

Systematic Review and Perspectives of Methane (CH₄) Classifications and Production Methods from CH₄ Hydrate Reservoirs

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Cite This: *Energy Fuels* 2024, 38, 19293–19335



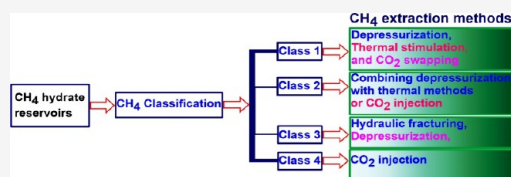
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ABSTRACT: Methane (CH₄) hydrates represent a promising yet intricate future energy source. Challenges in sustainable offshore extraction, such as fine sand production, CH₄ hydrate reformation, water production, and a possible increase in the bottom well pressure due to sand formation, highlight the need for ongoing research. This study provides a systematic review of CH₄ hydrate classification, evaluating its deposit composition, formation, stability, and extraction potential through various experimental, simulations, and field trial tests and highlighting the factors impairing their effectiveness. Critical factors, such as the kinetic behavior of CH₄ hydrate formation, the impact of geological structures on CH₄ migration and accumulation, and the environmental and technical challenges, are illustrated. The effects of sediment specific and sediment modification at varied temperatures, pressures, and salinity for developing efficient methods for CH₄ recovery from hydrate reserves and optimizing conditions for hydrate storage and transport technologies are also presented. The unique characteristics of Class 1, Class 2, Class 3, and Class 4 CH₄ hydrate reservoirs along with production methods, production factors like the injection rate, temperature, and pressure drop, as well as reservoir parameters such as the permeability, porosity, and surface area are revealed to influence gas production significantly. It is revealed that depressurization is widely recognized across all class types for its effectiveness due to the low economic cost and feasibility of implementation, particularly highlighted in Class 1 and Class 3 reservoirs, where it facilitates the dissociation of CH₄ hydrates for CH₄ recovery, indicating potential extraction rates of up to 75% over two decades. Thermal stimulation and CO₂ swapping also stand out, especially for Class 1 reservoirs, as viable methods contribute to CH₄ extraction by directly heating the reservoir to destabilize hydrates or injecting CO₂ to replace CH₄ in the hydrate structure, simultaneously sequestering CO₂. Class 2 reservoirs, characterized by low permeability, often require combining depressurization with thermal methods or innovative approaches like CO₂ injection to enhance CH₄ extraction efficiency, indicating potential extraction rates of up to 87.80%. Furthermore, hydraulic fracturing emerges as essential for Class 3 reservoirs by improving the permeability and facilitating gas flow, indicating potential extraction rates of up to 80.60%, thus enhancing CH₄ extraction. Additionally, this review emphasizes the current challenges and suggests potential interventions. The concise synthesis of findings, encompassing both experimental evidence and simulation deductions, as presented in this review, will enhance comprehension regarding screening, designing, and formulating CH₄ extraction strategies.



1. INTRODUCTION

Methane hydrates, comprising natural gas molecules trapped within a lattice of ice crystals under high-pressure and low-temperature conditions, present a significant yet largely untapped potential energy resource.¹ These compounds are abundant beneath the ocean floor and Arctic permafrost, as diagrammatically shown in Figures 1 and 2, positioning them as a focal point of interest in alternative energy resources.^{1,2} In the primary curves illustrated in Figure 1, the blue parts in permafrost and marine sediment regions are within the hydrate formation and stability zone. The curves Figure 1a and 1b are built on data on the pressure–temperature phase stability conditions and correspond with the reflection of acoustic wave data collected in these environments.³ Despite the fact that numerous different models have been developed describing the mechanism investigation and analysis involved in the

formation of CH₄ hydrate, there is a general agreement that the origination of the CH₄ hydrate in naturally existing hydrates is either generated by anaerobic decomposition of organic matter or made from the thermogenic decay of organic matter.^{3,4} The global volume of CH₄ hydrates is vast, estimated to be around 3000–30 000 trillion m³, signifying a considerable portion of the world's organic carbon, potentially surpassing the combined carbon content of known global fossil fuel reserves.⁵ This immense energy storage capacity coupled

