 hydrate−sand nanoparticle systems are essential for developing controlled CO_2 hydrate storage methods by providing information on how CO_2 hydrate can be encapsulated and stored within the sediment matrix. Additionally, the insight informs the design of improved storage materials and operational strategies, ultimately offering a viable potential solution for advancing the feasibility and effectiveness of CO_2 hydrate storage as a carbon capture and storage technology. Moreover, according to the study by Cao,[65] the particle radii of gas hydrates influence the increase in the potential energy of hydrate−sand nanoparticle systems, as shown in Figure 25a. The figure illustrates the increase in potential energy of hydrate−sand nanoparticle systems both before and after the nanoparticles have merged. It offers a consistent upward trend as the particle radii increase. The large particle radii of gas hydrates suggest the robust interactions between water and solids due to the extensive contact areas among these nanoparticles. The interaction forces between the nanoparticles can be correlated with the particle radii of both gas hydrates and sands. The intriguing variation in particle behavior, dependent on the radius, can be explained by the expanding regions of sintering between hydrate and sand particles. Water layer structures primarily characterize the sintering areas.

In addition, Deng et al.[17] performed a study using different graphite materials, including fluorinated graphenes FG-1 and FG-2 with different textural characteristics, to encapsulate CO_2

hydrate—graphite and graphene belong to this category of carbon-based nanostructures.[89,107] Graphene, a single layer of graphite arranged in a hexagonal lattice, possesses remarkable properties such as high surface area, mechanical strength, and electrical conductivity.[107−109] These features make graphene an excellent candidate for CO_2 storage in subseafloor saline sediments. By leveraging their unique nanostructures, graphite and graphene can enhance the controlled storage of CO_2 in such environments, offering potential solutions to mitigate climate change. Deng et al.[17] included CO_2 gas, ultrapure deionized water, irregular graphite (Gr), fluorinated graphite (FGr), and sodium dodecyl sulfate (SDS). The characterization involved analyzing the materials' morphology and water contact angles and conducting X-ray diffraction and nitrogen adsorption−desorption tests. The results revealed that fluorinated graphenes exhibit excellent hydrophobicity, high crystallinity, large specific surface area, and developed mesoporous channels—fluorinated graphene (FG) is a highly stable graphene derivative, with a certain amount of carbon atoms being covalently bonded to fluorine atoms, giving rise to modified properties such as high hydrophobicity and increased reactivity due to the presence of fluorine, which possesses the highest electronegativity among all elements.[110] The textural properties of the studied fluorinated graphenes (FG-1, FG-2) as per N_2 adsorption estimations are shown in Table 5. In the context of the study, as described in Table 5, FG-1 and FG-2 samples differ in their textural characteristics: FG-1 has a greater total pore volume (V_{tol}), micropore volume (V_{micro}), specific surface area (S_{BET}), and external surface area (S_{ext}) compared to FG-2. This implies that FG-1 provides a larger reactive surface area and mesoporous channels, which highly benefit CO_2 hydrate formation and stability. The greater micro- and mesopores in FG-1 can facilitate more effective mass transfer of CO_2 into the hydrate structure, enabling a higher storage capacity and possibly a higher formation rate of CO_2 hydrate. Therefore, while the study broadly discussed the advantageous properties of fluorinated graphenes, these differences between FG-1 and FG-2 result in discernible variations in performance in CO_2 hydrate formation and storage. FG-1's more pronounced textural characteristics likely contribute to its superior performance in promoting and stabilizing CO_2 hydrate encapsulation as compared to FG-2. Recognizing the nuances between different types of fluorinated graphenes is crucial in optimizing their use in carbon capture and storage technologies. The experimental procedures further included preparing SDS solutions, the hydration experiment, and the investigation of hydrate stability and decomposition process. The findings showed that the different graphite materials had varying effects on CO_2 hydrate formation and gas storage capacity, with fluorinated graphenes demonstrating superior performance, as shown in Figure 26. The implications of the results show that the surface properties and structure of hydrophobic materials play a crucial role in promoting CO_2 hydrate formation. According to the study by Deng et al.,[17] surfactants, such as sodium dodecyl sulfate (SDS), can significantly impact the gas−liquid interface and enhance gas storage capacity within the nanostructured encapsulation of CO_2 hydrate. The addition of SDS facilitated the formation of CO_2 hydrate within the encapsulation materials, leading to improved stability and gas storage efficiency, as described in Figure 27. This enhancement can be attributed to the surfactant's ability to modify the surface properties of the materials, promoting better interaction between the CO_2 gas and the surrounding water molecules. Furthermore, the presence of SDS likely influenced the interfacial tension, promoting a more favorable environment for CO_2 hydrate formation and storage. As a result, the study shows that incorporating surfactants like SDS holds promise for optimizing the performance of nanostructured encapsulation materials in controlled CO_2 hydrate storage, offering potential advancements in carbon capture and storage technologies. While the current understanding of the influence of nanoma-

Table 5. Textural Characteristics of Fluorinated Graphenes as per N_2 Adsorption Estimations[17,a]

Fluorinated Graphenes Samples	V_{tol} (cm^3/g)	V_{micro} (cm^3/g)	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{ext} (m^2/g)
Fluorinated graphenes-1 (FG-1)	0.270	0.040	269.500	81.900	187.600
Fluorinated graphenes-2 (FG-2)	0.200	0.020	171.40	46.900	124.500

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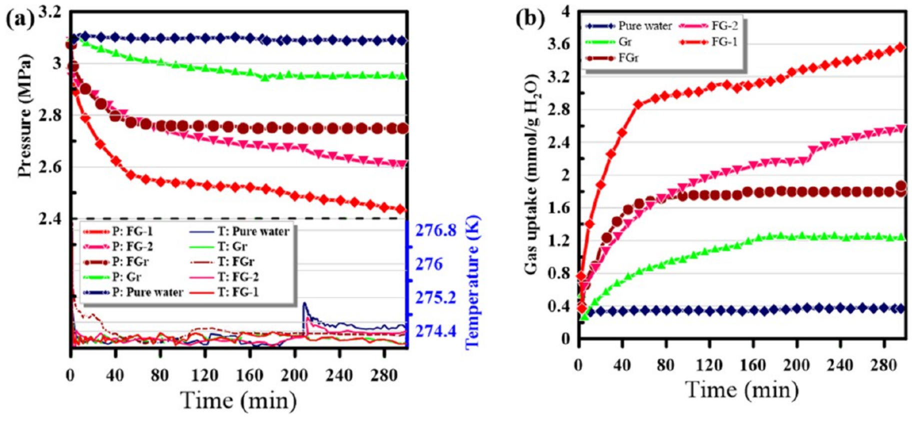

Figure 26. Impact of graphite materials on CO_2 hydrate formation and storage capacity at the pressure (P) of 3.1 MPa and temperature (T) of 274.2 K: (a) pressure and temperature and (b) storage of gas during the formation of CO_2 hydrates. Redrawn with permission from ref 17. Copyright 2023, Elsevier.

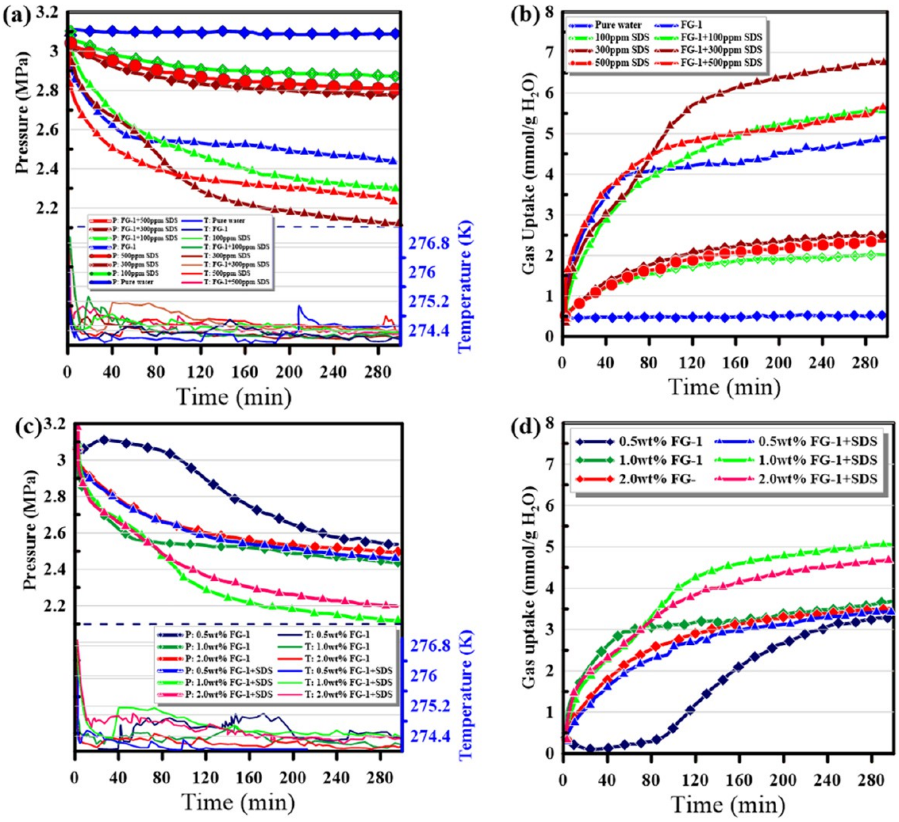

Figure 27. Effect of sodium dodecyl sulfate (SDS) on CO_2 hydrate encapsulation on enhancing CO_2 hydrate stability and storage efficiency at the pressure (P) of 3.1 MPa and temperature (T) of 274.2 K. (a, b) Effects of SDS concentrations. (c, d) Effects of different quantities of fluorinated graphene. Data retrieved from ref 17. Copyright 2023, Elsevier.

terials on CO_2 hydrate formation has advanced, there is still a need for more systematic and specific research to fully elucidate the micromechanisms and optimize the use of nanomaterials in this context.[82]

3.1.2. *Bioinspired Nanostructures and Biomimetics for Efficient CO_2 Hydrate Encapsulation.*

Bioinspired nanostructures draw inspiration from natural processes and biological systems to design materials with enhanced properties for CO_2 hydrate encapsulation. These structures mimic the features and functions found in nature, offering potential solutions for controlled CO_2 storage.[111] Biomimetic approaches aim to replicate biological processes, such as mineralization, to create nanostructured materials capable of efficiently encapsulating CO_2 in hydrate form.[111,112] Bioinspired nanostructures leverage principles observed in biological systems, such as hierarchical organization, surface modifications, and selective binding capabilities, to enhance CO_2 encapsulation.[113] By emulating the structural and functional characteristics of natural materials, bioinspired nanostructures offer the potential for improved CO_2 capture and storage efficiency.[113,114] For example, the replication of natural mineralization processes seen in marine organisms can inspire the development of nanostructured materials that promote CO_2 hydrate formation and stabilization in subseafloor saline sediments.[115,116] Biomimetic approaches for efficient CO_2 encapsulation focus on mimicking biological processes, such as self-assembly and molecular recognition, to create tailored nanostructures capable of capturing and encapsulating CO_2.[96] By harnessing the self-assembly properties found in biological systems, biomimetic nanostructures can be designed to facilitate the nucleation and growth of CO_2 hydrates, leading to controlled storage in subseafloor saline sediments.[96,117] Additionally, molecular recognition principles observed in biological systems can guide the development of selective binding sites within nanostructured materials, enabling targeted CO_2 encapsulation and enhanced stability within the saline sediments.[96,117]

Incorporating bioinspired nanostructures and biomimetic approaches into the study of nanomaterials for CO_2 hydrate formation holds promise for advancing the controlled CO_2 storage in subseafloor saline sediments. Biomimetic nanostructures such as red blood cells (RBCs) as nanostructured encapsulation materials have been shown to enhance the nucleation and growth of CO_2 hydrates, promoting controlled storage in subseafloor saline sediments.[96] This is achieved by manipulating the local hydrogen-bonding network among water molecules and facilitating the mass transfer of CO_2 molecules to the growth site with the help of suitable additives, such as magnesium. The methodology involves not the direct use of natural RBCs, which would face scalability and supply issues, but rather the nanoscale elements of their structure and membrane composition that are being mimicked.[96,118] This means extracting underlying design principles from the natural structure of human RBCs to engineer capsules capable of enhancing gas−liquid mass transfer, thus improving the kinetics of CO_2 hydrate formation for storage applications. The aim is to mimic the efficient oxygen and carbon dioxide transport capabilities of RBCs, applying these principles to engineer advanced materials and designs for CO_2 capture and storage.[96] The inspired structure mimics the rotational symmetry and specific geometric parameters of RBCs, using

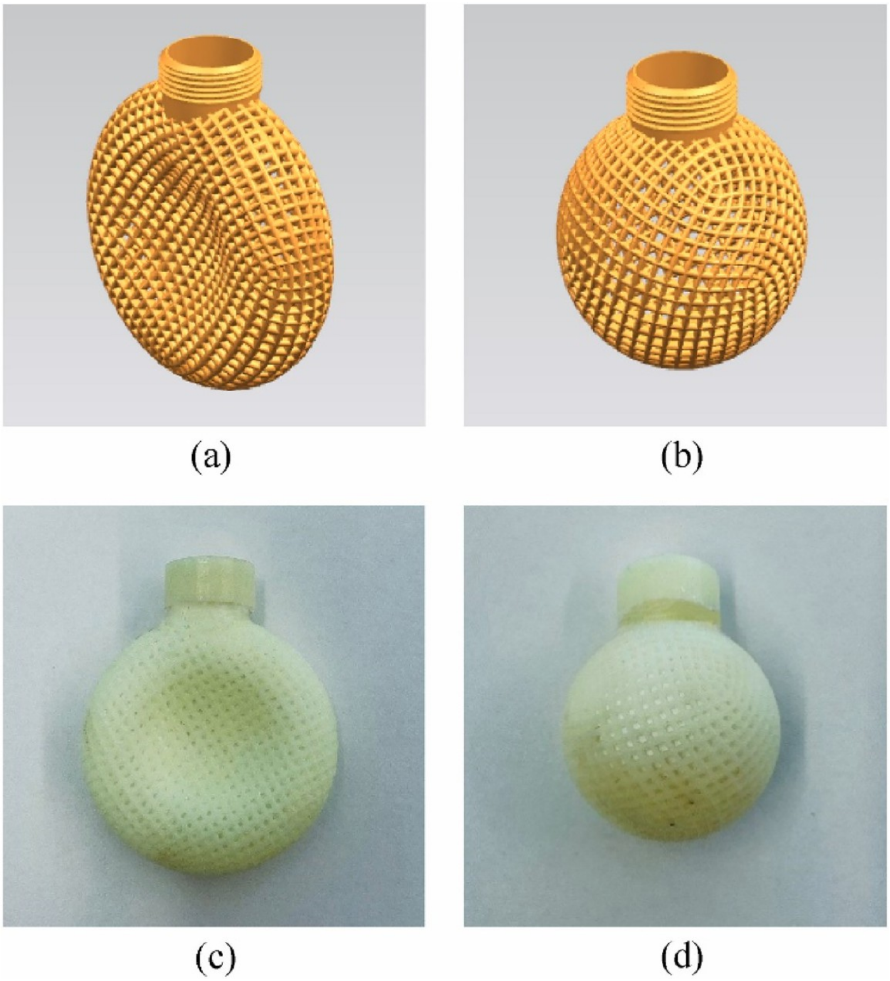

Figure 28. Types of skeletal models and 3D printed capsules with membranes: (a) a 3D representation of an RBC capsule, (b) a 3D representation of a spherical capsule, (c) the visual presentation of a 3D printed RBC capsule featuring a hydrophobic and breathable membrane, and (d) the visual presentation of a 3D printed spherical capsule with a hydrophobic and breathable membrane. Both capsules have an internal volume of 22.5 mL. Reproduced with permission from ref 96. Copyright 2023, Elsevier.

materials like poly(tetrafluoroethylene) (PTFE) for constructing hydrophobic and breathable membranes, alongside a supporting skeleton produced through 3D printing,[96] as diagrammatically shown in Figure 28. The initiative taps into the inherent properties of RBCs—high surface area to volume ratio and optimal shape for efficient gas exchange—reimagining these traits in a scalable, manufacturable format for CO_2 storage applications.[96,118] The molecular insights into CO_2 hydrate formation provide valuable information on the interactions and mechanisms involved in promoting the nucleation and growth of CO_2 hydrates. The molecular insight into the formation of CO_2 hydrate from saline solutions can provide theoretical support and practical implications for the development of biomimetic nanomaterials for CO_2 storage.[4] The influence of temperature, pressure, salt concentration, and CO_2 concentration on CO_2 hydrate formation is crucial for designing effective encapsulation systems. Biomimetic approaches can leverage this understanding to create tailored nanostructures for improved CO_2 storage.[4] Biomimetic and bioinspired approaches provide innovative and sustainable solutions for CO_2 storage in marine environments, offering opportunities to enhance the efficiency and adaptability of nanostructured encapsulation systems.[119]

Zhang et al.[96] performed a study on the biomimetic structure of red blood cell (RBC) capsules for CO_2 hydrate-based encapsulation for the first time, proposing CO_2 hydrate encapsulation as the technical concern of gas permeation via capsule shells of RBC to promote CO_2 hydrate formation kinetics. The study focuses on creating bioinspired nanostructures for efficient CO_2 hydrate encapsulation. The materials used include a hydrophobic and breathable membrane made of porous poly(tetrafluoroethylene) (PTFE), 3D printed RBC-shaped and spherical capsules, and a 32-wt % tetra-n-butylammonium bromide (TBAB) solution for CO_2 absorption. The findings reveal the successful formation of CO_2 hydrates within the capsules under specific experimental conditions, with the optimum structure of RBC capsules enhancing mass and heat transfer, leading to improved gas uptake efficiency at the lowest possible cost. Figure 29 shows that the maximum amount of hydrate at a specific time when it reaches 95% (t_{95}) for the spherical capsule is 580 min; however, for the RBC-shaped capsule, it decreases to 239 min, representing a reduction of 58.8% compared to the spherical capsule. The gas absorption efficiency of the RBC is 143% more than that of the spherical capsule. The mean rate of hydrate formation per unit surface area is 0.007290 mol m^{-2} min^{-1} for the spherical capsule and 0.01310 mol m^{-2} min^{-1} for

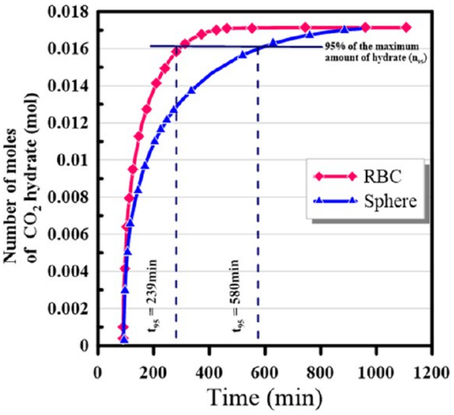

Figure 29. CO_2 hydrate formation kinetics at a specific time when it reaches 95% (t_{95}) for spherical and RBC-shaped capsules. Redrawn with permission from ref 96. Copyright 2023, Elsevier.

the RBC-shaped capsule. This illustrates the higher performance of the RBC-shaped structure in improving mass transfer. This advantage is due to the combination of a large surface area and a short diffusion distance of the RBC-shaped capsule. Furthermore, halting the reaction at t_{95} instead of attaining maximum capacity resulted in time savings of 46.7% and 38.6% for RBC and sphere, respectively.

An investigation has been conducted to examine the impact of capsule size on the kinetics of CO_2 hydrate formation, specifically focusing on the RBC-shaped capsule. Figure 30 indicates that the hydrate's growth rate increases when the capsule's size is higher, as this provides a greater surface area for mass transfer.[96] Nevertheless, the rate at which CO_2 hydrate formation occurs per unit volume reduces as the size increases, as evidenced by the data presented in Table 6. The longer gas diffusion distance in a bigger capsule necessitates CO_2 to diffuse through a thicker hydrate layer, resulting in a reduced effective diffusivity in order to react with the unreacted water solution in the core.[96] Hence, a smaller capsule size is favored to achieve greater efficiency in hydrate formation. However, it should be noted that in practical engineering applications, a smaller capsule is not always superior. Decreasing the size of the capsule will make it more difficult to encapsulate while also increasing the surface-to-volume ratio.[96] This means that a smaller capsule will require more membrane and supporting materials to take in the same quantity of gas. Hence, the choice of capsule size necessitates a thorough evaluation of parameters such as gas absorption efficiency, manufacturing complexity, and cost.

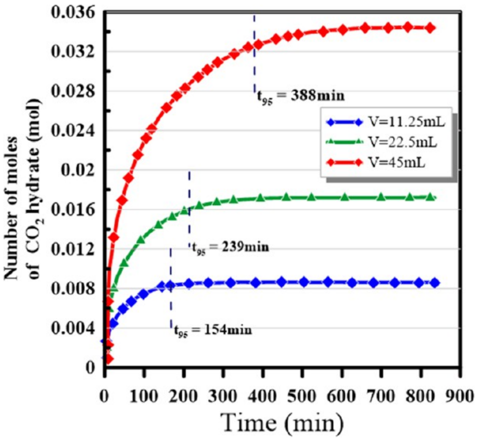

Figure 30. Effect of capsule size on CO_2 hydrate formation kinetics for red blood cell (RBC)-shaped capsule. Redrawn with permission from ref 96. Copyright 2023, Elsevier.

Table 6. CO_2 Hydrate Formation Rate for Red Blood Cell (RBC)-Shaped Capsules at Different Capsule Volumes[96,a]

Capsule Volume (mL)	Maximum Amount of Hydrate (mol)	Maximum Amount of Hydrate at a Specific Time (min)	Rate of Hydrate Formation per Unit Volume (mol min^{-1} m^{-3})
11.250	0.008161	154	4.710
22.500	0.01630	239	3.030
45.000	0.03270	388	1.870

[a] This table was reproduced with permission from ref 96. Copyright 2023, Elsevier.

3.2. CO_2 Hydrate Nanostructured Encapsulation Techniques.

Encapsulating CO_2 within nanostructures presents a promising avenue for controlled CO_2 hydrate storage within subseafloor saline sediments. Several techniques have emerged for this purpose, such as nanoemulsification, electrospinning, formation of nanostructures via cyclodextrins, metal−organic frameworks (MOFs), and nanoporous silica gel.[20,120,121] Each technique offers distinct advantages and challenges, as described in Table 7. The research on nanostructured encapsulation techniques for CO_2 hydrate storage offers a thorough exploration of various methods, their effectiveness, and the comparative analysis necessary for understanding their potential applications in subseafloor saline sediments. Their comparative effectiveness is crucial for informed decision-making in nanostructured encapsulation for controlled CO_2 hydrate storage.

Nanoemulsification is used as a nanostructured encapsulation technique for controlled CO_2 hydrate storage by leveraging the ability of nanoemulsions to encapsulate CO_2 molecules within their dispersed phase, forming stable emulsions. By utilizing surfactants and cosurfactants to stabilize the emulsion, nanoemulsions can encapsulate CO_2 molecules at the nanoscale, enhancing their solubility and facilitating controlled release.[122] This encapsulation strategy offers advantages such as increased surface area for CO_2 interaction and improved stability, thereby providing a promising approach for efficient and controlled CO_2 hydrate storage. Electrospinning is also used as a nanostructured encapsulation technique to optimize CO_2 hydrate storage by fabricating nanofibrous membranes or scaffolds with tailored properties.[124,128] These electrospun nanofibers, typically composed of polymers or polymer composites, provide a high surface area-to-volume ratio and tunable pore size, facilitating efficient CO_2 diffusion and adsorption.[128] By encapsulating CO_2 hydrate-forming materials within these nanostructured matrices, such as clathrate promoters or hydrate inhibitors, electrospinning enables precise control over the formation, stability, and release kinetics of CO_2 hydrates. This approach enhances the effectiveness and sustainability of CO_2 capture and storage processes, offering potential solutions for mitigating climate change. Furthermore, metal−organic frameworks (MOFs) are one of the nanostructured encapsulation techniques for controlled CO_2 hydrate storage due to their porous structure and high surface area.[127,129] These frameworks can adsorb CO_2 molecules within their pores, leading to the formation of CO_2

Table 7. Advantages and Challenges of Nanostructured Encapsulation Techniques for Controlled CO_2 Hydrate Storage

Encapsulation Technique	Advantages	Challenges	Refs
Nanoemulsification	High encapsulation efficiency and improved stability of CO_2 within nanostructures.	Challenges in large-scale application, potential issues with long-term stability.	122, 123
Electrospinning	Tailored morphology and structure.	Complex process and equipment requirements.	124
	High encapsulation efficiency, precise control over particle size, and suitability for controlled release applications.	Complexity in control of nanofiber alignment and scalability for industrial applications.	
		Potential aggregation of particles and difficulty in encapsulating large molecules.	
Formation through Cyclodextrins	Versatility in forming inclusion complexes, improved solubility and stability of encapsulated compounds.	Limited loading capacity, potential issues with molecular size and shape compatibility.	125
Nanoporous Silica Gels	Controlled nanoconfinement effects, tunable pore sizes for specific applications, insights into CO_2 capture kinetics and thermodynamics within varying pore sizes.	Scalability for large-scale CO_2 capture, potential issues with structural stability and durability over extended use.	120, 126
Metal–Organic Frameworks (MOFs)	High surface area and porosity, tunable structures for tailored applications, and enhanced CO_2 capture efficiency due to nanoparticle encapsulation within MOFs.	Instability under varying conditions, scalability for industrial applications, potential issues with structural degradation or loss of porosity over extended use.	127

hydrates under suitable conditions. The controlled release and storage of CO_2 can be achieved by manipulating the temperature and pressure within the MOF structure, allowing for efficient capture and storage of CO_2 molecules.[127] Moreover, nanoporous silica gels serve as effective nanostructured encapsulation techniques for controlled CO_2 hydrate storage by providing a porous matrix with a high surface area and tunable pore size.[120,126] These properties enable the absorption and confinement of CO_2 molecules within the nanopores of the silica gel, promoting the formation and stabilization of CO_2 hydrates.[120,130] Wang et al.[120] investigated CO_2 hydrate storage within different nanostructured silica gels, aiming to determine the impact of various pore sizes on the formation, equilibrium, and structure of CO_2 hydrates. Three silica gels—S9, S26, and S77—were examined based on their distinct pore sizes, as shown in Table 8. These gels underwent thorough analysis using high-pressure differential scanning calorimetry (DSC) and a high-pressure reactor system to determine CO_2 hydrate formation and dissociation behaviors under specific conditions of pressure and temperature. The findings revealed intriguing nuances across the silica gel variations. S9, characterized by strong nanoconfinement, exhibited the formation of both confined- and bulk-phase hydrates, while S26 and S77 predominantly formed bulk hydrates. This distinction impacted the equilibrium conditions, with confined-phase hydrates requiring higher pressures at given temperatures due to the nanoconfinement effect weakening water activity, as illustrated in Figure 31. Consequently, the study inferred the maximum pore size conducive to nanoconfined CO_2 hydrate formation, crucial for applications in controlled CO_2 hydrate storage. The kinetics of CO_2 hydrate formation were notably dissimilar among the silica gels. S9 exhibited slower formation kinetics due to stronger nanoconfinement, leading to longer formation times compared to S26 and S77, with an average time of 120 min, which is 2–3.5 times longer than that in S26 and S77 silica gels, as shown in Figure 32. Therefore, from a perspective of hydrate formation kinetics, the CO_2 hydrate formation in S26 and S77 is more favorable compared to that in S9. Additionally, the investigation into CO_2 capture amounts revealed a significant influence of water content and pressure on the effectiveness of CO_2 uptake, as diagrammatically described in Figure 33, highlighting the essential role of water

Table 8. Properties of Three Different Nanostructured Silica Gels with Varied Pore and Particle Sizes[a]

Silica Gel	Particle Size (μm)	Pore Size (nm)	Pore Volume ($cm^3 \cdot g^{-1}$)	BET Surface Area ($m^2 \cdot g^{-1}$)
S9	57.40	9.00	0.78	305.70
S26	60.60	26.00	0.70	73.40
S77	55.60	77.00	0.15	30.64

[a] This table was reproduced with permission from ref 120. Copyright 2022, Elsevier.[120]

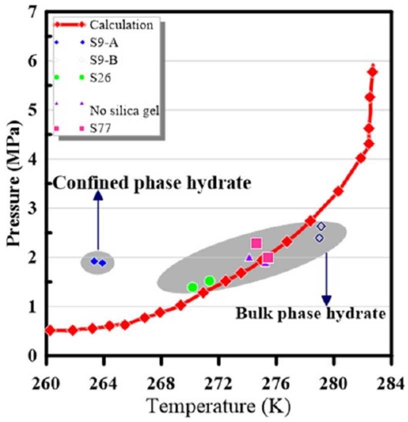

Figure 31. Effect of nanoconfinement on CO_2 hydrate equilibrium conditions. Redrawn with permission from ref 120. Copyright 2022, Elsevier.

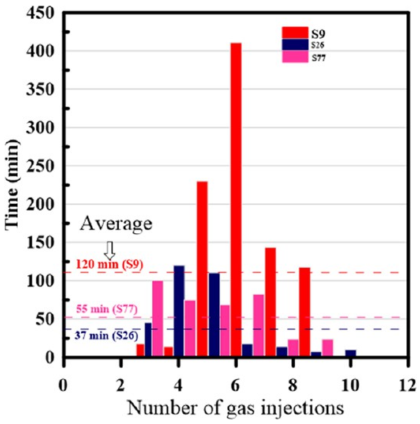

Figure 32. Comparison of CO_2 hydrate formation kinetics in different silica gels: S9, S26, and S77. Data retrieved from ref 120. Copyright 2022, Elsevier.

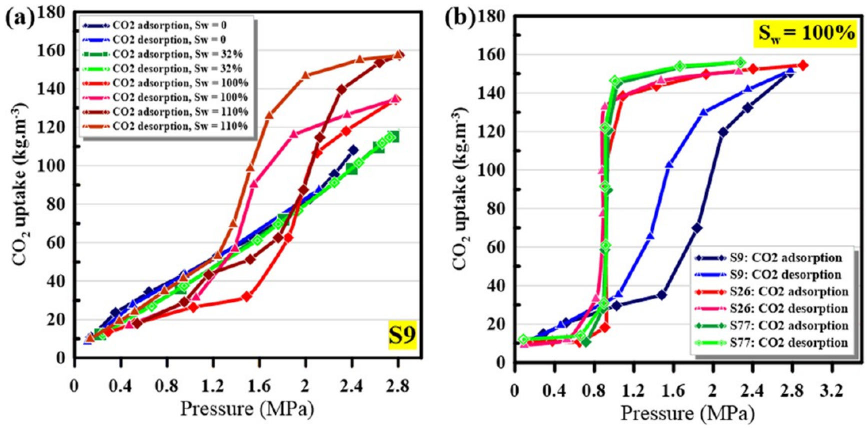

Figure 33. Effect of water content and pressure on CO_2 adsorption and CO_2 desorption: (a) in S9 with different Sw and (b) in S9, S26, and S77 with Sw = 100%. Data retrieved from ref 120. Copyright 2022, Elsevier.

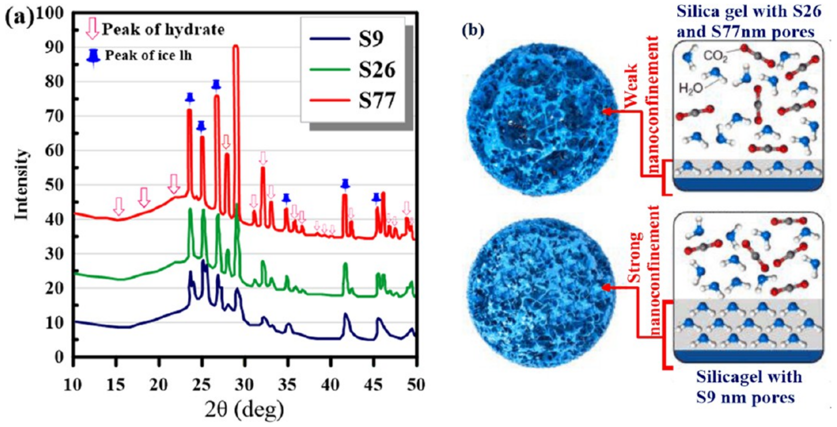

Figure 34. Effect of nanoconfinement on ice Ih formation in CO_2 hydrate. (a) X-ray diffraction (XRD) of CO_2 hydrate in S9, S26, and S77. (b) Microscopic views illustrating variations in nanoconfinement strength on the pore surface. Redrawn with permission from ref 120. Copyright 2022, Elsevier.

saturation in facilitating CO_2 capture over pressure changes. As shown in Figure 33 (a), dry S9 and S9 with water saturation (Sw) = 32% behaved similarly, whereas S9 with Sw = 32% had decreased CO_2 absorption, indicating that water occupies a portion of the pore space and forms few hydrates. S9′s CO_2 adsorption curves with Sw = 100% and 110% have a sharp jump and are identical. Due to mass transfer, the gas−liquid contact area decreases at larger water contents, causing the jump from 1.5 to 1.8 MPa for Sw = 100% and 110%, respectively. Because more CO_2 hydrate is generated at greater water levels, Sw 110% has a higher CO_2 uptake at 2.8 MPa than Sw = 100%. Thus, fully- or oversaturated silica gels trap CO_2 better than dry silica gel. In addition, Figure 33 (b) shows that the three types of silica gels with Sw = 100% had equal ultimate CO_2 uptake at 2.8 MPa. Two more rapid leaps are seen in S26 and S77′s adsorption curves but not in S9. This curve feature implies that CO_2 hydrate formation is faster in S26 and S77 than in S9. Further, S77 and S26 trap slightly more CO_2. Considering the hydrate formation rate, S77 and S26 are better than S9.

According to the study by Wang et al.[120] on the impact of nanoconfinement on the CO_2, hydrate structure revealed that the nanoconfinement had no notable effect on the CO_2 hydrate crystal structure. In contrast, intriguing variations in ice Ih formation under different nanoconfinement levels were noted, as illustrated in Figure 34. As shown in Figure 34(b), water molecules interact strongly with pores due to strong nanoconfinement, making it harder to create hydrate cages between water and CO_2 molecules. Due to significant water adsorption, nanoconfinement may decrease ice Ih's interplanar spacing parameter, as shown in Figure 14(a). Under weak nanoconfinement, water molecules can form CO_2 hydrates more freely, paving the way for future investigations into lattice property alterations under strong nanoconfinement. Due to the varying test conditions, it is not possible to definitively determine that the diameters of CO_2 hydrate crystals in silica gel were lower than those of pure hydrate. This comparison serves as a source of inspiration for future investigations into the distinct properties of CO_2 hydrate crystals under various confinement conditions.

In addition, cyclodextrins (CDs) are cyclic oligosaccharides notably studied in the context of carbon capture and storage (CCS) due to their unique structure, utilized as nanostructured encapsulation techniques for controlled CO_2 hydrate storage owing to their distinctive molecular structure featuring a hydrophobic cavity and hydrophilic exterior.[131] This structure allows CDs to form inclusion complexes with various guest molecules, including CO_2, by encapsulating CO_2 molecules within their hydrophobic cavities, which can be particularly valuable in creating controlled CO_2 hydrate storage systems.[125] This encapsulation process helps regulate the release and absorption of CO_2, making CDs promising candidates for

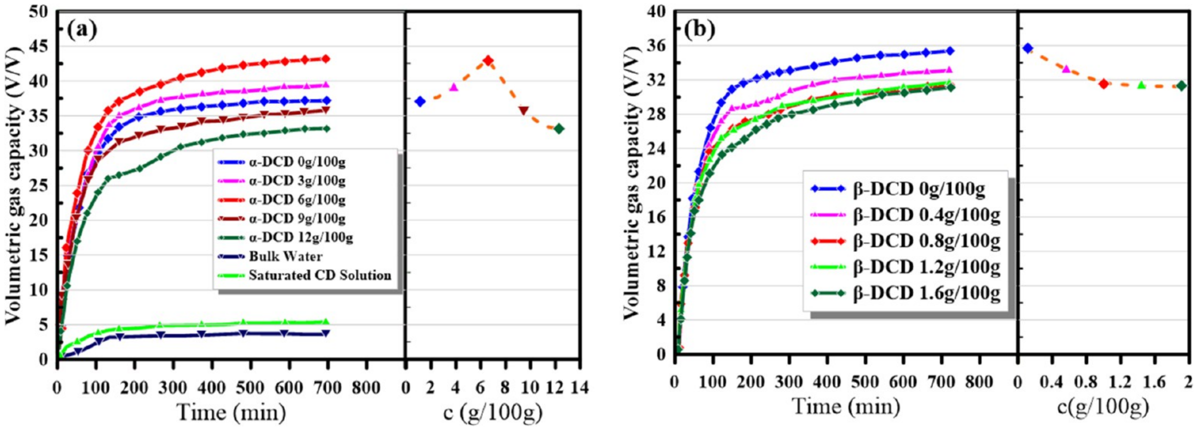

Figure 35. Formation of cyclodextrins (CDs)-CO_2 inclusion complexes, showing concentration-dependent enhancement of CO_2 adsorption. (a) α-CD-CO_2 at an initial pressure of 3.5 MPa. The right panel illustrates the correlation between the maximum gas adsorption capacity measured at 800 minutes and the concentrations of α-CD, respectively. (b) β-CD-CO_2 at an initial pressure of 3.5 MPa. The right panel depicts the relationship between the maximum gas adsorption capacity, measured at 800 min, and the concentrations of β-CD, respectively. Redrawn with permission from ref 125. Copyright 2018, Elsevier.

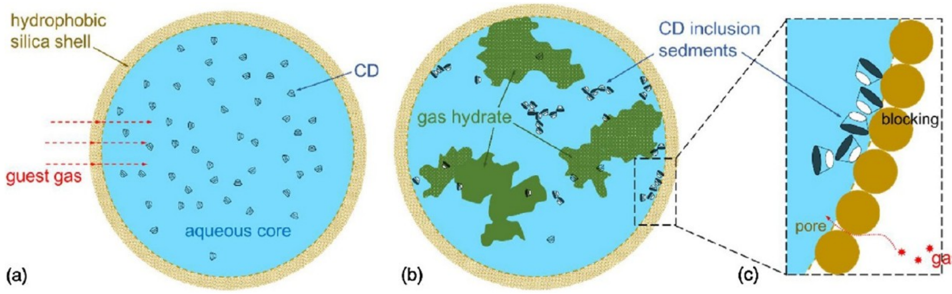

Figure 36. Schematic representation of CD inclusion complex sedimentation within the encapsulation system, indicating a reduction in gas adsorption in DW or DCD. (a) The initial phase, (b) hydrate and CD inclusion complex formation, and (c) blockage due to CD inclusion sedimentation. Reproduced with permission from ref 125. Copyright 2018, Elsevier.

applications in carbon capture and storage technologies aimed at mitigating climate change. Hou et al.[125] investigated the effect of cyclodextrins (CDs) on CO_2 hydrate nanostructured encapsulation. The experiment used pure CO_2 (99.99%) along with α-cyclodextrin (99.99%), β-cyclodextrin (99%), and hydrophobic silica particles. Cyclodextrins were prepared in various concentrations in water to form cyclodextrin solutions, which were then mixed with hydrophobic silica to synthesize dry-cyclodextrin-water (DCDs). Kinetics measurements were conducted using a miniature high-pressure reactor to observe gas adsorption under different temperatures and pressures. The study revealed significant insights into the dynamic interplay between cyclodextrins (CDs) inclusion complexes and gas adsorption kinetics on CO_2 hydrate nanostructured encapsulation. First, CDs, particularly α-CD and β-CD, were shown to facilitate the formation of inclusion complexes with CO_2 molecules, providing a conducive environment for gas encapsulation. The hydrophobic inner surface of CDs was found to attract and accommodate CO_2 molecules, effectively enhancing the gas adsorption capacity of the encapsulation system, as diagrammatically illustrated in Figure 35. The phenomenon observed is concentration-dependent, with an optimal CD concentration identified for maximizing CO_2 adsorption. Despite their structural similarities, α-CD and β-CD exhibited distinct behaviors in gas adsorption kinetics. β-CD, with a slightly larger cavity size compared to α-CD, was observed to have a faster sedimentation rate of inclusion complexes. Consequently, β-CD showed a more pronounced negative impact on gas adsorption compared to α-CD, indicating the significance of CD type in modulating gas encapsulation performance.

Furthermore, while CDs promote gas encapsulation through the formation of inclusion complexes, excessive CD concentrations could impede gas adsorption, as diagrammatically illustrated in Figure 35. According to a study by Hou et al.,[125] the sedimentation of CD inclusion complexes within the encapsulation system creates barriers that impede the diffusion of CO_2 molecules in dry water (DW) or DCD, as schematically represented in Figure 36, leading to reduced gas uptake efficiency. DW functions as a unique type of Pickering emulsion, wherein hydrophobic silica particles act as surfactants, stabilizing water. The formation of gas hydrate within dry water involves two consecutive steps: First, the guest gas permeates through the hydrophobic solid shell into the aqueous inner core, followed by (second) the formation of gas hydrates through interaction between the guest gas and liquid water. A detailed discussion of this gas adsorption process, including the two steps, is provided in the work by Li et al.[132] DW emerges as a promising material for capturing and storing CO_2 as clathrate hydrates.[125] The enhanced gas adsorption within DW's silica particle pores also accelerates the hydrate formation process.[125,133] Currently, enhancing DW's adsorption capacity and optimizing the gas hydrate formation rate remain critical challenges for its practical application. The dual influence of CDs on gas adsorption highlights the importance of carefully optimizing CD concentrations to achieve maximum gas adsorption capacity while mitigating potential blocking effects.

The studies by Wang et al.[120] and Hou et al.[125] offer valuable insights into nanostructured encapsulation techniques for controlled CO_2 hydrate storage. Wang et al.[120] explore the impact of nanoconfinement on CO_2 hydrate formation within silica gels of varying pore sizes, highlighting the nuances in hydrate equilibrium and formation kinetics, identifying that nanoconfinement influences hydrate formation rates and equilibrium conditions, with different silica gel types exhibiting varied performance in CO_2 uptake efficiency. On the other hand, Hou et al.[125] investigate the role of cyclodextrins (CDs) in CO_2 encapsulation, demonstrating how CDs can enhance gas adsorption through the formation of inclusion complexes; however, excessive concentrations may hinder gas uptake due to sedimentation effects, illustrating that careful optimization of CD concentrations is crucial for maximizing gas adsorption while mitigating blocking effects. Both studies emphasize the importance of understanding the interplay between nanostructure properties and gas encapsulation dynamics for advancing controlled CO_2 hydrate storage technologies.

3.3. CO_2 Hydrate Characterization Techniques for Nanostructured Encapsulation. Advanced analytical methods are crucial for assessing encapsulation efficiency and evaluating the properties of encapsulated CO_2 hydrates. Several specialized techniques have been developed for this purpose, such as advanced imaging techniques, spectroscopic methods, Thermal analysis techniques, and advanced diffraction techniques. These specialized techniques offer a comprehensive understanding of encapsulation efficiency and the properties of CO_2 hydrates within nanostructured encapsulation systems. Using these advanced analytical methods, researchers can gain valuable insights into the performance and behavior of encapsulated materials, contributing to the development of efficient and controlled CO_2 hydrate storage in subseafloor saline sediments.

3.3.1. Advanced Imaging Techniques. Imaging techniques, such as high-resolution scanning electron microscopy (HRSEM) and transmission electron microscopy (TEM), serve as essential analytical tools in the detailed characterization of CO_2 hydrates, particularly for nanostructured encapsulation.[134] The necessity for such advanced techniques arises from the need to understand the precise morphological features and crystallographic structures of encapsulated CO_2 hydrates, which play a significant role in carbon capture and sequestration efforts aimed at reducing the carbon footprint and meeting the goals of the Paris Agreement and COP26 conference commitments.[116]

HRSEM excels in providing topographical details and surface morphology through images demonstrating the high-resolution microstructure.[135] This approach is crucial as it contributes to a comprehensive understanding of how the surface characteristics of CO_2 hydrates can influence their behavior and stability within various environments.[135,136] The high level of detail achievable through HRSEM surpasses traditional SEM techniques by allowing researchers to examine aspects such as the size, shape, and distribution of nanomaterial on a surface.[136] Figure 37 shows the morphology and structure of synthesized ZnO nanoparticles analyzed using scanning electron microscopy (SEM). The characterization of ZnO nanoparticles presented in Figure 37 reveals promising attributes for their application in nanostructured encapsulation for CO_2 hydrate characterization. The nanoparticles exhibit an approximately spherical morphology within a diameter range of 20 to 40 nm, indicating uniformity conducive to efficient packing and distribution within an encapsulation matrix. Moreover, XRD analysis by Haghtalab et al.[137] confirmed the crystalline nature of the nanoparticles, matching the standard profile of hexagonal ZnO, which bodes well for their stability and long-term performance. The calculated average crystallite size of 11.5 nm by Haghtalab et al.[137] suggests a fine internal structure that could enhance mechanical and chemical properties relevant to CO_2 capture and storage within the encapsulation material. Additionally, the measured zeta potential of −35.1 mV indicates good stability of the ZnO nanoparticles in water-based nanofluid, a critical factor in maintaining the integrity of the encapsulation material over time and ensuring effective CO_2 capture and storage.[138] Conversely, TEM offers an even deeper dive into the internal structure, enabling scientists to see beyond the surface and attain direct structural information on nanostructured materials. This method reveals the significant crystallographic structures and interfacial interactions for understanding the fundamental properties of CO_2 hydrates and for practical applications in carbon sequestration.[139] The resolutions attained with TEM are powerful enough to visualize the atomic arrangements, providing insights into the structural integrity and chemical makeup of the CO_2 hydrate encapsulation matrix.[140]

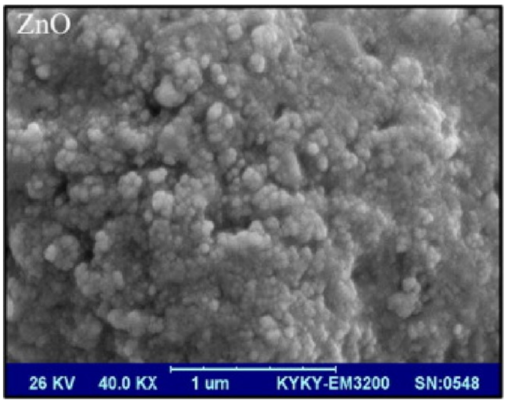

Figure 37. Scanning electron microscopy (SEM) depiction of synthesized zinc oxide (ZnO) nanoparticles from ref 138. Copyright 2016. Elsevier.