Received: July 15, 2024

Revised: September 13, 2024

Accepted: September 13, 2024

Published: September 26, 2024



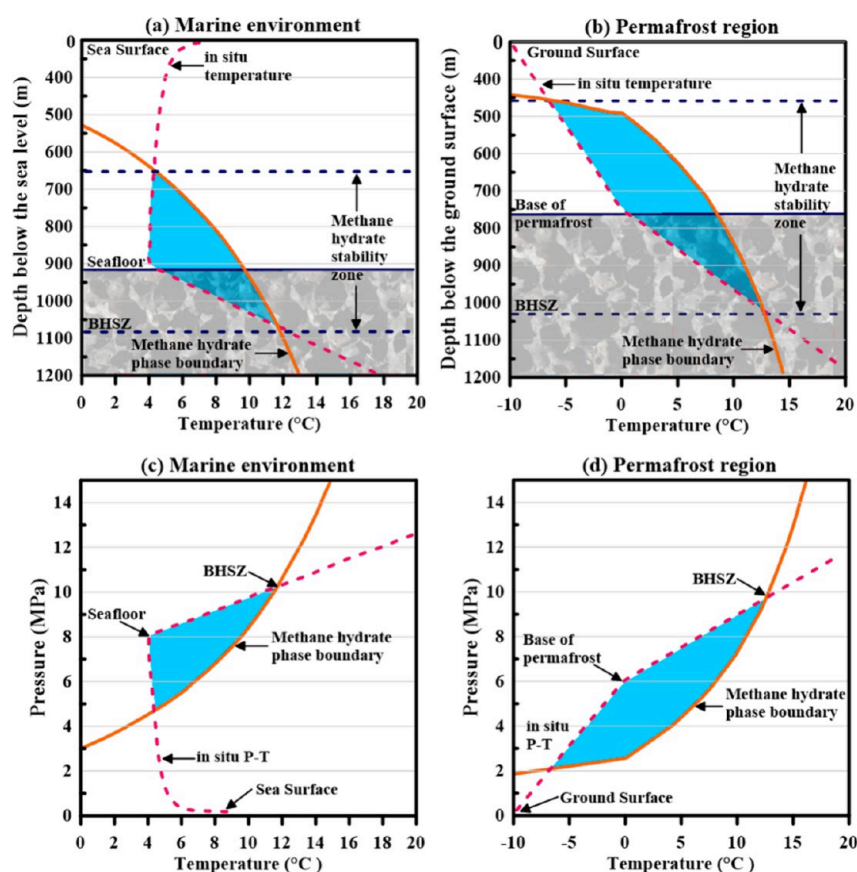


Figure 1. Methane (CH_4) hydrate stability zones in (a) a marine environment with a salinity of 3.5 wt % and (b) a permafrost region with a salinity of 0 wt %, alongside (c, d) the respective curves on P - T phase diagrams. The bends observed in the CH_4 hydrate phase boundaries in b and d, indicated by orange lines, align with the transition point of 0 °C, marking the range above which liquid water is stable and below which ice is stable. Data retrieved from ref 8. Available under a CC-BY 4.0 license. Copyright 2023 Pratama et al.