Compared to their typical applications, utilizing HRSEM and TEM for CO_2 hydrate analysis pushes the boundaries of what these instruments can reveal. Where traditional applications may focus on broader materials characterization, the use of HRSEM and TEM in the context of CO_2 hydrates leverages their high-resolution capabilities to explore critical nanoscale interactions and structural complexities that can dictate the performance of carbon capture materials.[141]

3.3.2. Spectroscopic Methods. Spectroscopic approaches, notably Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR), serve as indispensable tools for characterizing the chemical composition and molecular structures of the encapsulated CO_2 hydrates.[142,143] The necessity of these analytical techniques lies in their ability to provide molecular-level insights. Raman spectroscopy is exceptionally beneficial due to its sensitivity to vibrational modes, which can reveal alterations in the hydrate phases and the influence of nanoconfinement on structural integrity.[144] It allows for the detailed identification of different cages within the CO_2 hydrate structures by examining shifts and intensities in the characteristic Raman peaks as a result of the CO_2 molecules interacting with the surrounding water lattice in hydrate form[145] Figure 38 shows an example of Raman spectra of CO_2 in various states and hydrate structures, indicating spectral changes relevant for nanostructured encapsulation characterization. The sensitivity to structural changes makes Raman spectroscopy indispensable for studying CO_2 hydrates encapsulated within the nanostructures. In Figure 38, CO_2 hydrates' Raman spectra reveal distinct peak shifts and positions across different states and hydrate structures, serving as spectroscopic fingerprints for characterization. Variations in peak positions between solid, gaseous, and dissolved CO_2 and between sI and sII hydrates indicate changes in molecular environments and bonding. Figure 38(b) presents the Raman spectra of CO_2 within sI CO_2 hydrate and sII CO_2+THF hydrate. In the latter, the CO_2 peaks within the small cage are located around ~1274 and 1380 cm^{-1}. This contrasts with the large cage of sI CO_2 hydrate, where the lower frequency peak is situated at ~1277 cm^{-1}; a difference of ~3 cm^{-1} for the lower frequency peak and ~1 cm^{-1} for the higher frequency peak is noted. Reproducible measurements and averaging of peak positions enhance reliability, though challenges exist in determining shifts for closely spaced peaks. Understanding these spectroscopic features is crucial for characterizing CO_2 hydrates in nanostructured encapsulation, informing the development of CO_2 capture and storage technologies.

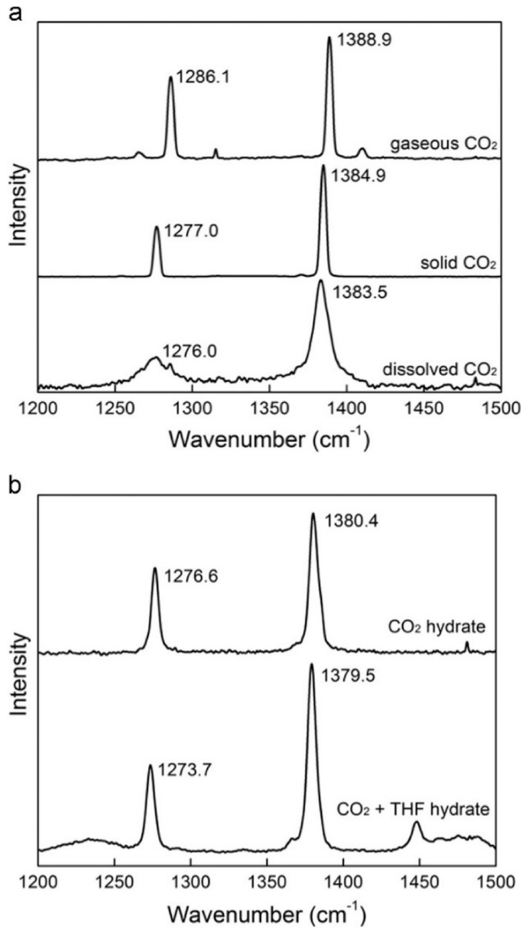

Figure 38. Raman spectra of CO_2 in various states and hydrate structures, indicating spectral changes relevant for nanostructured encapsulation characterization: (a) in gaseous, solid, and aqueous solutions and (b) in sI CO_2 hydrate and sII CO_2 + THF hydrate. Reproduced with permission from ref 142. Copyright 2015, Elsevier.

On the other hand, FTIR spectroscopy is equally crucial as it detects functional groups, providing a complementary analysis to Raman spectroscopy. It aids in identifying the molecular arrangements and potential interactions between the CO_2 hydrates and the encapsulating materials.[146,147] Particularly, it is proficient in detecting the infrared active vibrations, which can give insight into the presence of CO_2 and water in the hydrate via specific absorbance bands unique to the encapsulated CO_2 molecules and surrounding water molecules.[147]

The advancements of these techniques in characterizing nanostructured encapsulated CO_2 hydrates as compared to typical applications arise from their nondestructive nature and the level of detail, they provide without altering the sample. Specifically, using in situ measurements with these spectroscopic techniques offers real-time monitoring of hydrate formation and decomposition, which is a significant advancement over traditional methods.[148] Furthermore, the combination of Raman and FTIR techniques allows researchers to gather a more holistic understanding of both vibrational and rotational modes within a hydrate structure, something not possible with either technique alone. This dual-analysis approach enhances the understanding of the gas hydrate formation and the interactions within the nanostructured encapsulation.[149]

3.3.3. Thermal Analysis Techniques. The meticulous characterization of CO_2 hydrates using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) is indispensable for a profound understanding of these substances' thermal properties. These analytical techniques are crucial for determining the thermal stability, phase transitions, and decomposition behavior of CO_2 hydrates in a controlled environment.[150] The necessity of these techniques lies in their ability to elucidate critical thermodynamic parameters, which are essential for predicting the behavior of CO_2 hydrates under different pressure and temperature conditions.[151] DSC is adept at detecting specific signatures of CO_2 hydrates, like phase changes signaled by exothermic or endothermic events, and helps determine the precise temperatures at which these transitions manifest. DSC also yields insights into the heat capacities and transition heat closely associated with the thermal behavior of CO_2 hydrates.[152] TGA, on the other hand, effectively measures mass changes that occur on heating or cooling, which can indicate the kinetics of dehydration and desolvation or loss of stability through decomposition.[151] This dual approach can recognize distinct weight loss stages that detail the stepwise decomposition of CO_2 hydrates, providing a clearer picture of the compound's stability profile.

Furthermore, when used jointly, DSC and TGA provide a more comprehensive analysis than either technique alone, as one can correlate heat flow data with weight change to improve the understanding of the thermodynamic processes occurring within the sample.[153] This synergy between DSC and TGA is considered more informative than that of tradition.

3.3.4. Advanced Diffraction Techniques. CO_2 hydrate characterization using X-ray diffraction (XRD) is dominant for revealing intricate details about the crystalline structures, phase compositions, and orientation within a nanostructured encapsulation framework.[120,154] This characterization is necessary because understanding the crystalline structure is essential for applications that use CO_2 hydrates. By analyzing the position and intensity of diffraction peaks in an XRD pattern, one can identify the crystallographic phases and the stability of these hydrates under different environmental conditions, which is crucial for storing CO_2 hydrates.[120] The XRD technique provides unique signatures for CO_2 hydrates that include identification of the hydrate structure type (sI, sII, or sH), the occupancy of the hydrate cages by CO_2 molecules, and any lattice distortions that may occur due to changes in temperature or pressure.[155] These details are critical for predicting the behavior of hydrates in natural subseabed saline sediments. Liu et al.[156] characterized PXRD profiles of hexagonal ice formed in silica gel, as diagrammatically shown in Figure 39. The distinctive PXRD patterns revealed the stability of hexagonal ice crystal planes at various temperatures, with notable reductions observed between 258.1 and 271.1 K. These observations suggest that hexagonal ice becomes less stable within this temperature range, indicating conditions favorable for the transition to hydrate formation. This transition necessitates disrupting existing intermolecular forces among water molecules to establish new ones, facilitating the formation of CO_2 hydrate. The instability of hexagonal ice within this temperature range increases the possibility of hydrate formation, a critical consideration for nanostructured encapsulation strategies. These findings provide crucial insights into the dynamics of CO_2 hydrate formation and could inform the development of more efficient encapsulation techniques for various applications, ranging from gas storage to carbon capture and storage initiatives.

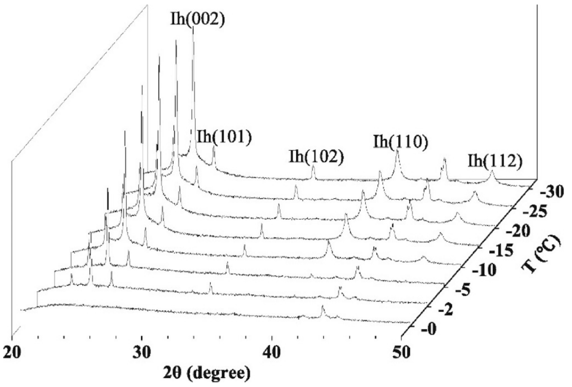

Figure 39. PXRD patterns of hexagonal ice formed in silica gel. Reproduced with permission from ref 156. Copyright 2018, Elsevier.

Compared to typical applications of XRD, the use of this technique in nanostructured encapsulation of CO_2 hydrates advances the field by allowing for the exploration of size-dependent phenomena. Nanoconfinement can significantly impact the rate of hydrate formation, the stability of hydrates, and even the storage capacity for CO_2.[120] With high-resolution XRD, it is possible to observe subtle changes in the crystal lattice that result from the interaction of the CO_2 molecules with the nanostructure confines, thus shedding light on the polymorphic transitions and potential alterations in the hydrate's properties.

4. ENHANCING CO_2 HYDRATE STABILITY AND STORAGE POTENTIAL WITH NANOPARTICLE-ASSISTED SURFACTANT/POLYMER FORMULATIONS

4.1. Rheological Characteristics of Nanoparticle-Assisted Surfactant and Polymer Formulations for CO_2 Hydrate formation. Rheology, the study of the flow and deformation of matter, particularly liquids and soft solids, plays a key role in elucidating the behavior of complex fluids, including those involved in hydrate formation processes.[157] Nanoparticles (NPs) incorporated into surfactant and polymer formulations profoundly impact the rheological properties of these systems. The rheological interactions and performance enhancements in nanoparticle-assisted surfactant−polymer formulations for CO_2 hydrate formation and stability are

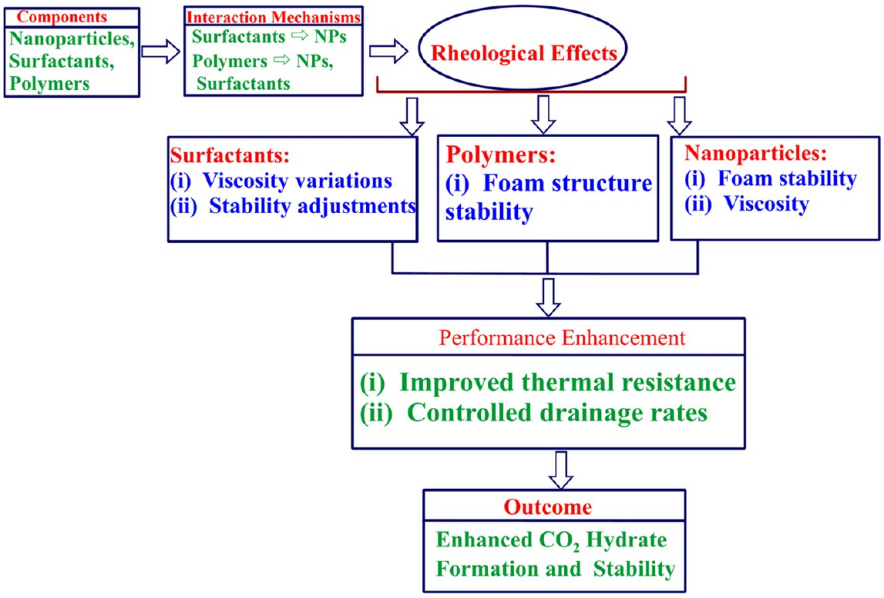

Figure 40. Schematic representation of rheological interactions and performance enhancements in nanoparticle-assisted surfactant−polymer formulations for CO_2 hydrate formation and stability.

schematically illustrated in Figure 40. Adding nanoparticles introduces alterations in viscosity, yield stress, and shear thinning behavior, crucial factors influencing CO_2 hydrate formation.[82] Studies indicate that nanoparticles can enhance the stability and kinetics of hydrate formation by controlling the rheological properties of the formulation.[82,122] The rheological behavior of nanoparticle-stabilized gaseous CO_2 foam, transitioning between shear thickening and shear thinning with varying shear rates, influences the structural properties of CO_2 hydrate formation.[122] When foam transitions from shear thickening—an increase in apparent viscosity with shear rate to shear thinning—a decrease in apparent viscosity with shear rate, it affects how the foam behaves under different conditions. At low shear rates, the foam exhibits shear thickening behavior, which can benefit processes requiring increased resistance to flow, potentially aiding in hydrate formation by providing stability and support to the hydrate structure.[122,158] Conversely, the foam transitions to shear thinning behavior at higher shear rates. Shear thinning behavior could enhance the mobility and fluidity of the foam, which might impact CO_2 hydrate formation differently. While shear thinning behavior may decrease apparent viscosity, it can promote better mixing and movement, potentially facilitating the dispersion of CO_2 and aiding in hydrate formation kinetics.[158] On the other hand, the maximal foam's apparent viscosity is crucial as it represents the highest viscosity achieved by the foam. High apparent viscosity is desirable for processes like CO_2 hydrate formation, as it indicates better structural integrity and stability, potentially aiding in maintaining the hydrate structure once formed.[159] While studies have provided valuable insights into the influence of nanoparticles on CO_2 hydrate formation, more systematic and specific research is needed to further explore the micro mechanism of their influence and optimize their application in promoting natural gas hydrate formation.

The interplay between nanoparticles and surfactant–polymer matrices significantly influences these systems' structural and colloidal properties.[126] Nanoparticles act as stabilizing agents, modifying the interfacial properties and affecting the adsorption behavior of surfactants on CO_2 hydrate surfaces.[122,126,160] This alteration in interfacial characteristics could potentially expedite the CO_2 hydrate nucleation and growth within subseafloor saline sediments, thereby impacting their rheological behavior.[83] Furthermore, the rheological behavior of nanoparticle-assisted systems can be assessed through techniques such as rheometry, providing insights into the viscoelastic properties and flow characteristics under varying pressure, temperature, and salinity conditions.[116,157] These rheological nuances are crucial for predicting and controlling the stability and formation kinetics of CO_2 hydrates in saline sediments,[157] particularly in subseafloor environments where conditions are inherently complex. Fu et al.[161] investigated the impact of materials—99.5% CO_2, NaCl, and nanosilica dispersion—on CO_2 foam formation in subseafloor saline sediments. Surfactants (SDS, Ecosurf EH-9, DTAB) and a polymer (HEC) from Sigma-Aldrich were employed to analyze foam stability and viscosity. Nanosilica properties, including surface modification and colloidal characteristics, were outlined, providing insight into their potential in foam stabilization. The experimental setup involved thermal chambers, ISCO pumps, accumulators, and pressure regulators to control CO_2 and nanosilica dispersion convergence. The foam rheology model, adopting the Hershel–Bulkley model, characterized foam viscosity—results demonstrate anionic sodium dodecyl sulfate (SDS)'s superior performance in stability and viscosity enhancement compared to nonionic and cationic counterparts. SDS concentration variations revealed increment improvements in foam viscosity and stability. Temperature variations reveal the vulnerability of foam stability and viscosity to raised temperatures, with SDS concentration mitigating this effect. Introducing a 2-hydroxyethyl cellulose (HEC) polymer into the system enhances foam stability and viscosity, particularly at higher temperatures, indicating a less sensitive response to thermal changes. Moreover, the synergistic interactions among nanosilica, surfactants, and polymers reveal a proposed interwoven structure at the bubble interfaces, boosting foam performance, as shown in Figure 41. These findings suggest a promising opportunity for enhancing CO_2 foam stability and rheological properties in high-pressure, high-salinity, and high-temperature subseafloor environments, vital for carbon sequestration strategies.

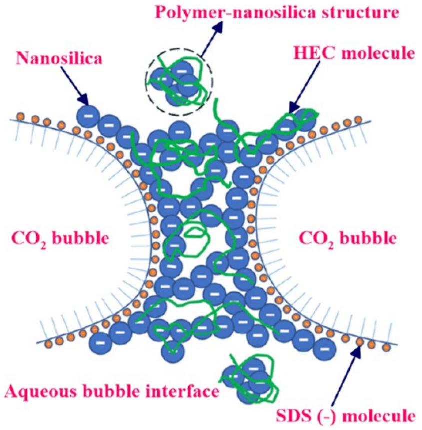

Figure 41. Illustration depicting the proposed interwoven interfacial structure formed by synergistic interactions among nanosilica, surfactants, and polymers, enhancing CO_2 foam performance. Reproduced with permission from ref 161. Copyright 2020, American Chemical Society.

The comprehensive analysis of rheological properties within nanoparticle-assisted surfactant–polymer systems sheds light on their potential for optimizing CO_2 hydrate formation and stability in subseafloor saline sediments. However, while these advancements hold promise, further research is essential to delineate the intricate interrelationships between nanoparticles, surfactants, polymers, and the resultant rheological alterations, paving the way for more efficient and sustainable strategies in carbon capture and sequestration technologies.

4.2. Role of Surfactants and Polymers in CO_2 Hydrate Formation Enhancement.

Using surfactants and polymers presents an essential way of improving CO_2 hydrate formation and boosting stability within subseafloor saline sediments. The complex interaction between these compounds illuminates their profound impact on the entire process, encompassing nucleation, growth, and stabilization of CO_2 hydrates. Surfactants, such as sodium dodecyl sulfate (SDS) or Tween series surfactants (e.g., Tween 20, Tween 80), have been found to play a multifaceted role in expediting CO_2 hydrate formation by influencing nucleation kinetics in marine sediments.[162] Their amphiphilic nature enables them to modify interfacial properties, reducing the energy barrier for nucleation. By adsorbing onto the gas−water interface, surfactants enhance the solubility of CO_2, fostering its migration into the aqueous phase.[163] This promotion of CO_2 dissolution amplifies the availability of CO_2 molecules for hydrate nucleation, expediting the initiation of the crystalline hydrate structure. Furthermore, the surfactant's ability to form micellar structures amplifies the surface area for hydrate formation.[47] The hydrophobic cores of micelles create microenvironments conducive to CO_2 accumulation, aiding in the creation of nucleation sites.[47,164] These collective mechanisms cumulatively accelerate the onset of CO_2 hydrate nucleation, expediting the process within saline sediments. Several surfactant-supported copromoters have been applied in CO_2 hydrate formation and have revealed different unique roles in CO_2 hydrate formation, as described in Table 9. Molokitina et al.[165] investigated the impact of dodecyl sulfate (SDS) concentration on CO_2 hydrate formation, examining CO_2 solubility in water, induction time, and hydrate growth mechanisms. SDS ranging from 100 to 5000 ppm did not affect CO_2 solubility. Under laminar stirring, SDS did not alter CO_2 equilibrium solubility, although, at high SDS concentrations, a slight enhancement in the CO_2 dissolving rate was observed. The induction time, measured during hydrate formation, notably increased with higher SDS concentrations, as described in Table 10. Typically, longer induction times suggest a delay in the onset of hydrate nucleation, indicating that higher SDS concentrations might hinder or slow down the formation of initial hydrate structures. This delay could be attributed to the altered interfacial properties or interactions between CO_2 molecules and water molecules in the presence of SDS. Further, it has been observed that at lower subcooling (small mass-transfer driving force), SDS lead to capillary-driven hydrate growth in the bulk liquid, contrasting the diffusion-driven growth at higher subcooling.[165] According to the study by Molokitina et al.[165] SDS did not affect the hydrate growth rate or film formation along the gas−liquid interface but significantly influenced hydrate growth mechanisms based on the mass-transfer driving force, emphasizing its role in altering CO_2 hydrate formation dynamics. Liu et al.[56] conducted laboratory experiments investigating the role of surfactants in enhancing CO_2 hydrate formation. Materials including tetrabutylammonium bromide (TBAB)—a typical ionic surfactant, and organic compounds as surfactant-supported copromoters such as tetrahydrofuran (THF), cyclopentane (CP), and deionized water were used. The study found that the addition of TBAB and THF led to the formation of a large amount of hydrate crystals, indicating their potential to enhance CO_2 hydrate formation. The induction time of hydrate formation is shorter for systems containing TBAB and THF than to pure water system, as illustrated in Figure 42(a). The crystal morphology of the additive systems was denser, with stronger gas storage capacity. As per Liu et al.[56] TBAB, THF, and CP significantly lower the surface tension for CO_2 hydrate formation. The decrease in surface tension indicates that these additives improve the movement of gas within the liquid phase, making it easier for CO_2 to dissolve and form hydrates more rapidly. TBAB—typical ionic surfactant solutions, in particular, showed a substantial reduction in surface tension, indicating enhanced gas−liquid interactions and faster hydrate formation compared to pure water, as shown in Figure 42(b). THF and CP solutions also contributed to reducing surface tension, although to a slightly lesser extent. These results indicate that TBAB has significant potential to

Table 9. Surfactant-Supported Copromoters in Enhancing CO_2 Hydrate formation

Surfactant-Supported Copromoters Type	Description	Role in CO_2 Hydrate Formation	Remark	Refs
Ionic Liquids	Organic salts in liquid state at low temperatures.	Act as surfactants to enhance CO_2 hydrate nucleation.	Ionic liquids with their unique surface-active properties can significantly reduce the energy barrier for hydrate formation.	166
Hydrophilic Surfactants	Nonionic or anionic surfactants.	Stabilize water-CO_2 interface, aiding in hydrate nucleation.	Due to their ability to interact with water molecules, these surfactants enhance water structure around CO_2, promoting nucleation.	167
Polymeric Additives	Polymers or copolymers (e.g., Polyvinyl Alcohol).	Modify water structure, favoring CO_2 hydrate formation.	Polymers modify the microstructure of water, creating a more favorable environment for hydrate formation through structural promotion.	168
Nanoparticles	e.g., silica nanoparticles and carbon nanotubes.	Surface characteristics assist in CO_2hydrate formation.	Nanoparticles offer high surface area and unique surface properties that can catalyze hydrate nucleation and growth efficiently.	126
Amino Acids	Certain amino acids or derivatives.	Enhance kinetics and stability of CO_2 hydrates.	Amino acids act as kinetic promoters and stabilizers, significantly accelerating the formation rate and enhancing hydrate stability.	169

Table 10. Effect of Sodium Dodecyl Sulfate (SDS) Concentrations on Induction Time of CO_2 Hydrate formation[165,a]

Solution	Number of Samples	Multiple Measurements per Sample	Induction Time for Each Sample (min)	Average Induction Time (min)	Remarks
Pure water	3	5, 5, 9	95, 62, 49	69 ± 24	Baseline induction time for CO_2 hydrate formation
SDS, 100 ppm	3	7, 6, 5	78, 93, 89	87 ± 8	Slightly decreased induction time compared to pure water
SDS, 1000 ppm	3	7, 9, 10	147, 100, 92	113 ± 30	Notable increase in induction time compared to lower SDS concentration and pure water
SDS, 5000 ppm	3	7, 7, 9	161, 131, 138	143 ± 16	Significant delay in CO_2 hydrate formation compared to other solutions

[a] This table was reproduced with permission from ref 165. Copyright 2019, Elsevier.

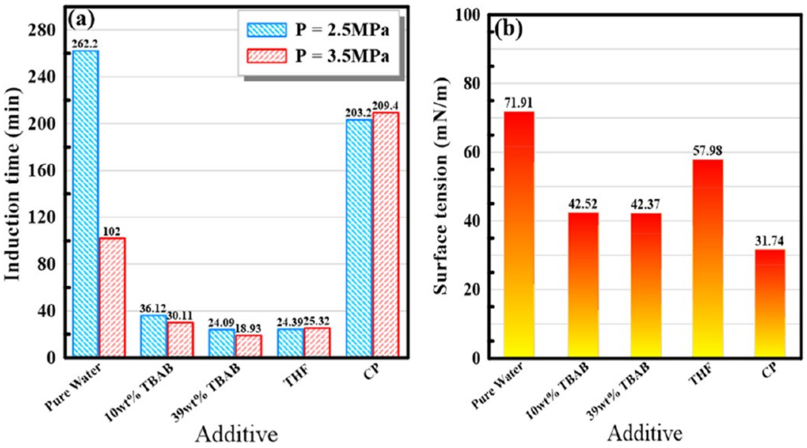

Figure 42. (a) The influence of surfactant on induction time for CO_2 hydrate formation in systems with TBAB (a typical ionic surfactant) and organic compounds (THF, CP) as surfactant-supported copromoters in pure water. (b) Effect of additives (TBAB, THF, CP) on surface tension and CO_2 hydrate formation. Redrawn with permission from ref 56. Copyright 2023, American Chemical Society.

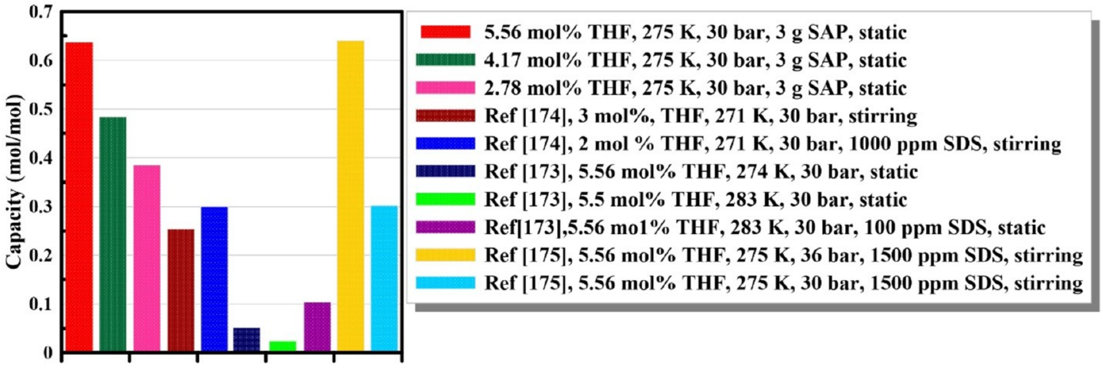

Figure 43. Effect of superabsorbent polymer (SAP) on THF-CO_2 hydrate formation and CO_2 storage capacity: comparison of CO_2 uptake from previous studies. Data retrieved from ref 60. Copyright 2022, Elsevier.

enhance CO_2 hydrate formation, which could have implications for improving CO_2 capture and storage technologies.

In parallel, polymers such as polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), and polyacrylamide (PAM) are known for their significant contributions to CO_2 hydrate formation and stability by altering the bulk properties of the system[170,171] Polymers, acting as kinetic inhibitors, modulate crystal growth by impeding the aggregation of hydrate particles.[170] Their presence hinders the coalescence of nascent hydrate crystals, promoting the development of smaller, more dispersed hydrate structures.[170] Moreover, certain polymers, particularly polyvinylpyrrolidone (PVP), have demonstrated a notable affinity for hydrate surfaces, enabling them to form protective coatings around the hydrate particles.[172] PVP polymer possesses properties that allow it to adhere to hydrate surfaces effectively. When introduced into the system, PVP molecules have been observed to interact with the hydrate crystals, forming a stable coating or encapsulation around the particles.[172] This encapsulation acts as a protective barrier, shielding the hydrate particles from external factors that could lead to their dissolution or destabilization. The formation of these protective coatings by polymers like PVP contributes significantly to enhancing CO_2 hydrate stability in subseafloor saline sediments. By preventing direct contact between the hydrate particles and surrounding water, these coatings mitigate the risks of crystal dissolution, thereby promoting the long-term stability of CO_2 hydrates within these environments. Kang et al.[60] investigated the impact of superabsorbent polymer (SAP) on THF-CO_2 hydrate formation and storage capacity at varied tetrahydrofuran (THF) concentration at various temperatures. The findings revealed that the SAP notably increased CO_2 uptake, making it a promising component for static CO_2 capture systems. Additionally, the CO_2 storage capabilities of THF-CO_2 hydrates were found to be directly proportional to THF concentrations. Lowering THF concentration decreased CO_2 storage significantly. By accessing the CO_2 storage capabilities of THF-CO_2 hydrates with the SAP from other multiple studies such as,[173−175] SAP emerges as an efficient enhancer for CO_2 capture, as diagrammatically illustrated in Figure 43. Compared to Veluswamy et al.'s findings,[173] the introduction of the SAP significantly enhanced CO_2 uptake by approximately three to four times under identical static conditions. Furthermore, the SAP's performance matched or surpassed mechanical agitation and surfactant scenarios,[174,175]. Given the substantial energy demands of mechanical agitation,[176] the SAP offers an energy-efficient alternative for CO_2 capture without stirring. Consequently, the THF solution within the SAP emerges as a viable candidate for hydrate-based CO_2 storage within a calm, undisturbed system. However, it has been observed that nucleation time varies with THF concentration and temperature. Different THF concentrations at the initial period have been observed to have similar induction periods at lower temperatures, indicating a consistent initiation period.[60,174,175] At lower THF concentrations, significantly <2.78 mol %, as observed by Kang et al.,[60] induction time increased with temperature. Therefore, a decrease in THF content may delay hydrate formation. Reduced THF availability to stabilize hydrate structures may delay nucleation, affecting hydrate formation rates. Thus, THF-CO_2 hydrates with the surfactant and polymer system can be a feasible candidate for hydrate-based CO_2 storage if and only if the concentration of THF is carefully accessed.

The combined application of surfactants and polymers for CO_2 hydrate formation yields a synergistic effect by enhancing nucleation kinetics and stability.[171] Surfactants reveal their role in expediting nucleation,[177] while polymers play a crucial role in inhibiting crystal growth and fortifying stability.[60] This cooperative action results in the formation of well-dispersed, stable CO_2 hydrates within subseafloor saline sediments, presenting a promising avenue in carbon capture and sequestration strategies.

4.2.1. Key Properties Required for Effective Surfactant/Polymer Formulations. For successful enhancement of CO_2 hydrate formation and stability in subseafloor saline sediments, formulating surfactant and polymer combinations necessitates a nuanced consideration of several key properties, such as CO_2 solubilization capacity, adsorption affinity, compatibility and synergistic interactions, and the stability in saline environments, as described in Table 11. The solubilization capacity of CO_2 in saline environments is essential for effective hydrate formation. Studies have shown that the phase equilibria and solubility of CO_2 in saline solutions are crucial factors.[178] The adsorption affinity of surfactants and polymers to sediment surfaces can significantly influence the stability and formation of CO_2 hydrates.[165] This can be attributed to the capillary-driven mechanism of gas hydrate growth under quiescent conditions, as observed in the presence of surfactants.[165] In addition, the compatibility and synergistic interactions between surfactants and polymers play a vital role in their effectiveness in enhancing CO_2 hydrate formation and stability. Super-

Table 11. Key Properties Influencing Surfactant and Polymer formulations for CO_2 Hydrate Enhancement in Subseafloor Environments

Property	Description	Remarks	Refs
CO_2 Solubilization Capacity	Surfactants' capability to dissolve CO_2 molecules into the aqueous phase efficiently. High solubility aids in accelerating CO_2 migration, increasing availability for hydrate nucleation.	Critical for expediting CO_2 availability for nucleation; influences the speed of the formation process.	179
Micellar Stability	The ability of surfactants to maintain stable micellar structures in saline conditions. Stable micelles provide increased surface area, fostering CO_2 hydrate nucleation by creating favorable microenvironments for crystallization.	Stable micelles amplify available surfaces for nucleation sites, which is key for enhancing the initiation of CO_2 hydrate formation.	180
Adsorption Affinity	Polymers' propensity to adhere to hydrate surfaces forms robust coatings that shield crystals from dissolution. This property is crucial for enhancing CO_2 hydrate stability by protecting the crystals from destabilizing factors.	Essential in preventing hydrate crystal dissolution and maintaining stability over time; crucial for long-term CO_2 sequestration.	181
Compatibility and Synergistic Interactions	The harmonious interaction between surfactants and polymers in a formulation. Compatibility ensures that the combined formulation maximizes the individual functionalities of both compounds, synergistically enhancing nucleation kinetics and stability.	The synergic between surfactants and polymers amplifies their individual properties, optimizing the CO_2 hydrate formation process in tandem.	162
Stability in Saline Environments	The resilience of formulations in high salinity conditions. Resistance to degradation or precipitation is essential for prolonged effectiveness, enabling sustained enhancement of CO_2 hydrate formation and stability in marine saline sediments.	Crucial for enduring effectiveness in challenging subsurface conditions; ensures longevity of CO_2 hydrate stability.	182
Eco-Friendly Nature	The environmental impact of surfactants and polymers. Sustainable, biodegradable, and low-toxicity substances reduce subseafloor ecological consequences.	Aligns with sustainability objectives, minimizing ecological risks; imperative for responsible utilization in subseafloor environments.	181, 183

Table 12. Effects of Different Nanoparticles (NPs) on CO_2 Hydrate Formation and Stability

Category of Nanoparticles (NPs)	Nanoparticle (NP)	Mechanism of Action	Refs
Metal Nanoparticles	Gold (Au)	Surface Catalysis - Provides active sites for CO_2 adsorption, promotes nucleation, and enhances CO_2 molecule interaction for hydrate formation.	188
	Silver (Ag)	Promotes nucleation and growth of CO_2 hydrate crystals by facilitating intermolecular interactions between CO_2 molecules.	189, 190
	Copper (Cu)	Acts as a catalyst, accelerating the conversion of CO_2 into hydrate crystals by providing reactive sites and enhancing molecular adsorption.	191
Carbon-Based Nanoparticles	Graphene	Provides a high surface area and promotes CO_2 adsorption, assisting in nucleation and stabilization of CO_2 hydrate structures.	97, 192
	Carbon Nanotubes (CNTs)	Enhances CO_2 adsorption and nucleation due to their unique structure, providing surfaces for CO_2 molecules to adhere to, thus stabilizing hydrate formation.	99, 193
	Carbon Dots	Facilitate CO_2 molecule interactions, increasing nucleation rate and promoting stable CO_2 hydrate crystal growth.	99
Polymer-Based Nanoparticles	Polyethylene Glycol (PEG)	Act as promoters, altering the water structure around CO_2 molecules enhancing hydrate formation and stability.	122, 194
	Polyvinylpyrrolidone (PVP)	Assist in nucleation and growth of CO_2 hydrates by providing a conducive environment for CO_2 molecule aggregation and stabilization.	195
	Poly(methyl methacrylate) (PMMA)	Modify the surface chemistry, aiding in CO_2 molecule adsorption and subsequent hydrate formation by altering interfacial interactions.	196
Hybrid Nanoparticles	Metal−Organic Frameworks (MOFs)	Offer high surface areas and tailored pore sizes, enhancing CO_2 adsorption, nucleation, and stabilization of hydrate structures.	105
	Core−Shell Nanoparticles	Utilize a core material (e.g., metal) to catalyze CO_2 adsorption and a shell material (e.g., polymer) to stabilize formed hydrate structures.	50
	Lipid-Based Nanoparticles	Modify CO_2-water interfaces, improving CO_2 adsorption and promoting stable CO_2 hydrate crystal growth.	96, 197

absorbent polymers have been demonstrated to accelerate the formation reaction and increase CO_2 uptake during CO_2 hydrate formation.[60,165] Furthermore, the stability of CO_2 hydrates in saline sediments is critical for long-term effectiveness. Research has indicated that CO_2 hydrates formed in deep-oceanic sediments are stable for extended periods, demonstrating their potential for long-term stability.[16] These properties dictate the effectiveness of these formulations in enhancing the desired processes and ensuring long-term stability within challenging subsurface environments.

4.3. Nanoparticles-Based Approaches for Enhancing CO_2 Hydrate Formation. *4.3.1. Nanoparticles (NPs).* NPs reveal higher reactivity than their bulk materials due to their reduced particle size, typically ranging from 1 to 100 nm, and increased surface-to-volume ratio.[184] NPs, particularly those with high surface area and tailored surface chemistry, such as functionalized graphene nanosheets, metal−organic frameworks (MOFs), or porous silica nanoparticles, tend to interact with CO_2 molecules during the CO_2 hydrate formation.[82,108] At the molecular level, NPs' surfaces, often modified with specific functional groups, possess an inherent affinity for CO_2 molecules. This affinity arises from electrostatic interactions, hydrogen bonding, and van der Waals forces between the NPs' surface functionalities and CO_2 molecules.[108,185] Such interactions facilitate the adsorption and concentration of CO_2 species near the NP surfaces, promoting the nucleation and growth of CO_2 hydrate crystals.[185] Furthermore, the unique morphology and size-dependent properties of NPs play a key role in influencing CO_2 hydrate formation.[83] NPs, due to their nanoscale dimensions, offer a high density of active sites, fostering heterogeneous nucleation sites for CO_2 hydrate crystals.[83,88] Their tunable size and shape allow for the modulation of nucleation kinetics and crystal growth, potentially optimizing CO_2 capture and sequestration processes within saline sediments.[88] Additionally, NPs within the CO_2 hydrate structures have been observed to impart structural reinforcement and stability.[88] Their incorporation into the hydrate matrix can influence the morphology and mechanical properties of the formed hydrate crystals, potentially improving their structural integrity and resistance to dissociation, thereby contributing to prolonged CO_2 storage within subseafloor sediments.

NPs based on category have been observed to possess different mechanisms of action on enhancing CO_2 hydrate formation kinetics and stability and how they interact with sediment composition in subseafloor saline sediments, as described in Table 12. NPs, like silica NPs, have shown compatibility with marine sediment compositions.[89] Research suggests that these NPs do not typically impose substantial environmental impacts due to their compatibility and potential nontoxic nature.[89,186] Ongoing research continuously assesses the long-term risks of NP deployment, emphasizing the need for regular monitoring and investigations to ensure their safe and sustainable use in diverse environments.[20,187]

NPs find versatile applications in forming CO_2 hydrates, categorized into distinct functional types, such as promoters, inhibitors, stabilizers and modifiers. First, as promoters, these nanoparticles amplify the rate of CO_2 hydrate formation or reinforce its structure, often comprising materials like metal oxides, carbon-based nanoparticles, or specialized polymers.[82] Conversely, nanoparticles can act as inhibitors, impeding or slowing the formation of CO_2 hydrates; these might include surfactant-coated nanoparticles or specific polymers like polyvinylpyrrolidone (PVP) disrupting hydrate creation.[82,89] Additionally, some nanoparticles like silica NPs, graphene oxide, or clay minerals serve as stabilizers, maintaining the integrity of formed CO_2 hydrates under varying conditions or pressures. They assist in upholding the hydrate structure once it is established. Furthermore, nanoparticles function as modifiers. NPs such as metal−organic frameworks (MOFs), zeolites, or functionalized carbon nanotubes are notable, altering CO_2 hydrates' properties and affecting dissociation kinetics, storage capacity, or other crucial characteristics.[14,89,198] Numerous experimental and numerical simulation studies have revealed that NPs, particularly silica NPs, graphite NPs, and metal NPs, have a positive effect on the

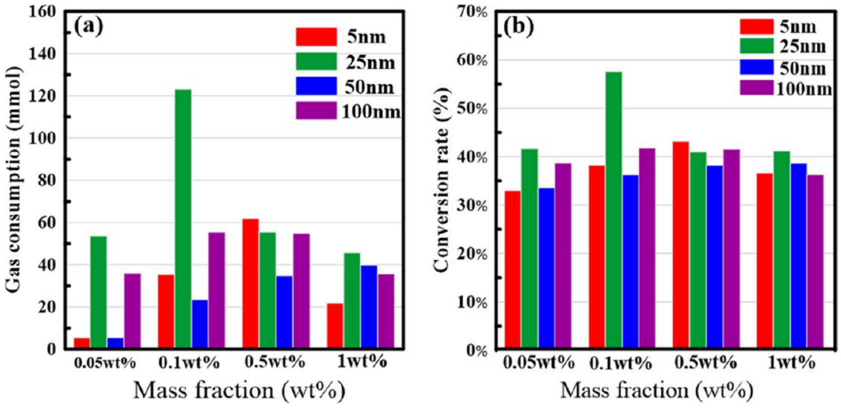

Figure 44. Nanoparticle (NP) size and concentration effects on gas consumption and conversion rate: (a) gas consumption and (b) conversion rate. Adapted from ref 83. Copyright 2022, Elsevier.

promotion of CO_2 hydrate formation and stability[65,199] The presence of NPs has been found to reduce the induction time and increase CO_2 gas consumption during the CO_2 hydrate formation process.[65,199,200] According to the study by Cao,[65] NPs were observed to enhance the stability of CO_2 hydrate structures. NPs contributed to the evolution of structural stability of CO_2 hydrate−sand nanoparticle systems, as evidenced by the evolutions of potential energy and the number of hydrogen bonds.

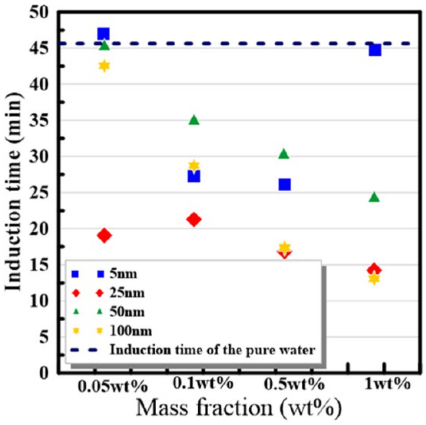

Figure 45. Influence of nanoparticle size and concentration on hydrate nucleation induction time. Adapted from ref 83. Copyright 2022, Elsevier.

NP size distribution analysis offers critical insights into the uniformity and dispersion of NPs in solution.[201] According to the study by Jiao et al.[83] revealed that uniform sizes or controlled distributions of NPs often lead to enhanced stability, as they minimize irregular interactions and promote more predictable behaviors within the CO_2 hydrate formation process. However, studies have demonstrated that small-sized NPs have less effect on gas consumption and conversion rate when the concentration is too low.[83] Figure 44 demonstrates this aspect, particularly at a low concentration of 0.05 wt % of silica NP, indicating that the gas conversion rate is relatively higher with 0.5 and 0.1 wt %. In contrast, NP agglomeration may occur at high concentrations, weakening the advantageous effects of reduced size and increased surface area.[83,202] Also, the hydrophilic nature of NPs leads to hydrogen bonds between water molecules and the hydroxyl groups on their surface, competing for hydrate cage formation.[202] This competition, particularly pronounced at higher concentrations, significantly inhibits hydrate formation.[202,203] When this inhibitory effect outweighs the NPs' promotion effect, the hydrate formation rate decreases, subsequently lowering the conversion rate. According to the study by Jiao et al.[83] on NPs size and concentrations optimization suggested that the optimal performance of the NPs occurs at a particle diameter of 25 nm, demonstrating the highest conversion rate at 57.47% at 0.1 wt %, 25 nm, a notable 39% increase compared to the pure water system's conversion rate of 34.94%. In addition, induction time—the initiation period of hydrate formation—varies based on the particle size and concentration of the NPs, as shown in Figure 45 for silica NP from experimental investigation by Jiao et al.[83] Figure 45 shows that smaller particle sizes and higher NP concentrations tend to decrease the induction time, accelerating the initiation of hydrate formation. Generally, systems with NPs exhibit a shorter induction time compared to pure water systems.[82,83,138] This observation indicates that the presence of NPs effectively reduces the time required for hydrate nucleation, leading to quicker initiation of the process. Numerous studies has revealed that the induction time reduces with rising NP concentrations.[82,83,138] Nevertheless, there is not a clear-cut law governing the impact of particle sizes within the 5−100 nm range, except for the observation that the shortest induction time occurs with particle sizes of 25 nm.[83] According to the study by Li et al.,[204] the thermal conductivity of tetrahydrofuran (THF) hydrate rises as NP concentration increases. Conversely, Liu et al.[205] suggested that the thermal conductivity of CO_2 hydrate declines as NP size increases. These findings indicate an inconsistency between the trends in induction time, nucleation temperature, and thermal conductivity. This shows that heat transfer has minimal influence during nucleation, mainly because of the substantial subcooling driving force. Instead, the effects of heterogeneous nucleation and mass transfer enhancement wield a more significant impact.

4.3.2. Nanoparticle-Surfactant Formulation. In recent research investigations, NP-assisted surfactant formulations have shown promising findings in enhancing CO_2 hydrate formation and stability in subseafloor saline sediments.[20,206] NPs, when combined with surfactants, have demonstrated the ability to modify interfacial properties and influence the behavior of gas hydrates in saline sediments.[206] Several studies have revealed that incorporating NPs in surfactant formulations can improve the dispersion and adsorption of surfactants

Table 13. Impact of SDBS Concentration on Surface Tension in Graphite NP (GN) Water Solution and Its Influence on CO_2 Hydrate Formation[208,a]

SDBS Concentration (%)	Surface Tension + Uncertainty (mN m^{-1})	Influence on CO_2 Hydrate Formation
0.000	72.900 ± 0.150	Negligible impact on surface tension; no significant influence on CO_2 hydrate formation.
0.020	44.200 ± 0.700	Initial decrease in surface tension; slight influence on CO_2 hydrate formation.
0.040	39.400 ± 0.800	A sharp decrease in surface tension, a conducive environment for CO_2 hydrate formation.
0.060	35.900 ± 0.400	Further reduction in surface tension; facilitates easier entry of gas molecules for hydrate formation.
0.080	34.300 ± 0.100	Continued decrease in surface tension; enhanced environment for CO_2 hydrate formation.
0.100	34.100 ± 0.200	Surface tension reduction plateaus; optimal concentration for efficient CO_2 hydrate formation.
SDBS Concentration (%) + GN (0.4%)	**Surface Tension + Uncertainty (mN m^{-1})**	**Influence on CO_2 Hydrate Formation**
0 + GN (0.4%)	70.9 ± 2.500	Baseline for graphite nanoparticle (GN) water solution.
0.02 + GN (0.4%)	70.2 ± 1.600	Minimal change from baseline; slight influence on CO_2 hydrate formation.
0.04 + GN (0.4%)	53.5 ± 0.800	Significant decrease in surface tension; conducive environment for CO_2 hydrate formation.
0.06 + GN (0.4%)	43.9 ± 0.100	Further reduction in surface tension facilitates easier entry of gas molecules for hydrate formation.
0.08 + GN (0.4%)	39.9 ± 0.100	Continued decrease in surface tension; enhanced environment for CO_2 hydrate formation.
0.1 + GN (0.4%)	36.2 ± 0.200	Surface tension reduction plateaus; optimal concentration for efficient CO_2 hydrate formation.
Pure water	73.3 ± 0.4	Baseline for pure water. No additives influencing CO_2 hydrate formation.

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at the gas−water interface, thereby enhancing the stability and formation kinetics of CO_2 hydrates.[138,162,206] Research has indicated that NP-assisted surfactant formulations can effectively alter saline sediments' wettability and interfacial tension, creating favorable conditions for CO_2 hydrate nucleation and growth.[162] The presence of NPs in surfactant formulations has been found to facilitate the formation of a stable hydrate phase by promoting the adsorption of surfactants at the gas−water interface, which in turn enhances the interaction between CO_2 and water molecules, leading to improved hydrate formation efficiency.[206] Moreover, studies have demonstrated that the synergistic effects of NPs and surfactants in formulations contribute to stabilizing CO_2 hydrates in subseafloor saline sediments.[55] Nanoparticles have been observed to act as nucleation sites for hydrate formation,[55,189] while surfactants aid in reducing surface tension and stabilizing the gas hydrate structure.[207] This combined approach has enhanced the overall CO_2 storage capacity and stability of hydrates in saline sediments,[55] offering potential benefits for carbon capture and storage applications in subseafloor environments.