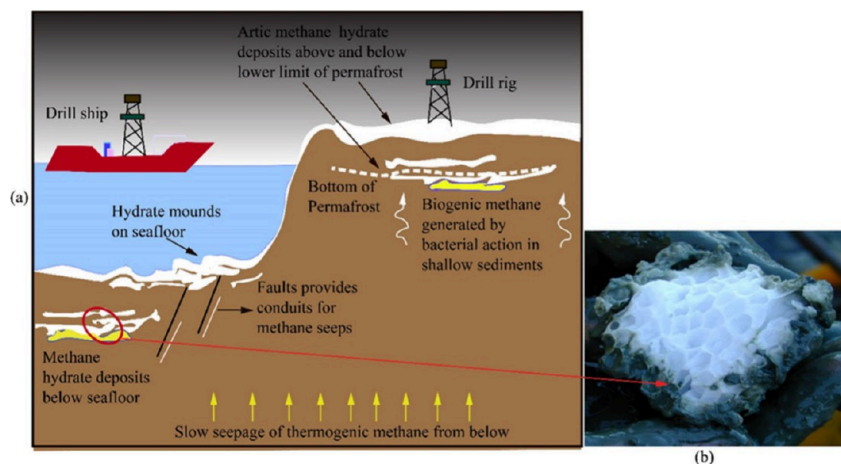


Figure 2. Methane (CH_4) hydrate deposits. Modified with data retrieved from ref 9. Copyright 2018 earthdoc.org.

with the geographic diversity of its deposits underscores its potential as a future clean energy source.^{1,2} Research and field trials have revealed the feasibility of energy production from CH_4 hydrate resources, suggesting a promising viewpoint for this unconventional hydrocarbon resource to meet the ever-growing energy demand while ensuring energy sustainability with minimal environmental impact.^{6,7}

The significance of CH_4 hydrates as an energy resource has necessitated classifying its deposits and developing efficient production methods. Traditional extraction techniques are

challenged by the unique solid nature of CH_4 hydrates, their distinct thermodynamic characteristics, and their occurrence in environments that demand innovative approaches for safe and sustainable extraction. The production of CH_4 from hydrates involves complex processes, including hydrate dissociation and the stabilization of the extraction process to avoid geohazards. Research in this area has brought forth a variety of production techniques, notably thermal stimulation, depressurization, and chemical injection strategies, each tailored to exploit different types of hydrate deposits efficiently.^{7,10} Furthermore, success-

Table 1. Summary of Key Review Articles Investigating CH₄ Hydrate Formation and Production Strategies: Recent Advances

| year | topic reviewed | study focus | refs |
|------|---|--|------|
| 2019 | mechanisms of CH ₄ hydrate formation in geological locations | primarily focuses on understanding the processes and conditions that lead to the formation of CH ₄ hydrates within geological environments | 17 |
| 2019 | natural gas hydrate reservoirs: formation, characteristics, and production strategies | primarily focuses on understanding the thermodynamics and reservoir properties of gas hydrates to aid in accurate modeling of hydrate flow in porous media | 18 |
| 2021 | gas hydrate reservoir production technologies, energy efficiency review | primarily focuses on evaluating the energy efficiency of different technologies used to produce gas from sedimentary layers containing gas hydrates | 19 |
| 2022 | state-of-the-art review and prospect of gas hydrate reservoir production methods | the study focuses on providing a comprehensive review and future outlook on innovative drilling techniques, strategies for scientific well location layout, wellbore structure and trajectory design, effective drilling fluid, and qualification systems for gas hydrate reservoir exploration and exploitation | 20 |

ful field trials in locations like the North Slope of Alaska have revealed the potential for yielding a steady flow of natural gas from CH₄ hydrates, marking significant progress toward realizing CH₄ hydrate's role as an integral component of the global energy mix.¹¹ This progress in classification and production methodologies is crucial for unlocking the vast energy potential locked within CH₄ hydrates efficiently and environmentally responsibly.