4.3.2.1. Interfacial Tension (IFT) Reducing. To reduce interfacial tension (IFT) of CO_2 hydrate formation, nanoparticle−surfactant must align at the gas−liquid interface, where the surfactant adsorbs on the nanoparticle's surface, creating a modified surface on the nanoparticles.[206,208] These complex molecules of surfactant nanoparticles are transported from the bulk of the fluid to the gas−liquid interface by the Brownian motion of the nanoparticles, where the interfacial energy is reduced.[208,209] Yu et al.[208] investigated the impact of sodium dodecyl benzene sulfonate (SDBS) on surface tension within a solution containing graphite NPs (GNs) in water, investigating its consequential effect on CO_2 hydrate formation. The addition of SDBS revealed a significant influence on surface tension, particularly evident beyond a threshold concentration of 0.02%. Up to this point, there was negligible impact on surface tension, as shown in Table 13, but as the concentration surpassed this level, there was a notable and sharp decrease in surface tension. This reduction is due to the gradual coverage of GN particle surfaces by SDBS molecules, creating a layer that lowered the surface energy and tension of the nanofluid. With increasing SDBS concentration, this effect became more pronounced, enabling easier entry of gas molecules into the liquid phase, thereby fostering an environment conducive to CO_2 hydrate formation. However, the reduction in surface tension plateaued beyond 0.04% SDBS concentration, suggesting an optimal concentration for maximizing the reduction in surface tension and facilitating gas dissolution critical for efficient hydrate formation.

Cheng et al.[210] explored the alterations in surface tension within the synergic solution of nanoparticle−surfactant on the process of CO_2 hydrate formation by using various materials—99.9% CO_2, surfactant tetrabutylammonium bromide (TBAB), nanoparticle (NP) solutions containing silicon dioxide (SiO_2), and aluminum oxide (Al_2O_3). The findings revealed a significant reduction in surface tension when SiO_2 and Al_2O_3 NPs were introduced into a surfactant solution (TBAB). This reduction in surface tension occurred across various concentrations of NPs, with Al_2O_3 revealing a more pronounced effect than SiO_2. The lowered surface tension facilitated faster gas dissolution, improving the gas−liquid interaction kinetics crucial for CO_2 hydrate formation, shown in Figure 46. This effect is particularly noteworthy as it potentially accelerates CO_2 capture within the solution, offering insights into more efficient methods for CO_2 sequestration. The more pronounced effect of Al_2O_3 compared to SiO_2 suggests differences in particle size, shape, surface chemistry, and dispersion stability. Smaller particle size, favorable surface chemistry, and improved dispersion of Al_2O_3 may enhance its interaction with

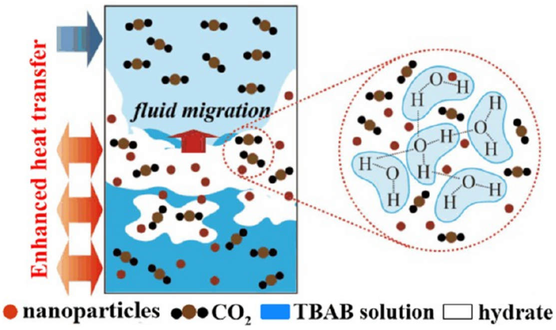

Figure 46. Effect of surface tension on gas dissolution and kinetics of CO_2 hydrate formation in the presence of NP−surfactant interaction. Adapted from ref 210. Copyright 2021, Elsevier.

surfactant molecules, leading to a more effective reduction in surface tension. Further, the inherent properties of SiO_2 and Al_2O_3, such as electronegativity and polarizability, may contribute to the observed variations. The concentration of NPs in the solution also plays a crucial role, influencing the degree of surface tension reduction.[192,211] Additionally, Cheng et al.[210] study hinted at temperature variations induced by different NPs (SiO_2/Al_2O_3) introduced into a surfactant (TBAB) solution, suggesting a possible correlation between thermal conductivity and the CO_2 hydrate formation process, as described in Figure 47.

In addition, Wu et al.[180] investigated the influence of interfacial tension, specifically at the gas−water interface, within the context of CO_2 hydrate formation enhanced by alumina NP−surfactant formulations. It unveiled that the introduced surfactants, notably sodium dodecyl sulfate (SDS) and alkyl polyglucoside (APG), were instrumental in modifying interfacial tension. These amphiphilic agents adsorbed at the gas−water interface, reducing the interfacial tension significantly. This reduction wielded profound effects on the kinetics of hydrate formation: it expedited CO_2 gas diffusion into the water phase, hastening the encapsulation of gas molecules within the hydrate structure. Notably, the presence of surfactants decreased the induction period, a critical phase in hydrate formation, compared to systems lacking these agents. The alteration of interfacial tension favored hydrate aggregation, influencing the spatial distribution and characteristics of the resulting hydrate structure.

4.3.2.2. Induction Time Reduction. Nanoparticle−surfactant interactions at the gas−liquid interface are widely studied to regulate CO_2 hydrate formation induction time.[180,208,210] The premise implies that aligning these entities at this interface is crucial. Surfactant molecules bind to nanoparticle surfaces, changing their properties.[180] Brownian motion helps the surfactant-coated nanoparticle complex travel from the fluid's bulk to the gas−liquid interface.[208] This interface interaction modifies nanoparticle surface characteristics, which may reduce CO_2 hydrate formation induction time.[82,208] According to the study by Yu et al.[208] the investigation into induction time reduction with the synergic interaction of graphite NPs (GNs) and dodecyl benzenesulfonate (SDBS) during CO_2 hydrate formation revealed that, as the concentration of SDBS increased ranging between 0 to 0.08%, so did the induction time. This is due to the SDBS's impact on slowing down the dispersion of gas in the solution, resulting in a delayed supersaturation state necessary for hydrate formation initiation. However, at a critical point, notably with 0.04% SDBS concentration, a significant reversal occurred, as diagrammatically shown in Figure 48. Beyond this threshold, the induction time saw a remarkable reduction. Surprisingly, under this optimal SDBS concentration, the solution reached the supersaturated state much faster than systems lacking SDBS or containing lower concentrations. This faster initiation of hydrate formation indicated the effectiveness of the 0.04% SDBS concentration in expediting the process. Despite the initial increase in induction time with lower SDBS concentrations, as shown in Figure 48, the comprehensive assessment of gas consumption, CO_2 hydrate conversion, and stability highlighted the key role of 0.04% SDBS concentration. While this concentration initially prolonged the induction time compared to pure water, it significantly outperformed systems containing only water and graphite NPs, showcasing a substantial 62.4% decrease in induction time. In essence, while lower SDBS concentrations momentarily extended the time required for the solution to reach a supersaturated state, the optimal concentration of 0.04% SDBS acted as a catalyst,

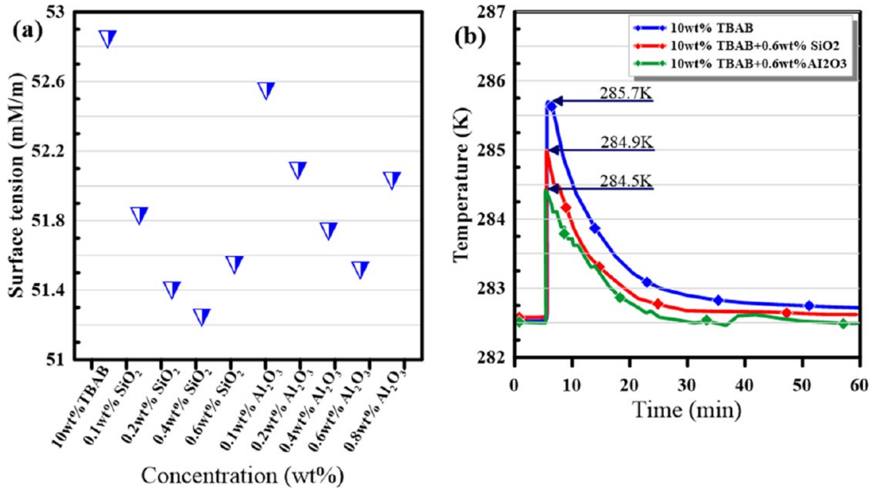

Figure 47. (a) Variation in surface tension with 10 wt % surfactant solution (TBAB) and different concentrations of NPs. (b) Temperature shift during Co_2 hydrate formation in 10 wt % surfactant solution (TBAB) + 0.6 wt % SiO_2/Al_2O_3 NPs over 60 min. Data retrieved from ref 210. Copyright 2021, Elsevier.

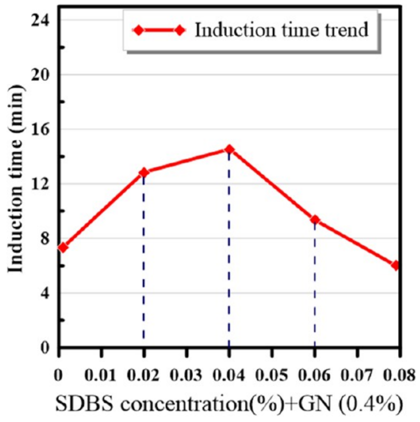

Figure 48. Influence of dodecyl benzenesulfonate (SDBS) concentration on CO_2 hydrate formation induction time in the presence of graphite NPs (GNs). Redrawn with permission from ref 208. Copyright 2018, Elsevier.

substantially reducing the induction time. This acceleration played a crucial role in hastening CO_2 hydrate formation, contributing to improved overall formation and stability.

The study by Cheng et al.[210] introduced nanoparticle (NP) solutions containing silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) into a surfactant solution (TBAB). The findings revealed a significant correlation between TBAB concentration and the induction time required for CO_2 hydrate formation. SiO_2 and Al_2O_3 NPs revealed a significant reduction in induction time when introduced into TBAB solution, particularly at 10 wt % TBAB. This reduction in induction time occurred across various concentrations of NPs, as shown in Figure 49(a). Higher concentrations of TBAB resulted in notably shorter induction times, indicating a clear relationship between the two variables. However, at 19 wt % TBAB, the induction time decreased substantially compared to lower concentrations, indicating a trend of faster nucleation with increased TBAB concentration, as shown in Figure 49(b). Nevertheless, despite this trend, there is a degree of randomness can be seen in hydrate formation kinetics even at higher TBAB concentrations, as evidenced by a concentration of 32 wt % TBAB compared to low observed concentrations of TBAB as illustrated in Figure 49(b), therefore suggesting that the relationship might not strictly follow a concentration-dependent pattern.

Wu et al.[180] discovered the remarkable reduction of induction time during CO_2 hydrate formation, primarily influenced by surfactants, sodium dodecyl sulfate (SDS) and alkyl polyglucoside (APG), alongside alumina NPs. The investigation unveiled a substantial decrease in the time needed for nucleation and growth of CO_2 hydrates when these surfactants were introduced. This acceleration is due to the surfactants' ability to lower surface tension, facilitating swift gas diffusion into the solution. Moreover, combining SDS and APG demonstrated a synergistic effect, further expediting hydrate formation compared to their individual effects. The compounded systems revealed notably shorter induction periods and lower residual pressures, indicating superior efficiency in promoting hydrate formation. Additionally, including alumina NPs significantly speeds up the process, underscoring their role in boosting the efficacy of CO_2 hydrate formation, as shown in Figure 50.

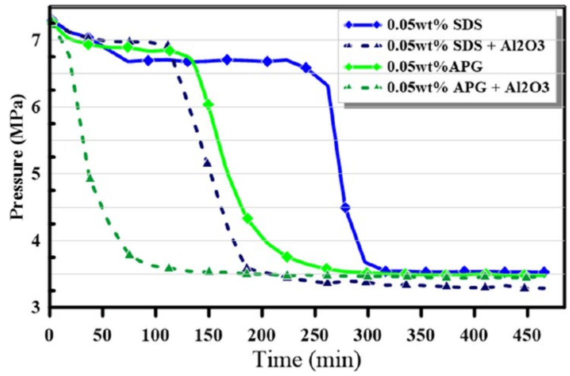

Figure 50. Influence of different surfactants (SDS and APG) and alumina NP on CO_2 hydrate formation induction time. Redrawn with permission from ref 180. Copyright 2021, Elsevier.

4.3.2.3. Gas Consumption, Storage Capacity, and Water-to-Hydrate Conversion Rate.

The mechanism of gas consumption, storage capacity, and water-to-hydrate con-

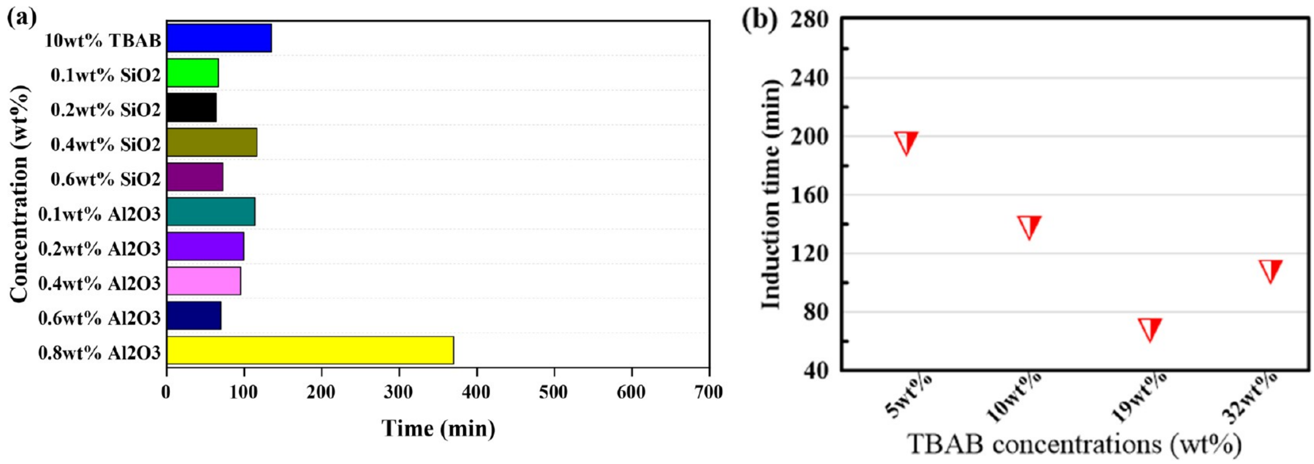

Figure 49. (a) Influence of SiO_2/Al_2O_3 NP solutions at varying concentrations on CO_2 hydrate formation induction time in the presence of 10 wt % TBAB. (b) Induction time needed for CO_2 hydrate formation at different TBAB concentrations. Adapted with permission from ref 210. Copyright 2021, Elsevier.

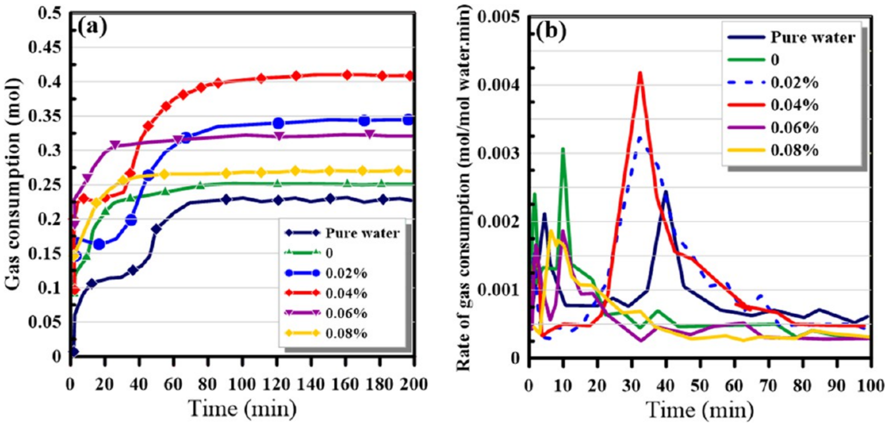

Figure 51. Influence of SDBS concentration (0—0.08%) on gas consumption in the presence of GNs (0.4%) NPs during CO_2 hydrate formation: (a) gas consumption and (b) rate of gas consumption. Modified from ref 208. Copyright 2018, Elsevier.

version rate for CO_2 hydrate formation involves the process of CO_2 molecules being captured and stored within the water lattice structure to form CO_2 hydrates.[212] During this process, the amount of gas consumed and the storage capacity are crucial factors that determine the efficiency of CO_2 capture.[212,213] The water-to-hydrate conversion rate reflects how effectively CO_2 molecules are incorporated into the hydrate structure. Factors such as temperature, pressure, and the presence of additives can influence these mechanisms,[213] ultimately impacting the efficiency and stability of CO_2 hydrate formation for potential applications in carbon capture and storage. The synergistic interaction of NPs and surfactants can impact the mechanism of gas consumption, storage capacity, and water-to-hydrate conversion rate for CO_2 hydrate formation and stability. According to the study by Yu et al.[208] revealed that the addition of graphite NPs (GNs) and sodium dodecyl benzenesulfonate (SDBS) influenced gas consumption; the gas uptake initially rose due to dissolved CO_2 and reached a steady state before hydrate formation commenced. As illustrated in Figure 51, lower SDBS concentrations restricted gas dispersion, while 0.04% SDBS notably increased gas dissolution, raising final consumption by 86.4%. Similarly, storage capacity saw a significant boost at 0.04% SDBS, as diagrammatically illustrated in Figure 52, increasing by 35.8% compared to pure water systems; this concentration facilitated better gas storage within the hydrates, enhancing overall capacity. The water-to-hydrate conversion ratio peaked at 0.04% SDBS, reaching 21.1%. This increase of 85.1% compared to pure water showcased more efficient hydrate formation at this concentration. Table 14 details the final water-to-hydrate conversion in CO_2 hydrate formation.

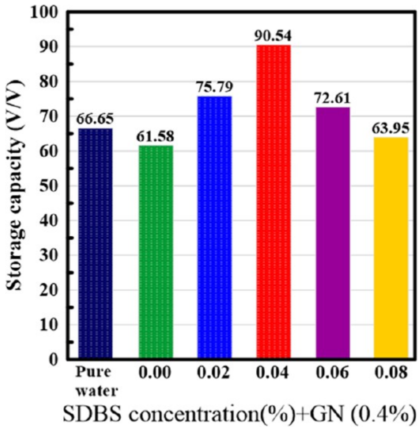

Figure 52. Effect of SDBS concentration on gas storage capacity within CO_2 hydrates presence of graphite NPs (GNs). Data retrieved from ref 208. Copyright 2018, Elsevier.

The comprehensive investigation into CO_2 hydrate formation by Cheng et al.[210] unveiled a complex interplay between various factors, notably the concentrations of surfactant (TBAB) and NPs (SiO_2, Al_2O_3), influencing gas consumption, storage capacity, and the water-to-hydrate conversion rate. The study revealed that higher concentrations of TBAB accelerated gas consumption and storage capacity. However, excessively high concentrations led to the formation of pure TBAB hydrates, limiting CO_2 storage potential, as shown in Figure 53(a). At lower concentrations, the presence of NPs significantly increased the rates of gas consumption and conversion, as illustrated in Figure 53(b). This is due to boosting quicker nucleation and promoting multiple hydrate formations. However, high NP concentrations showed inhibition influence these processes due to agglomeration, affecting both the conversion rate and gas storage capacity.

Wu et al.[180] investigations remarkably, the surfactants—sodium dodecyl sulfate (SDS) and alkyl polyglucoside (APG), combined presence further accelerated gas uptake, indicating enhanced efficiency in gas consumption compared to individual surfactant solutions. The accelerated gas uptake and improved efficiency likely stem from their complementary actions, as illustrated in Figure 54. SDS, an ionic surfactant, reduces surface tension, aiding CO_2 gas penetration into the water phase. In contrast, APG, a nonionic surfactant, potentially fosters micelle formation or aggregated structures, creating favorable sites for gas interaction. These surfactants synergize to modify solution properties, boosting gas dissolution and facilitating quicker CO_2 hydrate nucleation and growth, ultimately enhancing gas uptake efficiency during hydrate formation. Moreover, the compound systems, incorporating alumina NP, revealed high gas storage density, suggesting a synergistic effect between surfactants and NPs in boosting storage capacity within the formed hydrates. The synergistic effects of alumina NPs and SDS/APG surfactants compound systems on the hydrate storage density and gas consumption are shown in Figure 55. Notably, the surfactants' amphiphilic properties significantly influenced the efficiency of

Table 14. GN (0.4%) + SDBS Concentration (%) Effect on Water-to-Hydrate Conversion in CO_2 Hydrate Formation[208,a]

GN (0.4%) + SDBS Concentration (%)	Induction Time ± Uncertainty (min)	Final Water-to-Hydrate Conversion (mol %)	Influence on CO_2 Hydrate Formation	Remark
Pure water	8.600	11.400	Base level (baseline) for comparison.	Provides a reference point for understanding the effects of additives.
0.000	7.32 ± 1.760	12.9 ± 0.700	Slightly enhancement in the hydrate formation rate.	Graphite NPs (GNs) reduced induction time by approximately 14.88% compared to pure water, less impact by temperature and pressure changes.
0.020	12.83 ± 1.930	17.7 ± 0.400	Considerably moderate improvement in hydrate formation rate.	Adding SDBS slightly reduces GN's effect on induction time but increases water-to-hydrate conversion.
0.040	14.51 ± 1.740	21.1 ± 0.600	Significantly enhanced hydrate formation.	Optimal concentration for balance between reduced induction time and increased conversion. Gas consumption increased noticeably.
0.060	9.36 ± 1.830	16.5 ± 0.700	Moderate enhancement	Superior to pure GN, but diminishing returns as SDBS concentration increases.
0.080	6.02 ± 1.670	13.8 ± 0.400	Slight enhancement	Further increase in SDBS concentration might not significantly boost formation efficiency.

[a] This table was reproduced with permission from ref 208. Copyright 2018, Elsevier.

water-to-hydrate conversion, impacting surface tension, gas diffusion, and micelle formation.

4.3.3. Nanoparticle–Polymer Formulation. Incorporating polymers into NP-assisted formulations can significantly improve the stability of CO_2 hydrates in saline sediments.[50,82,89] The synergistic effects of NPs and polymers have been shown to enhance the mechanical strength and adhesion properties of CO_2 hydrates, thereby reducing the chances of hydrate dissociation and improving their long-term stability within the sediment matrix.[82,214] Research has revealed that selecting specific NPs and polymers can be tailored to optimize the formation and stability of CO_2 hydrates in saline sediments.[50] Certain nanoparticle types, such as silica NPs, exhibit a high affinity for CO_2 molecules, effectively promoting their adsorption and subsequent conversion into hydrates.[215] Combined with polymers that enhance the hydrate matrix's interfacial properties and structural integrity, these NP–polymer formulations yield improved CO_2 hydrate formation and stability under subseafloor conditions. Additionally, investigations have highlighted the role of NP–polymer formulations in mitigating the potential challenges associated with CO_2 hydrate formation, such as kinetic limitations and sediment heterogeneity.[82,197] By facilitating the nucleation and growth of CO_2 hydrates while simultaneously reinforcing their stability within the sediment matrix, NP–polymer formulations offer a promising approach to overcoming these challenges and enhancing the overall efficiency of CO_2 sequestration in subseafloor saline sediments.[197] Table 15 shows various effects of incorporating nanoparticles (NPs) and polymer formulations for enhancing CO_2 hydrate formation and stability.