Significant progress has been made in understanding CH₄ hydrate's vast potential as an alternative energy resource and its extraction mechanisms. However, the manuscripts have partially presented the comprehensive details on CH₄ hydrate classification based on deposits, composition, and formation mechanisms under their respective stability conditions in varying environmental parameters. While numerous existing review studies have investigated the physical and chemical properties of CH₄ hydrates, different technologies used to produce CH₄ hydrate, and innovative CH₄ hydrate drilling techniques, as described in Table 1, there remains a lack of unified criteria for CH₄ hydrate deposit and composition-based classifications, which hinders the optimization of extraction methods tailored to specific hydrate deposits and compositions. The detailed CH₄ hydrate's exploration due to sand production alongside CH₄ has not been extensively explored, which raises concerns, such as gas hydrate stability, which complicates extraction efforts, the variable and site-specific nature of CH₄ release from hydrate decomposition processes creating unpredictability in production rates, and geohazards associated with hydrate extraction posing safety and environmental risks. To address these challenges, various numerical reservoir simulators have been developed. These simulators offer insights into the feasibility of hydrate production under various reservoir deposits and composition conditions, comparing different CH₄ classes and how they affect production efficiency and environmental impact. Among them are Garapati's model for hydrate dissociation using CO₂/N₂ injection,¹² Wilder's model dealing with complex combinations of fluid, heat, and mass transport equations,¹¹ the TOUGH+HYDRATE simulator developed by the National Energy Technology Laboratory (NETL), which is a U.S. Department of Energy (DOE) national laboratory focused on advancing energy technology research and development¹³ and well recognized for its capability in modeling multiphase fluid and heat flow in porous media, specifically tailored for CH₄ hydrate deposits,^{13,14} the four-phase flow model for an unconsolidated CH₄ hydrate reservoir which simulates the Mallik production tests,¹⁵ and HydrateResSim, focusing on the mathematical simulation of CH₄ production in hydrate reservoirs.¹⁶ This work illustrated a comprehensive evaluation of the feasibility of hydrate production under various reservoir

deposit and composition conditions, comparing different CH₄ classes and how they affect production efficiency and environmental impact. We analyzed several field trials, numerical simulations, computational findings on CH₄ deposits, and composition-based classifications with production methods from various CH₄ hydrate classes, emphasizing successes and limitations. The study identifies the research gaps in current field trials and simulation studies and proposes potential solutions. Furthermore, recent advancements in exploration techniques, CH₄ production techniques, and CH₄ classification approaches considering stability, accessibility, and extraction potential are also presented. This article is presented in the following outline: first, an introduction of the study, followed by CH₄ hydrate formation and distribution, factors influencing CH₄ hydrate stability and occurrence, CH₄ hydrate classification, production methods for CH₄ extraction, case studies, and field applications. This is followed by challenges, research gaps, future perspectives, and the study's conclusion.

2. METHANE (CH₄) HYDRATES: FORMATION AND DISTRIBUTION

2.1. Geological Processes Leading to CH₄ Hydrate Formation.

CH₄ hydrate formation within geological systems is a complex and multifaceted process that is dictated by a confluence of physical, chemical, and geological factors, such as CH₄ and water interaction, microbial origin, continental margins, vapor-phase CH₄, and influence of sedimentary content, as described in Table 2. Table 3 provides a comparative analysis that underscores the novelty of this section in several key areas. By examining the nuances of CH₄ and water transport mechanics, the specific role of vapor-phase CH₄, the detailed impact of sedimentary content, particularly Illite clays, and the intricate processes around microbial CH₄ production, this section offers fresh perspectives and insights into the complex dynamics of CH₄ hydrate formation in geological systems. Furthermore, our focused recommendations, as presented in Table 2, for enhancing transport mechanisms to the reaction front, managing the impacts of vapor-phase CH₄, manipulating sediment content, and targeting microbial activity provide actionable avenues for future research and exploration. These novel contributions are positioned to encourage innovative studies that can improve the efficiency and predictability of CH₄ hydrate formation in geological settings, potentially influencing energy resources management and environmental considerations.