According to the study by Zhao et al.,[50] polystyrenesulfonate@Fe_3O_4 nanospheres (PNS) in the context of CO_2 hydrate formation unveiled intriguing insights into their performance, particularly when coexisting with fine marine sediments. Polystyrenesulfonate (PSS) is a polymer of styrene units and sulfonate groups.[214,219] The polymer may have sodium ions associated with the sulfonate groups, making it water-soluble and potentially introducing charged sites on the polymer.[214] PSS and Fe_3O_4 (iron(II, III) oxide, also known as magnetite) nanoparticles form a PNS formulation that enhances hydrate formation and stability in marine sediments.[50] Through isothermal experiments conducted by Zhao et al.,[50] the CO_2 storage capacity remained consistent at 55v/v under isothermal formation conditions in the absence of marine sediments. However, when PNS samples and marine sediments were introduced into the solution, a remarkable CO_2 storage capacity was observed, reaching 71.5 ± 9.3v/v, as diagrammatically illustrated in Figure 56. This enhancement is attributed to the unique surface characteristics of PNS nanoparticles and marine sediments. The negative charges and organic matter on sediment surfaces provided nucleation sites for CO_2 hydrate growth, while the $- SO_3-$ groups on PNS nanoparticles facilitated adsorption onto sediments, creating an environment conducive to CO_2 hydrate formation. This synergistic effect highlights the potential of PNS and marine sediments to significantly improve CO_2 storage capacity in hydrate formations, suggesting a promising avenue for efficient seabed CO_2 sequestration.

In addition, the research on synergic graphene–polymer (GP) formulations for enhancing CO_2 hydrate formation and stability has yielded significant insights through molecular dynamics simulation.[216] Meconi et al.[216] investigated gra-

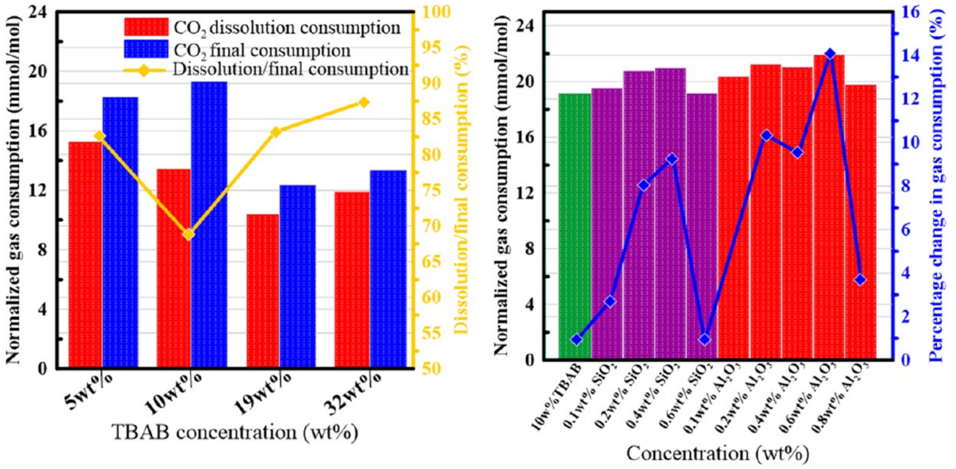

Figure 53. (a) The ultimate normalized CO_2 gas uptake and dissolution consumption during the CO_2 hydrate formation process across various TBAB concentration levels. (b) Gas consumption normalized for CO_2 hydrate formation in solutions of 10 wt % TBAB with varying concentrations of NPs (SiO_2, Al_2O_3). Data retrieved from ref 210. Copyright 2021, Elsevier.

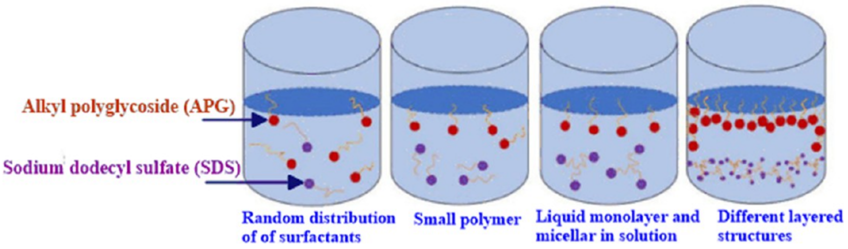

Figure 54. Synergistic effects of surfactant (SDS and APG) combinations on gas uptake and hydrate formation. Adapted from ref 180. Copyright 2021, Elsevier.

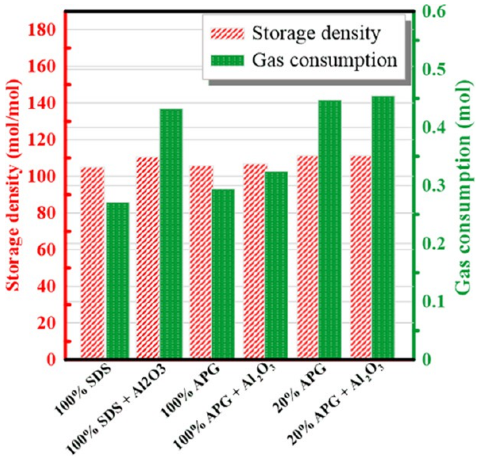

Figure 55. Enhanced CO_2 hydrate storage in alumina NPs and SDS/APG surfactants compound systems. Redrawn with permission from ref 180. Copyright 2021, Elsevier.

phene–polymer (GP) with six different polymers, including poly(methyl methacrylate) (PMMA), poly(2-aminoethyl methacrylate) (PEAM), poly(3-diamin-(aminomethyl)propyl methacrylate) (DAPM), poly(aniline methacrylamide) (PAAM), poly(N-(3,5-diaminophenyl)methacrylamide) (PDAFMA), and poly(styrene) (PS), to understand their influence on CO_2 adsorption. Notably, the morphology of polymers on graphene nanoparticle surfaces varied, impacting adsorption modes and strengths. Polymers with higher numbers of protic groups, such as amines and amides, revealed stronger cohesive forces, leading to increased aggregation and enhanced CO_2 adsorption, as illustrated in Figure 57. Hydrogen bonding played a crucial role, particularly at low pressures, contributing significantly to the binding of CO_2. The GP composite materials preferred CO_2 adsorption over nitrogen gas (N_2) and methane (CH_4), indicating potential selectivity. Despite a slight reduction compared to bare graphene, GP composites, especially those with protic polymers, have proved competitive in enhancing CO_2 hydrate formation and stability.

Table 15. Synergistic Nanoparticle–Polymer Formulations for Enhancing CO_2 Hydrate Formation and Stability

Polymer	Nanoparticle	Properties	Effects on CO_2 Hydrate Formation and Stability	Refs
Polyethylene	Graphene Oxide	High surface area, excellent dispersion, hydrophobic.	Enhanced formation rate, storage capacity, and slow release.	216
Polyvinyl	Silica	Porous structure, high surface area, hydrophilic.	Accelerate formation, Improve stability.	217
Polyacrylamide	Iron Oxide	Rheological control, biocompatible.	Controlled formation, Faster storage rate, prolonged stability.	218

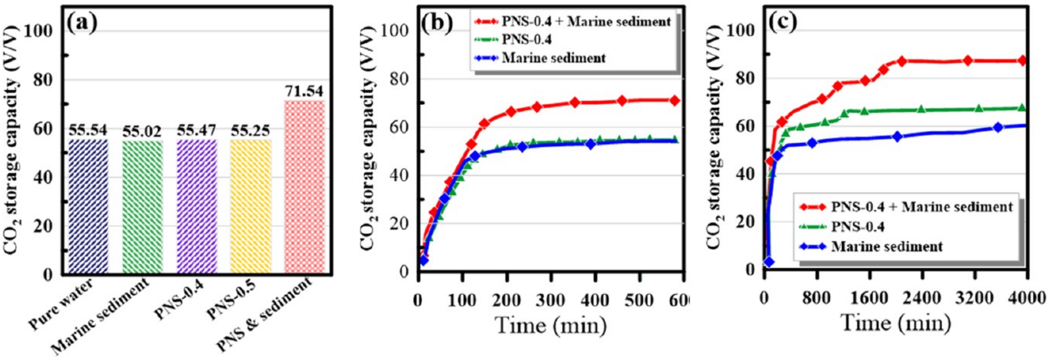

Figure 56. Enhanced CO_2 storage capacity in the presence of polystyrene sulfonate@Fe_3O_4 nanospheres (PNS) and marine sediments. (a) Maximum CO_2 storage capacities in pure water, marine sediments, PNS-0.4, and PNS-0.5. (b, c) The curves depicting CO_2 consumption for marine sediments and samples coexisting with PNS-0.4 in short-period (b) and long-period (c) isothermal experiments. Data retrieved from ref 50. Copyright 2022, American Chemical Society.

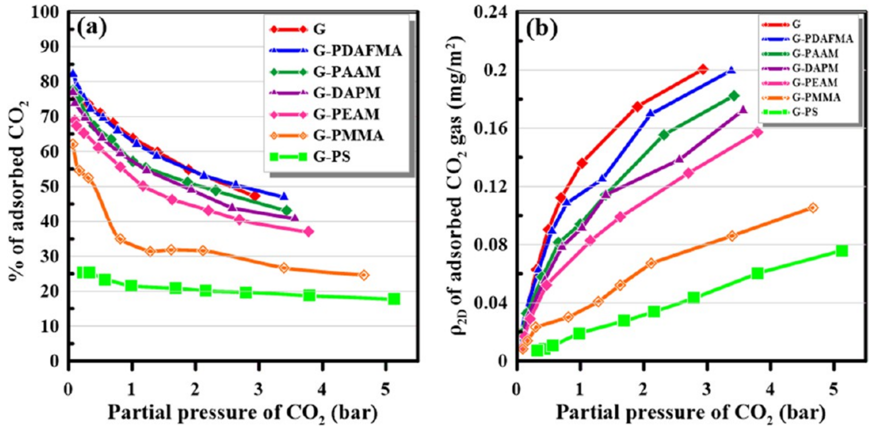

Figure 57. Influence of graphene−polymer composite surfaces and bare graphene on CO_2 gas adsorption at 300 K. (a) The percentage of CO_2 molecules adsorbed at the surface relative to the total number of CO_2. (b) The two-dimensional density (ρ_{2D}) of adsorbed CO_2 gas. Redrawn with permission from ref 216. Copyright 2019, Elsevier.

Table 16. Summary of Strategies for Optimizing Nanoparticle-Assisted Surfactant and Polymer Formulations to Enhance CO_2 Hydrate Formation and Stability in Subseafloor Saline Sediments

Strategy	Optimization Strategy
Nanoparticle Selection	Careful selection of nanoparticles based on their catalytic properties, size, and surface chemistry to enhance CO_2 hydrate nucleation and growth.
Surfactant Synergy	Identifying surfactant combinations that promote CO_2 solubility, stabilize hydrate surfaces, and facilitate nucleation in saline sediments.
Polymer Design	Tailor polymers act as hydrate stabilizers, inhibiting agglomeration and maintaining structure integrity.
Concentration Optimization	Systematically adjust concentrations of nanoparticles, surfactants, and polymers to find optimal ratios for enhanced CO_2 hydrate formation.
Temperature Control	Investigating the impact of temperature on the efficiency of formulations, optimizing for subseafloor conditions.
Pressure Sensitivity	Consider the influence of pressure on hydrate stability and tailor formulations for subseafloor pressures.
Rheological Studies	Assess the rheological properties of formulations to ensure adequate mobility and distribution in sediments.
Long-Term Stability	Evaluate the stability of CO_2 hydrates over extended periods, considering potential sediment interactions.

4.3.4. Synergistic of Nanoparticle/Surfactant/Polymer Formulations. Research investigations have revealed that adding NPs to surfactant and polymer formulations can significantly enhance the nucleation and growth of CO_2 hydrates in saline sediments.[82,195,206] Several strategies can be employed to tailor these formulations for enhanced CO_2 hydrate formation and stability, as summarized in Table 16. NPs provide nucleation sites for hydrate formation, leading to increased rates of hydrate growth and improved overall conversion of CO_2 into hydrates.[122,192] Incorporating NPs into surfactant and polymer formulations improves the stability of CO_2 hydrates.[161,195] NPs can act as stabilizers, preventing the dissociation of CO_2 hydrates and contributing to long-term stability under varying environmental conditions in subseafloor saline sediments.[98,99,210] NP-assisted surfactant and polymer formulations also allow tuning CO_2 hydrate properties. The careful selection and design of NPs, surfactants, and polymers have allowed researchers to control the size, shape, and distribution of CO_2 hydrate crystals.[206,220] This level of control has led to tailored properties that are advantageous for storage and sequestration applications. For example, manipulating the properties of CO_2 hydrate crystals can result in enhanced

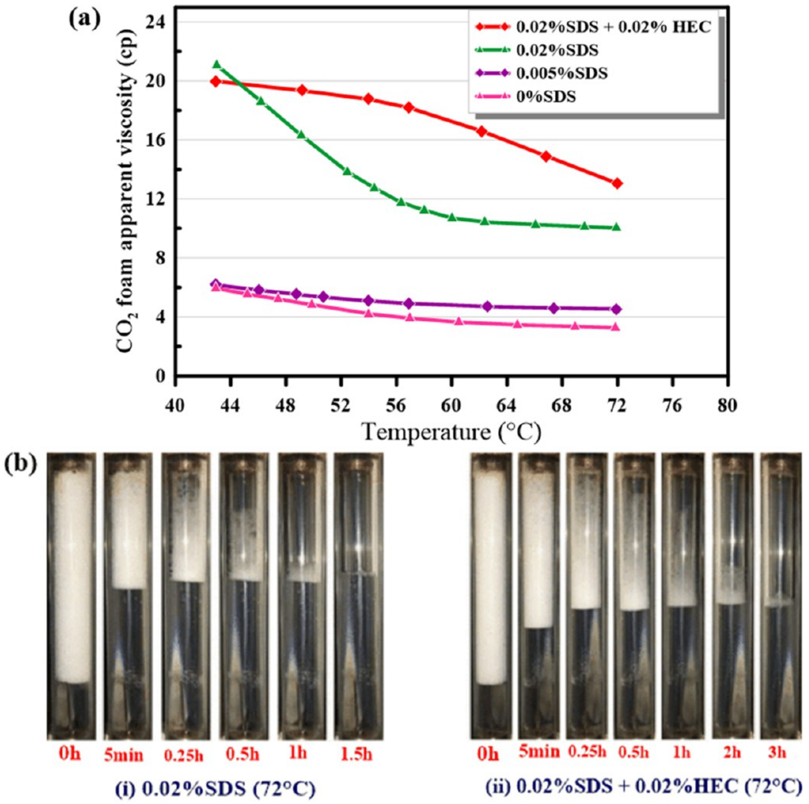

Figure 58. (a) Enhanced CO$_2$ foam stability through hydroxyethyl cellulose (HEC) polymer integration in nanosilica-SDS-stabilized CO$_2$ foam system. (b) Illustration of changes in CO$_2$ foam height over time, with and without adding HEC polymer. Adapted from ref 161. Copyright 2020, American Chemical Society.

storage capacity, improved stability, and optimized conditions for CO$_2$ sequestration in subseafloor saline sediments.[206] Moreover, combining NPs with surfactants and polymers has been demonstrated to enhance the transport properties of CO$_2$ within hydrate-bearing sediments.[89,221] This advancement has significant implications for CO$_2$ storage and transport efficiency in marine sediments; by improving the transport properties of CO$_2$, this approach contributes to more effective and secure CO$_2$ storage, ultimately aiding in the mitigation of greenhouse gas emissions and the development of sustainable energy solutions.

According to the study by Fu et al.[161] into the synergistic effects of nanoparticle−surfactant−polymer formulations for CO$_2$ foam formation and stability using materials that include anionic surfactant SDS, nonionic surfactant Ecosurf EH-9, cationic surfactant DTAB, and hydroxyethyl cellulose (HEC) polymer revealed compelling findings. The effects of different surfactants on nanosilica-stabilized CO$_2$ foam generation, apparent viscosity, and stability were examined. The anionic surfactant SDS revealed substantial influence, enhancing CO$_2$ foam stability and apparent viscosity compared to nonionic Ecosurf and cationic DTAB surfactants. The study highlighted the significance of the negatively charged nanosilica working synergistically with SDS, resulting in improved electrostatic repulsion and reduced interfacial tension. Surfactant concentration variations in the aqueous nanosilica solution demonstrated a proportional increase in foam apparent viscosity with increasing SDS concentration, establishing a threshold concentration. High temperatures were identified as a factor diminishing CO$_2$ foam stability and apparent viscosity. Yet, the addition of SDS mitigated this effect, emphasizing the crucial role of surfactant concentration in maintaining foam properties under such conditions. Furthermore, introducing HEC polymer into the nanosilica-SDS-stabilized CO$_2$ foam system enhanced thermal resistance. The polymer's ability to solidify the nanosilica distribution at the bubble interface strengthened the spatial network, resulting in improved foam stability, as shown in Figure 58. The stability of CO$_2$ foam, achieved through carefully selected components and their interactions, positively influences the formation and stability of CO$_2$ hydrates, offering potential applications in carbon capture and storage (CCS), ensuring effective trapping and secure storage of CO$_2$.

4.4. Feasibility Analysis of Nanoparticle-Assisted Surfactant/Polymer Formulations for Enhanced CO$_2$ Hydrate Storage.

4.4.1. Availability of Nanoparticle, Surfactant, and Polymer Additives for CO$_2$ Hydrate Storage. The development and application of NPs, surfactants, and polymers play a crucial role in enhancing the formation and stability of CO$_2$ hydrates for potential subseafloor storage solutions. The availability of NPs such as aluminum oxide (Al$_2$O$_3$) has been shown to significantly enhance CO$_2$ hydrate formation rates when combined with surfactants like sodium dodecyl sulfate (SDS), indicating promising results in laboratory studies.[222] Moreover, superabsorbent polymers (SAPs) have been utilized to improve CO$_2$ uptake in binary THF-CO$_2$ hydrate formation under static conditions, indicating a tangible advancement in the polymer field related to CO$_2$ storage enhancements.[60] The use of surfactant-assisted NPs is not only limited to enhancing the physical properties of hydrates but also ensures the colloidal suspension's stability, which is crucial for practical applications.[223] This supports the notion that an assortment of suitable NPs, surfactants, and polymers is readily available for research and development toward CO_2 hydrate stability and storage efficiency. However, there are notable challenges and limitations associated with the scalability and sourcing of these nanomaterials and chemicals. The production of NPs and surfactants at a scale that is feasible for industrial applications of CO_2 hydrate storage faces potential constraints. Issues such as the high cost of large-scale production, the environmental impact of sourcing raw materials, and the technical challenges in maintaining the quality and specifications of NPs and surfactants can hinder their widespread adoption.[82] Additionally, the stability of surfactants under varying environmental conditions, particularly in subseafloor sediments, requires careful consideration to ensure the long-term efficacy of the hydrate storage system, primarily due to the challenges posed by slow CO_2 hydrate formation kinetics and a limited understanding of the stability dynamics of CO_2 hydrates.[177,187] Identifying and addressing these challenges is essential for the practical implementation of nanoparticle-assisted surfactant–polymer formulations in enhancing CO_2 hydrate storage solutions.

4.4.2. Cost Considerations. Utilizing nanoparticle-assisted surfactant–polymer formulations for enhanced CO_2 hydrate storage comes with certain cost implications, as described in Table 17. These innovative materials and advanced technologies contribute to a higher initial investment compared to traditional additives methods for CO_2 hydrate storage, such as simple salts or low-cost surfactants.[84,224] While traditional additives may offer lower upfront costs, they often lack the tailored functionalities and effectiveness of nanoparticle-assisted formulations in terms of hydrate formation kinetics and stability enhancement.[107,210] However, nanoparticle-assisted surfactant–polymer formulations' superior efficiency and performance in CO_2 storage significantly outweigh these initial costs in the long term. The high efficiency in CO_2 capture and storage achieved through these formulations could reduce the need for frequent reinjections, ultimately saving operational costs.[55,84]

4.4.2.1. Cost-Effectiveness Comparison. When evaluating the cost effectiveness of NPs, surfactants, and polymer additives against traditional additives CO_2 hydrate storage methods, it is evident that NPs formulations offer better long-term savings. They are more effective in enhancing CO_2 storage capacity and stability, leading to significant improvements in operational efficiency.[84] Although the initial costs are higher, the reduction in operational expenses and the need for less frequent interventions make them more cost effective in the long run.[84,225]

4.4.2.2. Potential Cost-Saving Measures. Several cost-saving measures can be implemented to improve the economic viability of using NP formulations. Optimizing the synthesis process to reduce the production costs of NPs is one strategy.[225] Moreover, employing low-cost materials, such as silica NPs, at minimal concentrations without compromising performance can significantly reduce costs.[225] Combining these additives with cost-effective surfactants and polymers can further enhance the cost effectiveness by leveraging the synergistic effects of these compounds.[224,225]

4.4.3. Technological Readiness and Implementation Challenges. The technological readiness of nanoparticle-assisted surfactant–polymer formulations for practical application in CO_2 hydrate storage projects has seen promising developments. These formulations have been successfully

Table 17. Comparative Cost Analysis of Nanoparticle-Assisted Surfactant/Polymer Formulations versus Traditional CO_2 Hydrate Storage Methods

Factor	Nanoparticle (NPs) Formulations	Traditional Methods	Cost Effectiveness	Cost-Saving Strategies	Refs
Initial Investment	High due to innovative materials and technologies	Lower, as they rely on established processes	Nanoparticles offer long-term savings due to enhanced efficiency and reduced need for reinjection.	Optimize nanoparticle synthesisand utilization processes.	55,84, 224, 225
Operational Cost	Varies with formulation specifics but is generally higher due to specialized additives.	Comparatively lower	Nanoparticles reduce overall operational costs by improving the CO_2 storage capacity and stability.	Employ low-cost nanoparticles (NPs), like silica, in minimal concentrations.	84, 224, 225
Efficiency and Performance	Significantly improve CO_2 storage efficiency and stability	Less efficient, may require more frequent interventions	High with nanoparticles due to better CO_2 capture and storage performance.	Combine nanoparticles with cost-effective surfactants and polymers for synergistic effects.	55, 84, 224, 225
Environmental Impact	Potentially lower due to reduced need for chemicals and reinjections	Higher, as traditional methods may require more material and energy	Nanoparticles offer an environmentally sustainable option by enhancing CO_2 storage with minimal intervention.	Implement green synthesis of nanoparticles and recycle materials where possible.	55, 84, 224

applied in enhanced oil recovery (EOR) processes due to their ability to reduce interfacial tension (IFT), improve emulsion stability, and alter wettability under a range of environmental conditions, including high temperature and salinity.[184,226] The added NPs enhance the stability of these formulations, making them more resilient to the harsh conditions encountered in subseafloor saline sediments.[227] This improvement in stability and performance underscores a critical step toward the practical application of these technologies in CO_2 hydrate storage projects, suggesting a moderate level of technological readiness. However, several potential technical challenges or barriers need to be addressed. The success of nanoparticle-assisted surfactant–polymer formulations in CO_2 hydrate storage hinges on the compatibility of these formulations with specific reservoir conditions, including the chemistry of the sediment and the surrounding water.[228] Moreover, the long-term stability of these formulations under extreme pressure and temperatures characteristic of subseafloor environments remains a substantial challenge. Additionally, ensuring that these NP formulations do not adversely affect marine ecosystems presents another critical barrier to implementation. Addressing these technical challenges is vital for the successful deployment of this technology. Ongoing research efforts are intensely focused on overcoming these challenges to ensure the successful implementation of nanoparticle-assisted surfactant–polymer formulations in CO_2 hydrate storage projects. Advances in material science are enabling the modification of surface properties of NPs to improve their compatibility with various reservoir conditions.[82,91,229] Additionally, research into the synergistic effects between surfactants and NPs aims to optimize formulations for reduced IFT, better stability, and minimal environmental impact.[82,162,229] Emerging technologies, such as nonionic surfactants for the stabilization of polymeric NPs, are being explored for their potential to enhance the efficacy and environmental sustainability of these formulations in CO_2 hydrate storage applications.[230,231]