At its most basic, the formation of CH₄ hydrates requires the presence of CH₄ and water under conditions where they can combine to form solid hydrates.²¹ These conditions typically emerge in regions with high pressure and low temperature, such as deep-sea sediments along continental margins and

Table 2. Summary of Geological Processes Leading to Methane (CH₄) Hydrate Formation

| process/factor | mechanism | effects on sediments | influence on CH ₄ formation | recommendation | refs |
|--|---|---|--|--|-------|
| CH ₄ and water interaction | requires both CH ₄ and water; the formation rate is limited by the transport of either to the reaction front | consumes all available pore water in some cases | the interaction is essential for hydrate formation, but the rate is significantly constrained by the transport efficiency of CH ₄ and water to the reaction zone | enhancement of transport mechanisms is necessary for both CH ₄ and water to the reaction front to improve hydrate formation efficiency | 21 |
| vapor-phase CH ₄ | with enough vapor-phase CH ₄ , it can consume all available pore water | renders remaining water is too saline for further formation | vapor-phase CH ₄ 's ability to consume all available pore water indicates a potent influencing factor for hydrate formation, acting as a limiting condition when water becomes too saline | potential manipulation of the phase conditions to control the consumption of pore water and salinity increase to favor hydrate formation is vital | 21,22 |
| influence of sedimentary content | varies with accumulation and distribution in sediments, such as different Illite clay contents | impacts simulation of reservoir diversity | high Illite content in sediments notably enhances CH ₄ hydrate formation and content, pointing to the significant role sediment composition plays in hydrate dynamics | sediment composition analysis is crucial, particularly Illite clay content, to optimize conditions for CH ₄ hydrate formation; considering manipulating sediment content where feasible | 23 |
| microbial origin and continental margins | CH ₄ is primarily microbial in origin and found along continental margins | affects where CH ₄ hydrate is commonly found | the microbial origin of CH ₄ is primarily found along continental margins due to the biodegradation of organic matter, which underscores the ecological and geological conditions favoring CH ₄ hydrate presence | focus research and exploration efforts on continental margins with indications of high microbial activity and organic matter presence for potential CH ₄ hydrate formations; considering the ecological impacts of exploration activities | 22,25 |

Table 3. Comparative Analysis of CH₄ Hydrate Formation: Unveiling Novel Insights and Mechanisms beyond Previous Research Studies

| aspect | published studies ¹⁷ | this review (this section) | novelty justification |
|--|--|--|--|
| CH ₄ and water interaction | describes the basic requirements for hydrate formation | delves into the transport mechanics and limitations of CH ₄ and water to the reaction zone, providing a deepened understanding of transport efficiency | offers a focused examination of transport mechanisms to enhance CH ₄ hydrate formation efficiency, not extensively elaborated in prior literature |
| vapor-phase CH ₄ | general mention of its role in hydrate formation | discusses how vapor-phase CH ₄ can lead to saline conditions that inhibit further hydrate formation with suggestions for potential manipulation of conditions | introduces strategic considerations for managing vapor-phase CH ₄ 's impacts on formation rates and salinity, presenting novel angles for research and application |
| influence of sedimentary content | acknowledges the role of sedimentary content | explores the specific influence of different Illite clay contents and grain sizes on CH ₄ hydrate formation kinetics | enhances the understanding of sedimentary content's impact on hydrate kinetics, emphasizing the role of Illite clays, which adds granularity to existing knowledge |
| microbial origin and continental margins | highlights microbial CH ₄ contribution to hydrate formation | provides detailed insights into the biodegradation of organic matter and its effect on CH ₄ production, focusing on continental margins with favorable conditions | deepens the discussion on microbial CH ₄ sources along continental margins, offering refined strategies for research and exploration efforts based on microbial activity and organic presence |

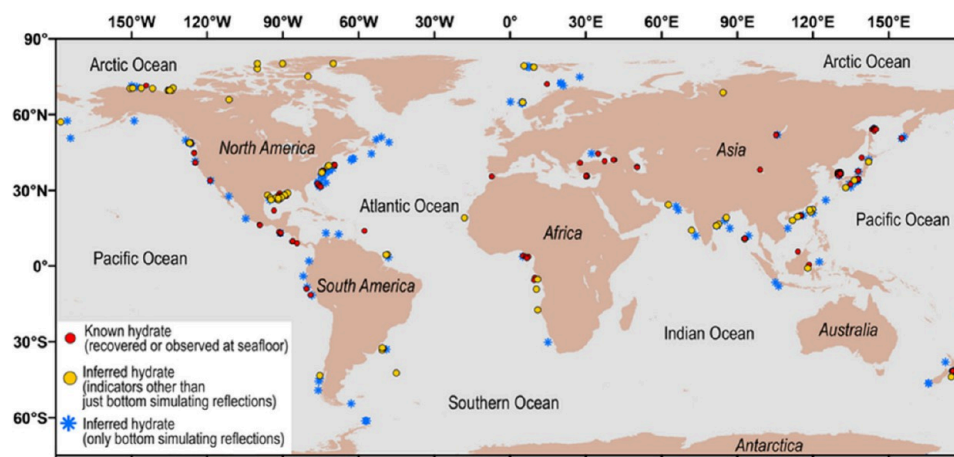


Figure 3. Global distribution of gas hydrate with recovered or observed occurrences represented by red circles and inferred occurrences by yellow circles and blue symbols, based on data from the preliminary U.S. Geological Survey database up to the end of 2019. Inferred hydrate occurrences are primarily identified through bottom-simulating reflections, borehole logs, and chlorinity anomalies linked to pore water freshening upon hydrate dissociation. Blue symbols represent inferences solely based on bottom-simulating reflections. At the same time, yellow circles indicate inferences supported by at least one additional indicator of gas hydrate, sometimes in conjunction with bottom-simulating reflections. Adapted with permission from ref 29. Copyright 2020 Elsevier.