4.4.4. Environmental and Regulatory Considerations. The integration of NPs within surfactant–polymer systems for the purpose of enhancing CO_2 hydrate storage brings forth significant environmental considerations. The environmental impact of these nanoparticle-assisted additives is multifaceted. On the one hand, specific NPs like carbon nanofibers, nanocellulose, titanium dioxide (TiO_2), and silver (Ag) have been shown to cause a 10-fold increase in Natural Resource Extraction Use (NREU) such as energy, water, and raw materials like metals or carbon sources, and Global Warming Potential (GWP) compared to their unfilled polymer matrix counterparts.[232] This indicates a substantial potential for contributing to environmental degradation if not properly managed or if used extensively without adequate controls. However, the complexity of these impacts, as the specific environmental consequences, may vary based on the type and quantity of NPs used, as well as their lifecycle management practices.[232]

The adoption of nanoparticle-assisted surfactant–polymer additives in CO_2 hydrate storage applications is subject to an evolving landscape of legislation and regulatory frameworks aimed at ensuring the safe use of nanotechnology. Different jurisdictions may have varying requirements and regulatory bodies contributing to a complex global regulatory environment. Although specific regulations tailored to NP use in CO_2 hydrate storage are not widespread, general regulations concerning NP safety, environmental release, and waste management apply. For instance, the regulation of nanomaterials within the EU under the Cosmetics Regulation (EC No. 1223/2009) provides a relevant regulatory framework by addressing the classification, labeling, and safety assessment of nanomaterials.[233] This indicates a trajectory toward more comprehensive oversight, which could encompass the use of NPs in CO_2 hydrate storage, emphasizing the necessity for compliance and adaptation to these regulatory standards. Proper navigation through these regulations is crucial for the successful and ethical implementation of nanoparticle-assisted technologies in CO_2 storage applications.[233,234]

4.5. Nanoparticles (NPs) Recovery: Mitigating Environmental Hazards.

The utilization of NPs in the process of CO_2 hydrate formation, stability, and storage presents a novel approach to greenhouse gas reduction. However, the environmental consequences of NP disposal are a significant concern. NPs, due to their unique properties such as high specific surface area and excellent thermal conductivity, improve the kinetics of CO_2 hydration processes but also pose risks when disposed of improperly.[14,82] If released into marine ecosystems, these particles may aggregate, potentially affecting aquatic life through ingestion or physical harm. The environmental impact is thus not just related to the effective capture of CO_2 but also to the eventual fate of the NPs used in these processes.[82] Developing effective methods for recovering NPs after their role in CO_2 hydrate formation is crucial for minimizing environmental risks. Given the potential for NPs to cause ecological harm, their recovery ensures that the benefits of CO_2 storage in hydrate form do not come at the expense of marine health. The recovery methods, such as magnetic retrieval/recyclable of NPs, present a novel approach where NPs can be easily separated from the sediment or hydrate matrix, minimizing the environmental impact associated with NPs dispersion and contributing to the sustainability of the process by allowing for the reuse of nanoparticles in subsequent hydrate formation cycles, thus reducing the need for continuous production of new NPs.[82,235] This advancement in technology offers promising avenues for the effective recovery of NPs from subseafloor sediments post-CO_2 hydrate formation. The advantage of this approach lies in its precision and minimal invasiveness, significantly reducing the potential for ecological disturbance. Additionally, the reusability of the recovered NPs fosters a sustainable cycle of application. Nonetheless, the limitation stems from the need for nanoparticles to be inherently magnetic or coated with magnetic materials, potentially restricting the choice of nanoparticles and affecting their hydrate promotion efficacy.[89,236]

Furthermore, the use of engineered NPs with specific structures, such as multilayer core–shell structures, facilitates their recovery by providing unique chemical or physical properties that can be exploited during the recovery process.[50] The advantage of this approach lies in their enhanced recoverability due to the unique chemical or physical properties they possess, the outer shell of these NPs can be tailored to interact selectively with certain substances or to exhibit increased buoyancy, facilitating their separation from the sediment or hydrate matrix. Nonetheless, the limitation of this approach stems from the complexity and cost associated with engineering NPs with specific structures. Achieving precise control over the composition and morphology of these NPs requires sophisticated synthesis techniques, which may not always be practical or economically viable. Addition-

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Table 18. Comparative Analysis of Optimization Strategies for CO_2 Hydrate Formation and Stability

Aspect	This Study (This Section)	Previous Studies
Focus	Integration of thermal and pressure management for CO_2 hydrate stability.	General overview of formation-decomposition mechanisms and CO_2 sequestration potentiality.[15]
Novelty	Detailed multifaceted strategies combining thermal and pressure controls.	Broad discussions on molecular dynamics simulations, experiments, and sequestration potentiality.[237]
Application	Tailored strategies for seafloor sediment environments.	Various settings, including porous media and methane (CH_4) hydrate reservoirs.[15,47,237]
Methodology	Hybrid and multistage approaches for optimized conditions.	Primarily focused on individual aspects of hydrate formation and decomposition.[15,47,238]
Impact	Implications for efficient and sustainable CO_2 capture and energy storage methods.	Overview of current knowledge without explicit focus on optimization strategies.

ally, the introduction of engineered NPs into the environment raises concerns about potential unintended consequences and long-term impacts on ecosystem health.

Another recovery technique focuses on the utilization of biodegradable NPs, designed to degrade into environmentally benign components after fulfilling their role in hydrate formation and stabilization. This strategy circumvents the need for physical recovery processes, thereby mitigating the environmental hazards associated with NPs accumulation in marine ecosystems. The advantage of this approach lies in its inherent alignment with environmental protection goals, offering a self-mitigating solution to NPs dispersion. However, the limitations are linked to the control over the degradation process, ensuring that it only occurs once the NPs have served their purpose. This requires precise engineering of NPs composition and stability, posing challenges in balancing efficacy in hydrate promotion with environmental safety considerations.[82]

A multifaceted approach could be adopted to enhance efficiency and sustainability in NPs recovery post-CO_2 hydrate formation. Integrating multiple recovery techniques, such as magnetic retrieval/recycling and engineered nanoparticles with specific structures, can offer complementary benefits. Combining these techniques can achieve a holistic approach, balancing efficacy in hydrate promotion with environmental safety considerations, thus ensuring sustainable NPs utilization in CO_2 hydrate storage. Despite these innovations, several challenges remain in the field of NPs recovery post-CO_2 hydrate formation. The development of cost-effective and efficient recovery technologies that can operate under the extreme conditions of subseafloor environments, such as varying sediment chemical composition and sediment heterogeneity, and overly high or low pressure, temperature and salinity, is crucial. Research on improving recovery rates and understanding the interaction between NPs, hydrate formations, and marine ecosystems is vital. This involves interdisciplinary approaches combining material science, environmental science, and engineering to address these complex issues.

5. OPTIMIZING CO_2 HYDRATE FORMATION AND STABILITY VIA THERMAL AND PRESSURE MANAGEMENT

The novelty of this section lies in the comprehensive analysis and synthesis of recent advancements in optimizing CO_2 hydrate formation and stability through thermal and pressure management strategies, particularly applicable to seafloor sediment environments. This approach is contrasted against previously published studies to underscore the unique contributions and perspectives it offers within the context of CO_2 sequestration and energy applications. The following comparative analysis, as presented in Table 18, highlights this section's distinctive focus and contributions.

The presented study in this section extends beyond the scope of the previous studies by providing a detailed exploration of how thermal and pressure management can be synergistically applied in subseafloor environments to enhance CO_2 hydrate formation and stability. It addresses the necessity for precise manipulation of these influential factors within seafloor sediment contexts, where the balance between thermal conditions and pressure dynamics critically determines the feasibility and efficiency of CO_2 hydrate-based carbon capture and storage (CCS) technologies. By presenting a systematic analysis of the latest developments in thermal and pressure management techniques, including innovative hybrid methodologies and multistage approaches, this work contributes a novel perspective to the body of research on CO_2 hydrate formation. It emphasizes the potential of these advanced strategies to significantly improve CO_2 hydrate stability and formation rates, underscoring their importance in advancing carbon sequestration efforts and energy solutions. Furthermore, through the comparative analysis of different optimization strategies, this work elucidates the advantages of combining thermal and pressure adjustments in attaining maximum CO_2 hydrate stability. It presents a compelling argument for the critical role of tailored, comprehensive strategies in overcoming the challenges associated with CO_2 hydrate formation in seafloor sediments, highlighting the potential for groundbreaking advancements in the field of CO_2 sequestration and CCS technologies.

5.1. Impact of Temperature, Pressure, and Salinity on CO_2 Hydrate Formation and Stability.

In recent research investigations, the impact of temperature, pressure, and salinity on CO_2 hydrate stability and formation kinetics has been a focal point.[47,239,240] These influential factors are crucial in understanding and optimizing CO_2 hydrate formation and stability in subseafloor saline sediments.[240] Temperature has been revealed to significantly influence CO_2 hydrate stability and formation kinetics. 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.[47,213] Liu et al.[4] 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.[187] reported that the stability of CO_2 hydrates in oceanic sediments at depths of 1km with a higher pressure from 10 MPa and low temperatures between 276.15 to 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,

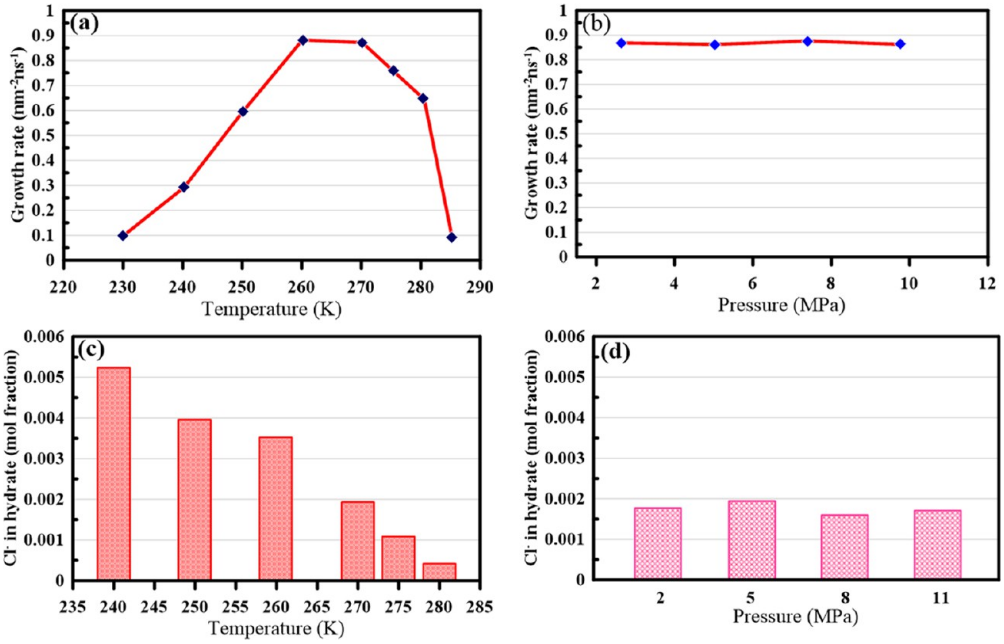

Figure 59. Temperature and pressure dependence analysis of CO_2 hydrate growth rate. (a, b) The growth rate of CO_2 hydrate in NaCl solution to temperature and pressure dependencies. (c, d) Cl^- concentration's temperature and pressure dependencies in the newly formed hydrate phase. Redrawn with permission from ref 247. Copyright 2023, American Chemical Society.

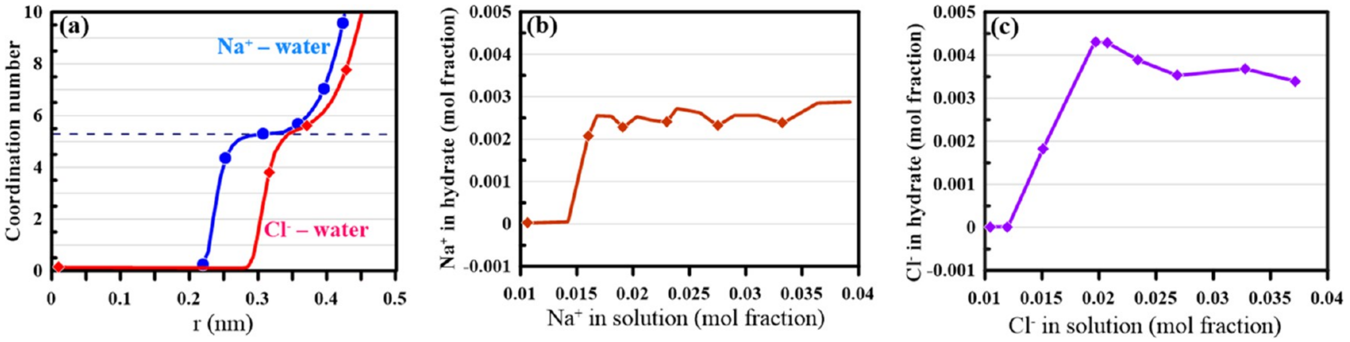

Figure 60. Relationship between ion incorporation, salinity, and hydrate structure distortion. (a) Coordination of the number of water molecules surrounding ions in the solution phase at 260 K and 5 MPa. (b, c) Correlation between solution salinity and ion concentration in the newly formed hydrate phase. Data retrieved from ref 247. Copyright 2023, American Chemical Society.

especially in subseafloor 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.[241,242] However, molecular simulation investigation by Liu et al.[4] 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.[243] 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 subseafloor saline sediments can impact the equilibrium conditions and kinetics of CO_2 hydrate formation.[38] 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.[244] Thus, the influence of salinity variations provides valuable insights for tailored and controlled CO_2 release.[245] 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,[206,246] particularly in the context of carbon capture and storage technologies.

Zhao et al.[247] 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 × 4 × 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

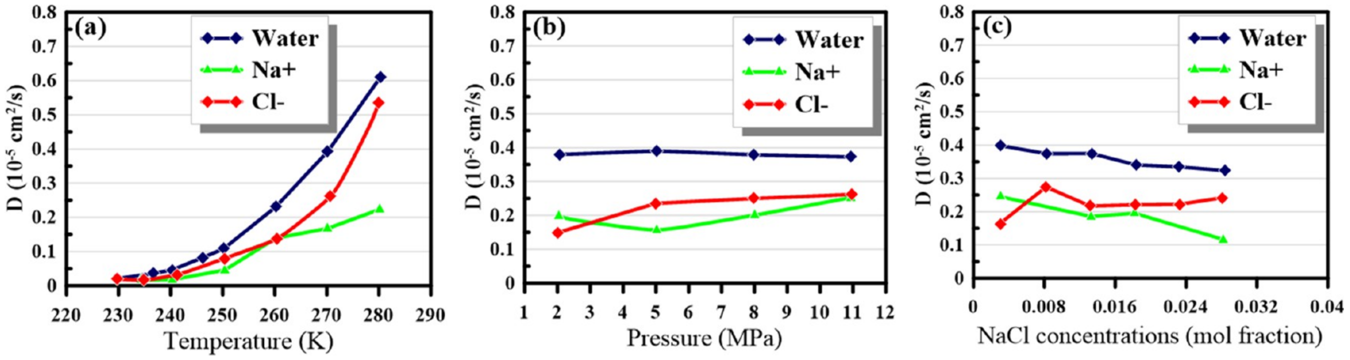

Figure 61. Influence of temperature on ion diffusion and incorporation into CO_2 hydrate structure during growth with respect to pressure and ion concentrations: (a) temperature, (b) pressure, and (c) varying NaCl concentrations. Redrawn with permission from ref 247. Copyright 2023, American Chemical Society.

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 revealed 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 Figure 59. 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.[247] revealed 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 Figure 60. 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.[47,182] Specifically, the dynamic properties refer to the ability of ions to diffuse and move within the solution.[247,248] 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.[247] 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 Figure 61(a). In contrast, ions exhibit rapid diffusion at higher temperatures, as shown in Figure 61(a), reducing the probability of being trapped in the hydrate phase.[247] 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.[4] 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 Figure 62. 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

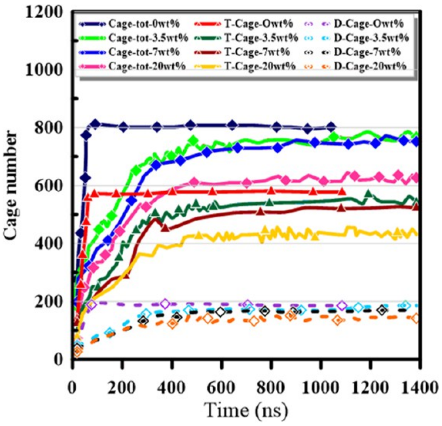

Figure 62. Influence of sodium chloride (NaCl) concentration on CO_2 hydrate cage formation and stability at 255 K, 30 MPa. Redrawn with permission from ref 4. Copyright 2021, RSC Advances.

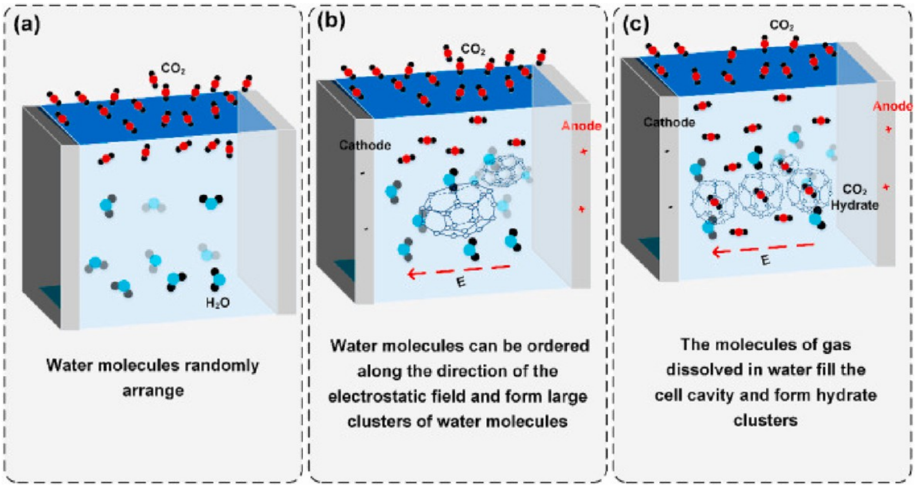

Figure 63. Formation of CO_2 hydrate under the influence of an electrostatic field. Reproduced with permission from ref 249. Copyright 2023, Elsevier.

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.[4] 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.[21,43] 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 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.[47] Furthermore, the experiments conducted by Husebø et al.[244] using bentheim sandstone as a porous medium demonstrate 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.

The comparative analysis of the discussed studies reveals several key insights into the factors influencing CO_2 hydrate formation and stability in subseafloor saline sediments. Temperature, pressure, and salinity all play significant roles in shaping the kinetics and stability of CO_2 hydrates. While temperature exerts a pronounced effect on hydrate growth rates, pressure primarily impacts hydrate nucleus formation rather than individual crystal growth. Additionally, salt ions, particularly sodium chloride (NaCl), influence hydrate formation kinetics, with lower salinity areas being more conducive to CO_2 hydrate formation and stability. Molecular dynamics simulations highlight the intricate dynamics of ion incorporation into the hydrate structure, with temperature influencing ion diffusion rates and their incorporation into the growing hydrate lattice. Despite the inhibitory effect of salt ions on CO_2 hydrate growth, experiments suggest that higher initial salinity may lead to longer induction times and less hydrate formation, with the physical structure of the porous medium interacting with temperature and pressure dynamics impacting the overall process. Thus, a comprehensive understanding of these factors is essential for optimizing CO_2 hydrate formation and stability, particularly in saline sediment environments, with implications for carbon capture and storage technologies.

5.2. Thermal Management Techniques for Optimizing CO_2 Hydrate formation. Controlled heating methods are essential in optimizing CO_2 hydrate formation and stability in subseafloor saline sediments. One prominent approach involves using electrical heating systems,[249] as diagrammatically illustrated in Figure 63. 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.[249,250] Additionally, microwave heating is another noteworthy technique employed in this context. Microwave energy can be selectively delivered to specific regions of subseafloor sediments, promoting efficient heating and enhancing the kinetics of CO_2 hydrate formation.[251] 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.[252,253] This approach capitalizes on the natural temperature gradients in subseafloor environments. By strategically placing heat sources in specific locations within the sediments, researchers can harness

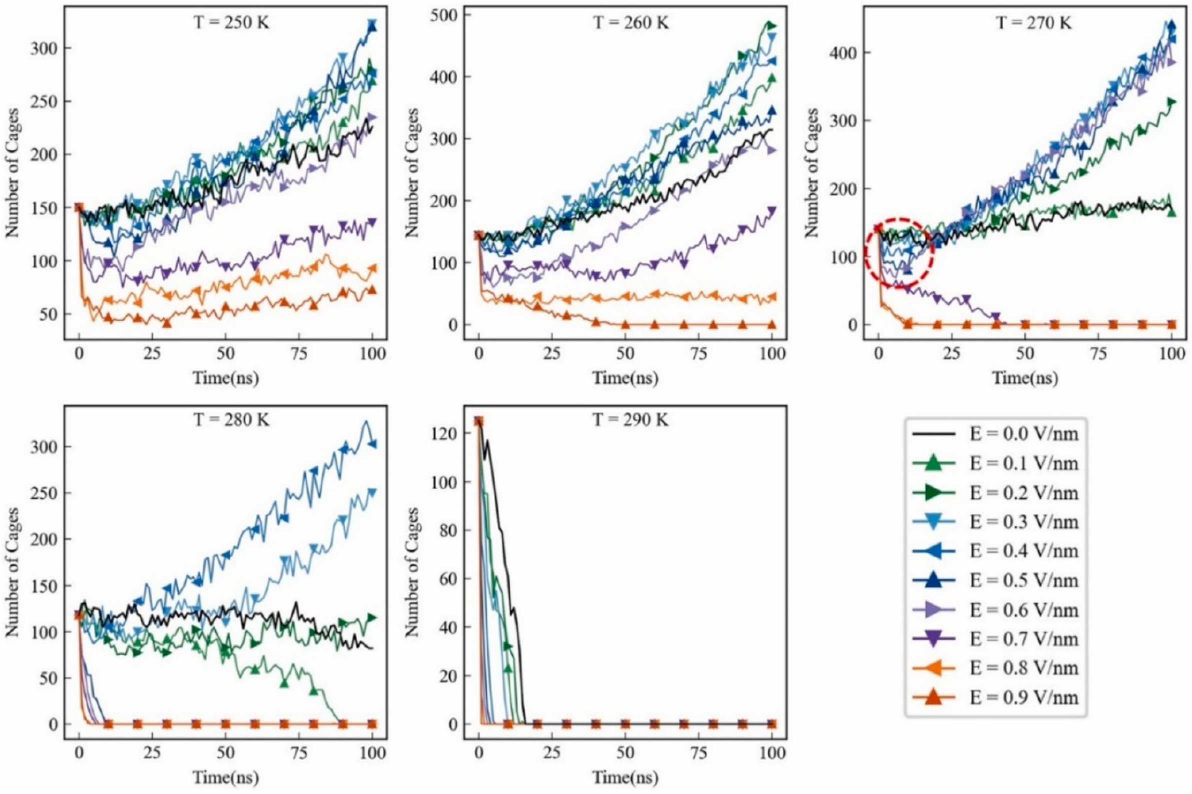

Figure 64. Changes in the number of CO_2 hydrate cages across varying temperature (K) and electrical field (V/nm) conditions. The red dotted circle at T = 270 K graph shows the fluctuating phase observed at the beginning of the simulation. Reproduced with permission from ref 250. Copyright 2023, Elsevier.

geothermal energy to induce localized heating.[254,255] 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 subseafloor saline sediments.[255,256] 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.