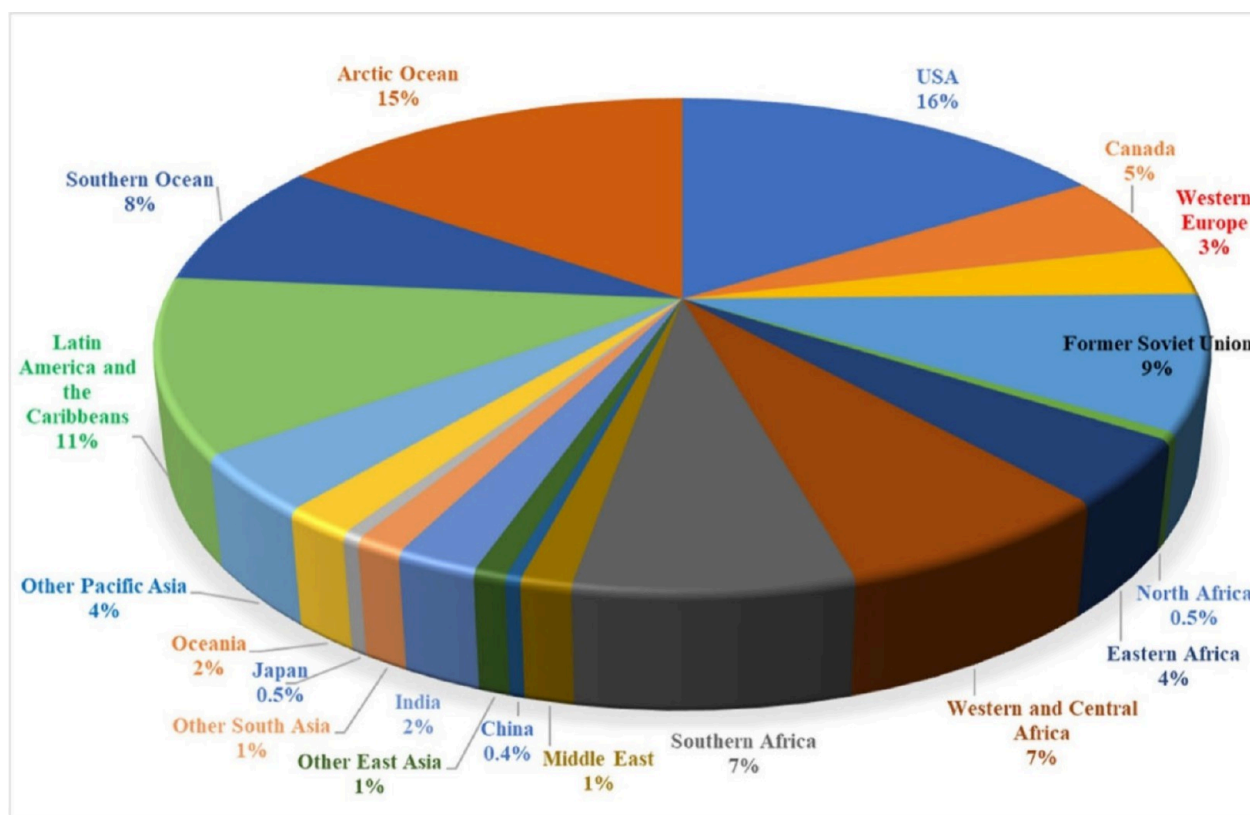


Figure 4. Main distribution of inferred gas hydrate accumulations and their respective estimated gas storages in global. Reproduced from ref 5. Available under a CC-BY 4.0 license. Copyright 2023 Gajanayake et al.

within and beneath permafrost.^{21,22} The formation of CH₄ hydrates in geological settings is significantly influenced by the transport mechanics of CH₄ and water to the reaction sites where hydrates can form.²¹ When the movement of either CH₄ or water is limited, the hydrate formation rate is restricted. In scenarios where CH₄ transport is the limiting factor, as gas fingers extend into the hydrate stability zone (HSZ), hydrates promptly form at the gas–water interface.²² This immediate formation highlights the dynamic interplay between CH₄

migration and hydrate crystallization. Additionally, the hydrate formation process in porous media such as marine sediments might encounter a natural halt when the hydrate formation consumes all available pore waters.^{22,23} This consumption not only stops further hydrate formation but also leads to an increase in the salinity of the remaining water.²² The increase in salinity essentially makes the environment unfriendly for additional hydrate formation under existing pressure–temperature conditions. Moreover, geologic processes and changes

within the ocean–atmosphere system, such as temperature variations, can precipitate the formation and dissociation of CH₄ hydrates.²² These changes can lead to the dissolution of existing hydrates or the creation of new ones in certain reservoirs, demonstrating the dynamic equilibrium of CH₄ hydrate presence in geological systems influenced by external environmental factors. On top of that, the sedimentary content, including the mineral composition and size of grains, significantly influences CH₄ hydrate formation.^{23,24} Different sediments offer varying surfaces for hydrate nucleation and growth, affecting the kinetics of CH₄ hydrate formation. Chen et al.²³ revealed that the presence of Illite clay minerals with different grain sizes promotes CH₄ hydrate formation, suggesting that the geological matrix plays a key role in the natural occurrence of hydrates. Microbial activity, especially in continental margin settings, releases CH₄ through organic matter decomposition.²⁴ This microbial CH₄ is a key contributor to hydrate formation in marine sediments, particularly along continental margins with favorable pressure and temperature conditions. Organic matter degradation by microbial consortia leads to CH₄ production, facilitating CH₄ hydrate formation in permafrost and deep water marine sediments.²⁴