5.5.1. 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 0.2−0.6 V/nm that significantly promotes the growth of CO_2 hydrate crystals.[250] Electric fields within the intensity window enhance the solubility of CO_2 molecules, offering a mechanism for promoting CO_2 hydrate growth.[250] 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.[71,250] This alignment facilitates the growth of CO_2 hydrate crystals within the identified intensity window. Meng et al.[250] 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 Figure 64—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.[250,257] 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.[250,258] This parameter can be determined analytically by computing the dihedral angle formed by two neighboring water molecules within the system, as specified in eq 1.[250] 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.[250,259] 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.[250,260] These values align with the expected behavior of water molecules in different phases. It is 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.

$$F_4 = 1/n \sum_{i=1}^{n} \cos(3\varphi_i) \tag{1}$$

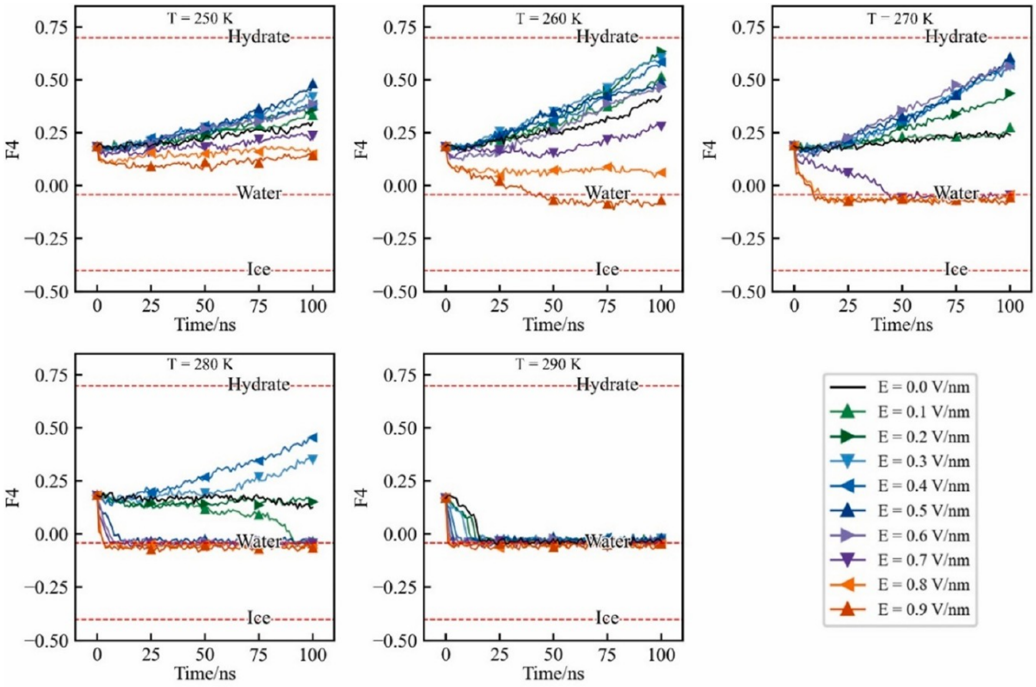

Figure 65. F4 structural order parameters at different temperatures (K) and electrical field (Vnm) conditions. Reproduced with permission from ref 250. Copyright 2023, Elsevier.

Table 19. Conditions for Hydrate Formation in Various Systems under the Influence of an Electrostatic Field[249,a]

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

[a] This table was reproduced with permission from ref 249. Copyright 2023, Elsevier.

In eq 1, indicating the F4 order parameter, φ_i represents the torsional angle of H−O···O−H, and n denotes the number of oxygen−oxygen pairs among water molecules located within a radius of a selected molecule. Figure 65 depicts the variation curves of F4 over simulation time for different temperatures (K) and electrical field systems (Vnm) as observed from Meng et al.[250] 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 2.[250] 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.[205] 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.[250] 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

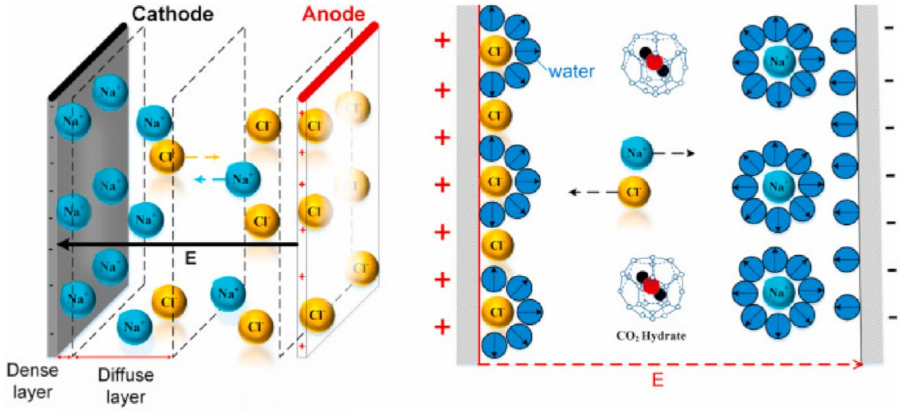

Figure 66. Influence of electrostatic field on CO_2 hydrate formation in saltwater system. Illustration of the arrangement of ions in the salt solution system when subjected to an electrostatic field. Reproduced with permission from ref 249. Copyright 2023, Elsevier.

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.

$$\mathrm{MSD} = R(t) = \langle |\vec{r}(i) - \vec{r}(0)|^2 \rangle = 1/N \sum_{i=1}^{N} \langle |R_i(t) - R_i(t_0)^2 \rangle \tag{2}$$

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.[249] reported that applying a 150 V 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 19, 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 19. 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.[249] 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 Figure 66.

The comparative analysis of the discussed studies reveals the diverse effects of electrical fields on CO_2 hydrate formation in different systems. While Meng et al.[250] revealed that specific electric field strengths within an intensity window (0.2−0.6 V/nm) significantly promote CO_2 hydrate growth by altering water molecule alignment and increasing solubility, Zhao et al.[249] showcased varying outcomes depending on the solution composition. In freshwater systems, the electrostatic field enhances hydrate formation by facilitating water molecule aggregation, but its impact diminishes in memory water systems, where residual hydrate cage fragments remain after decomposition. In saltwater systems, the field influences the entire formation process, enhancing hydrate formation initially but inhibiting growth due to intense collision between ions and nuclei. Despite its disruptive effects, the field promotes hydrate formation by influencing ion distribution in specific directions. These findings underscore the complexity of CO_2 hydrate formation dynamics under the influence of the electrical field and highlight the need for comprehensive understanding when applying such techniques in diverse environments.

5.3. Pressure Management Strategies for Optimizing CO_2 Hydrate formation.

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.[261] Pressures exceeding 800m depth are typically high enough to maintain CO_2 in a condensed state, which is ideal for maximizing storage capacity.[261] 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 subseafloor saline sediments, have been identified as crucial factors in promoting efficient CO_2 hydrate formation and ensuring long-term stability.[262] The interplay between pressure and temperature also plays a critical role.[47,263]

When injecting CO_2, pressure increases within a structural closure must be carefully monitored. Appropriate management of this pressure is crucial for the integrity of the CO_2 formation and storage and maximizing the useable space within the reservoir.[264] 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.[265] 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.[47] CO_2 hydrates form more readily and are more stable at high pressures and low temperatures.[47,263] These conditions can also influence the hydrate formation rate and dissociation.[263] Therefore, pressure control is key in mitigating the risks associated with CO_2 hydrate dissociation,[230,266] emphasizing the importance of integrating pressure management strategies into comprehensive risk assessment and mitigation frameworks for subseafloor 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.[187] 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.[267] These high-pressure reactor systems are instrumental in advancing CO_2 hydrate formation and developing pressure management strategies for carbon capture and storage applications.[263,267]

5.3.1. 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 subseafloor saline sediments.[164,268] 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 subseafloor saline sediments.[269] 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 nonlinear 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.[164,268,270] 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.[185] These predictive tools allow the control systems to adjust to environmental changes and maintain optimal CO_2 hydrate formation and stability conditions.[185] 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 environment.[263,271] Table 20 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

Table 20. 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	Refs
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	116
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.	272
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.	273
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.	116, 267

control in subseafloor 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.[274,275] 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.[275] On the other hand, depressurization techniques focus on controlled pressure reduction to induce phase transitions and optimize hydrate dissociation.[276,277] 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.[277] Both hydraulic fracturing and depressurization, individually or combined, have shown promise in improving gas production efficiency from marine hydrate reservoirs.[278] 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.[279] The findings from various research investigations, as described in Table 21, 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.[280] 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.[281]

5.4. 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. Optimizing 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 multistage approaches that boost CO_2 hydrate formation efficiency. Table 22 provides a comparative analysis of the relevance and efficiency of these two techniques from various research investigations.

5.4.1. 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 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.[286] 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

Table 21. 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	Refs
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.	274, 282
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.	283
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.	276, 284
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.	280, 285

Table 22. Comparative Analysis of CO_2 Hydrate Formation Techniques: Hybrid Methodologies and Multistage Approaches

Research Investigation	Hybrid Methodology (*Thermal and Pressure*)	Multistage Approach	Key Findings	Relevance and Efficiency	Refs
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.	116
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.	2
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.	290
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.	230
Multilayered 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 multistage approach considering sediment layering could enhance overall CO_2 hydrate formation efficiency.	7
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.	187
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.	144
Dendrite Growth Rate	Yes (Temperature Control)	No	Growth rate studies show that controlling temperature can lead to 3 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.	291
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.	292

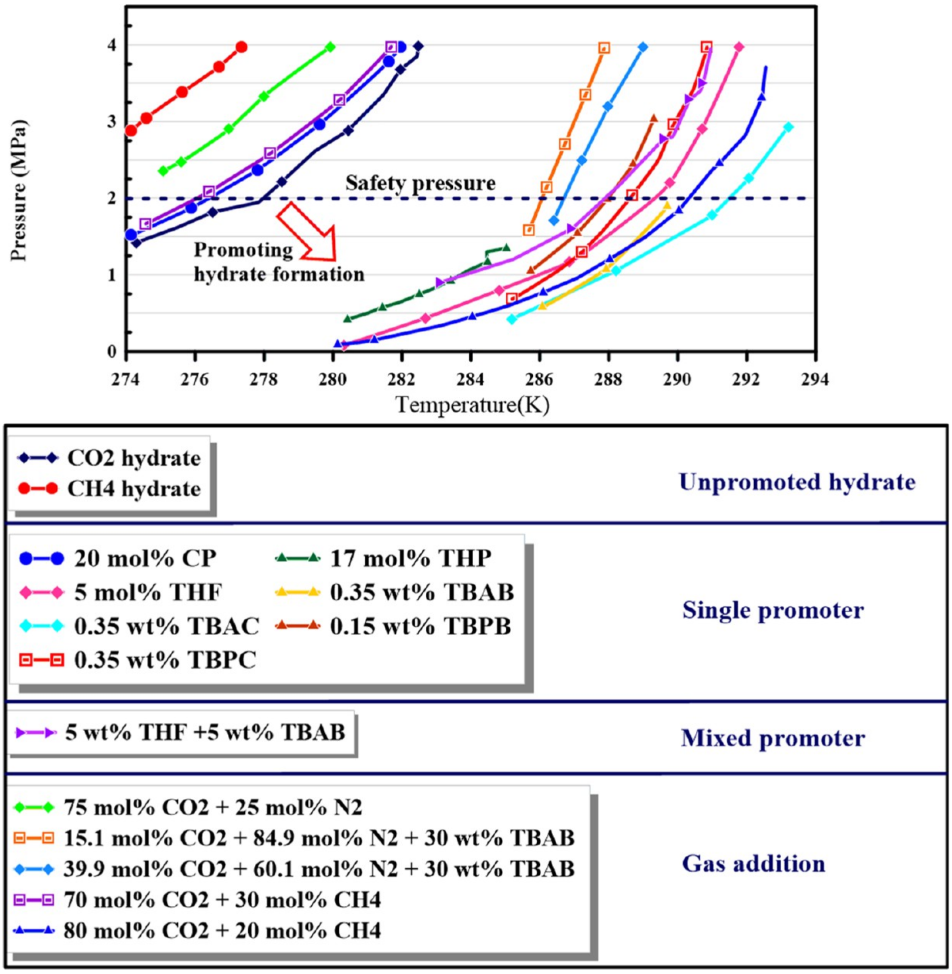

Figure 67. Synergistic effects of temperature and pressure alongside different additives on CO_2 hydrate formation and stability: illustration of equilibrium shift with parameters variation. Adapted from ref 238. Copyright 2023, Elsevier.

(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.[287] Such systems can be customized to manage temperature conditions precisely, ensuring they remain within the target range, which promotes the stable growth of CO_2 hydrates. The synergy between these thermal management techniques, such as composite PCMs incorporating materials like expanded graphite, surfactant, and organic compounds as surfactant-supported copromoters such as tetrahydrofuran (THF), cyclopentane (CP), enhances their performance within the thermal management system.[56,287] 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, as illustrated in Figure 67. 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.[23,206] This increases the rate of hydrate nucleation and shortens the induction time for hydrate formation.[23] 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.[116,164,185] 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 Figure 67, 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.[144] 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.[230,238] 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.[143,230,238]

5.4.2. Multistage Approaches for Enhanced Formation Efficiency. Multistage 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.[4,56,116,288] 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/stepped 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.[40,144,185,289]

5.5. Comparative Analysis: Optimization Strategies for CO_2 Hydrate Formation and Stability. The advancements in CO_2 hydrate formation techniques highlight a nuanced approach to optimizing conditions for maximum stability, which is crucial for CO_2 sequestration and gas storage applications. Hybrid methodologies integrating thermal and pressure management are essential, providing a synergetic effect that enhances CO_2 hydrate stability. These methods, including using phase change materials and pressure oscillation, as illustrated in Figure 67, effectively manage the temperature and pressure conditions favorable for hydrate formation. Additionally, multistage approaches, which sequentially apply various techniques to promote nucleation and growth, as described in Table 22, show significant promise in improving the efficiency and sustainability of the hydrate formation process. By leveraging the intrinsic dynamics of CO_2 and water under controlled conditions, both strategies offer avenues for more reliable and efficient CO_2 hydrate synthesis, addressing challenges in formation rates and stability. These innovative developments represent a key shift toward achieving greater control over the formation and stability of CO_2 hydrates, with implications for energy applications and CO_2 capture strategies.

6. CHALLENGES, RESEARCH GAPS, AND FUTURE PERSPECTIVES

6.1. Challenges. According to research findings, exploring carbon capture and storage (CCS) using CO_2 hydrate formation within subseafloor saline sediments faces multifaceted challenges.[19,51] This encompasses technical and economic feasibility, environmental implications, and the inherent variability of subseafloor conditions. Addressing these challenges requires a multidisciplinary approach integrating advancements in geophysical methods, sedimentology, fluid mechanics, and environmental science. Continuous research and technological development are crucial in overcoming these obstacles, enabling the realization of CO_2 hydrate storage as a viable and sustainable carbon sequestration method.

6.1.1. Sediment Microstructural Heterogeneity. The complex and heterogeneous nature of subseabed sediments presents a significant challenge in predicting and optimizing CO_2 hydrate formation and stability. Sediments' varying microstructures, impacted by factors like pore types, mineralogy, and environmental conditions, play a crucial role in gas hydrate saturation and accumulation.[51] A comprehensive understanding of these microstructures is vital, demanding advanced research that effectively characterizes sediment microstructures, impacting CO_2 hydrate stability and storage capacity.[51]

6.1.2. Sediment Chemical Compositions. The impact of sediment chemical compositions on CO_2 hydrate stability is another challenge. Clayey sediments, in particular, can lead to the formation of diverse hydrate structures with varying stabilities. These sediment characteristics, coupled with water chemistry, can significantly influence hydrate cap density and permeability—directly affecting CO_2 hydrate stability and leakage potential. The variability within sediment types and their properties adds layers of complexity to hydrate formation processes, underscoring the importance of understanding sedimentary chemical properties.[51]

6.1.3. Temperature, Salinity, and Chemical Additives. Subseabed sediment temperature and salinity, along with the application of chemical additives, pose significant challenges to CO_2 hydrate formation and long-term storage. For instance, temperature fluctuations can lead to hydrate dissociation, and salinity variations can affect hydrate formation efficiency. The effectiveness of chemical additives, such as kinetic promoters, can be compromised by irregular sediment characteristics—highlighting the delicate balance required in optimizing additive use for effective CO_2 hydrate formation.[51]

6.1.4. Economic and Environmental Considerations. The economic viability of large-scale application of these strategies remains a significant hurdle. High costs associated with chemical additives and advanced technologies limit practical application feasibility. Moreover, environmental concerns, including the potential ecotoxicity of nanomaterials and their interaction with marine ecosystems, necessitate careful consideration and thorough risk assessment to mitigate adverse effects.[19,51] Sustainable implementation of CCS technologies demands a cautious evaluation of economic and environmental impacts, ensuring the adoption of financially plausible and ecologically responsible strategies.

6.2. Research Gaps and Future Perspectives. *6.2.1. Microstructural Understanding in Sediment Dynamics.* A pronounced research gap exists in understanding sediment-specific microstructural influences on the CO_2 hydrate storage potential within subseafloor saline sediments. Few studies have elucidated the types of pores in gas hydrate reservoirs and the impact of grain size, sorting, and biological components.[51,293] Yet, the intricate heterogeneity of gas hydrate formation and saturation remains largely unexplored. Translating laboratory-based findings to the varied, often fine-grained sediments of actual subseabed environments poses significant challenges. Advanced characterization techniques, such as scanning electron microscopy (SEM) and computed tomography (CT), alongside in situ observations and large-scale performance assessments, are crucial in providing a comprehensive understanding of the microstructural controls on CO_2 hydrate stability and effectiveness in marine sediments.[294]

6.2.2. Chemical Composition'S Role at the Microscale. The interplay of CO_2 with varying mineralogical make-ups, organic matter content, salts, and in situ chemicals necessitates a closer examination. These factors are speculated to notably influence the kinetics of hydrate formation, the distribution of hydrate phases within pores, and the CO_2 trapping capacity over prolonged periods.[241] Emphasis on extending research to encompass a broader range of sediment chemistries derived from diverse subseabed environments is essential for optimizing CO_2 hydrate storage strategies and improving predictive models for potential leakage and environmental impacts.[295]

6.2.3. Nanomaterials and Surface Modifications. Nanoparticle-based sediment modifications, including the combination of nanoparticles with surfactants and polymers, show promise in promoting efficient CO_2 hydrate formation. Optimization of these combinations, understanding the interaction mechanisms between nanoparticles, surfactants, and CO_2, and establishing the optimal size of nanoparticles relative to pore sizes are areas needing further exploration.[253] Electrokinetic approaches, leveraging electric fields for particle migration and sediment property alteration, present additional avenues for enhancing CO_2 hydrate storage in subseafloor environments. However, the mechanisms behind these techniques require deeper investigation.[20]

6.2.4. Field Trials and Practical Implementation. There is a significant need for comprehensive field trials to elucidate the formation, stability, and long-term storage capabilities of CO_2 hydrates in saline sediments beneath the seafloor. These trials should delve into the thermodynamic and kinetic behavior of CO_2 hydrates under varying environmental conditions, aiming to develop strategies for enhancing stability and formation.[18] Exploring the effects of sediment heterogeneity on hydrate distribution and storage capacity, alongside perfecting chemical additive formulations for optimized hydrate formation, is crucial for advancing CO_2 sequestration techniques in offshore settings.[296]

Addressing these identified gaps requires multidisciplinary collaborations integrating geochemical analyses, experimental hydrate synthesis with varied sediment chemistries, and advanced modeling techniques. Pursuing innovative nanostructured encapsulation materials, tailored nanoparticle—surfactant—polymer systems, and computational modeling to predict and optimize subseabed CO_2 hydrate storage dynamics holds great promise. These efforts will propel the field toward realizing its full potential for long-term, effective CO_2 storage and contribute significantly to global warming mitigation strategies.

7. CONCLUSIONS

The extensive review of the approaches to enhance CO_2 hydrate formation efficiency through sediment-specific modifications and advanced techniques has led to several significant findings. The interactions between subseafloor sediments and various factors, including temperature, salinity, and chemical additives such as L-leucine (an amino acid), inorganic emulsifiers, surfactants, polymers, and nanomaterials, such as carbon nanotubes, graphene oxide, red blood cell (RBC)-inspired encapsulation, and nanoparticles, play a critical role in the formation, stability, and long-term storage potential of CO_2 hydrates. The following conclusions were made:

(1) It is evident that sediment characteristics such as porosity, permeability, grain size distribution, and mineral composition crucially affect CO_2 hydrate formation. Sediments with ideal features provide conducive environments for CO_2 migration and hydrate crystal nucleation and growth, showcasing the importance of selecting appropriate sediment matrices for effective CO_2 storage in subseafloor saline sediments.

(2) Sediment modification techniques present promising avenues for optimizing CO_2 hydrate storage systems. From surface roughening to chemical functionalization and the use of nanotechnology, these modifications aim to enhance nucleation sites, improve CO_2 adsorption, and stabilize hydrate formation. In particular, nanoparticle-based modifications have emerged as a potent method for promoting CO_2 hydrate formation and stability, although challenges such as nanoparticle agglomeration and environmental impacts need to be addressed.

(3) Effective thermal and pressure management strategies, such as electrical heating systems, microwave heating, utilizing geothermal gradients for localized heating, cyclic injection and withdrawal of fluids to induce pressure variations, as well as controlled oscillations in pressure levels, hydraulic fracturing, or depressurization techniques, have been identified as vital for optimizing CO_2 hydrate formation and stability. Adjustments to thermal and pressure conditions can mitigate issues arising from salinity variations and ensure the conditions align with the CO_2 hydrate stability window, thus enhancing CO_2 storage efficiency. However, challenges such as the need for precise control mechanisms and the environmental feasibility of heating systems pose hurdles to the widespread application of these strategies.

(4) The comprehensive analysis of CO_2 hydrate formation and the exploration of sediment-specific strategies underscore the potential of CO_2 hydrates in climate change mitigation and various practical applications. Significantly, CO_2 hydrate technology finds relevance in fields such as CO_2 capture and storage, gas replacement in the exploitation of natural gas hydrates, seawater desalination, and refrigeration systems. The ability to capture and store CO_2 in hydrates in subseafloor sediments offers a promising avenue for reducing atmospheric CO_2 levels, thereby contributing to global efforts to combat climate change. Moreover, replacing methane (CH_4) with CO_2 in natural gas hydrates represents an innovative method for both realizing energy extraction and achieving greenhouse gas sequestration simultaneously. In desalination and refrigeration, the unique properties of CO_2 hydrates can be harnessed to develop more energy-efficient and environmentally friendly technologies. Furthermore, the advancements in understanding and optimizing CO_2 hydrate formation within different sediment types pave the way for practical innovations in the design and implementation of subsea CO_2 sequestration strategies. Improving sediment suitability and stability conditions through targeted modifications makes it feasible to enhance the efficiency and capacity of CO_2 storage in subseafloor environments. This progresses the narrative from theoretical exploration to actionable solutions, demonstrating a significant leap toward the practical application of these findings in real-world scenarios.

(5) Despite the promising potential for CO_2 hydrate storage in subseafloor saline sediments, several challenges

remain. These include the need for further research on the impacts of sediment heterogeneity, the optimization of chemical additives, and the environmental compliance of nanoparticle-based modifications. Overcoming these obstacles will require a multifaceted approach that leverages advances in sedimentology, thermodynamics, and sustainable engineering practices. The journey toward efficient and environmentally responsible CO_2 hydrate storage in subseafloor saline sediments is ongoing. It is critical to continue exploratory research, field trials, and the development of innovative technologies and methodologies. With concerted efforts, CO_2 hydrate storage could play a significant role in the global endeavor to mitigate climate change by providing a secure and sustainable solution for CO_2 sequestration.

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Notes

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ACKNOWLEDGMENTS

The authors acknowledge the support from the China University of Geosciences, Wuhan, China, and the Chinese Scholarship Council.

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