2.2. CH₄ Hydrates Global Distribution Patterns and Reservoir Characteristics. **2.2.1. CH₄ Hydrates Global Distribution Patterns.** CH₄ hydrates are predominantly located in sediment layers around marine continental margins, stable in areas where water depths exceed roughly 450–700 m.²⁶ Estimates suggest that the total volume of CH₄ gas from hydrates in ocean sediment could be around 1.2×10^{17} m³ when expanded to atmospheric conditions, equivalent to approximately 74 400 Gt.²⁷ According to Archer et al.,²⁸ the model predicts the global CH₄ inventory as hydrate and bubbles below the sea floor to be about 1600–2000 Pg of carbon, supporting CH₄ hydrates as a considerable component of the global carbon cycle and energy resource pool. Figure 3 describes the main distribution of natural gas hydrate deposits globally, and Figure 4 illustrates the geographical distribution of inferred gas hydrate accumulations and their respective estimated gas storages. The global distribution of natural gas hydrates varies across different reservoir types, in which deep water sandstone formations contain 0.95%, nonsandstone marine sediments contain 2.70%, Arctic sandstones under existing infrastructure hold 0.01%, Arctic sandstones away from infrastructure contain 0.10%, surficial and shallow nodular hydrates hold 0.95%, while the marine reservoirs with limited permeability account for the majority at 95.29%.⁵

2.2.2. CH₄ Hydrates Reservoir Characteristics. CH₄ hydrate reservoirs represent a significant yet challenging future energy resource. Each CH₄ hydrate reservoir offers unique opportunities and challenges for hydrate exploration and production due to the varied accumulation characteristics in different deposits owing to geological feature differences, such as faulted systems,³⁰ shallow subsurface and seafloor,²¹ porous sediments,^{29,31} and marine deposits with dip angles,³² as described in Table 4. For instance, in the Qiongdongnan Basin of the northern South China Sea, the gas hydrate stability zone (GHSZ) thickness typically ranges between 200 and 400 m at water depths greater than 500 m.³³ This area's estimated gas hydrate inventory is approximately 6.5×10^9 t of carbon.³³ Favorable areas for hydrate accumulation in this basin have been identified, with high deposition rates, thick Cenozoic sediment, rich biogenic and thermogenic gas supplies, and

Table 4. Summary of CH₄ Hydrate Accumulation Characteristics in Different Geological Deposits

| geological structure | accumulation behavior | influential geological factors | effect on CH ₄ hydrate formation | highlights | challenges | refs |
|---------------------------------|--|--|---|---|--|------|
| faulted system | varies with the combination of fault system and gas source | fault systems, gas sources | the formation is influenced by fault permeability and gas flow direction | hydrate accumulations in faults depend significantly on the interplay between fault systems and gas sources; these geological features can lead to varied accumulation characteristics in seabed systems | managing gas leakage and ensuring the stability of hydrate formations | 30 |
| porous sediments | influenced by the kinetics of hydrate formation | attributes of sedimentary hosts, growth kinetics | particle size and sediment composition affect kinetic rates of formation | sedimentary host attributes and kinetics of hydrate formation play critical roles in how CH ₄ hydrates accumulate in different porous sediment settings | overcoming challenges in predicting accurately where hydrates will form due to heterogeneous sediment properties | 42 |
| marine deposits with dip angles | affected by dip angle, CH ₄ leakage rate, water salinity, and layer heterogeneity | dip angle, CH ₄ leakage rate, water salinity, layer heterogeneity | dip angle and salinity play crucial roles in hydrate stability and distribution | key factors like the formation's dip angle, CH ₄ leakage rates, water salinity, and layer heterogeneity are crucial in understanding hydrate formation in marine deposits; these aspects significantly influence CH ₄ migration and subsequent hydrate formation | difficulty in modeling long-term hydrate behavior in complex marine systems | 32 |
| shallow subsurface and seafloor | concentrated distribution, high saturation, easy access | depth of occurrence, formation environment | high saturation enables easier methane recovery but poses risks of sudden release | their high saturation and accessibility distinguish hydrate accumulations in the shallow subsurface and seafloor due to their concentrated distribution at relatively shallow depths; the formation environment plays a significant role in shaping the structure of these hydrate deposits | addressing the environmental impact and preventing potential hazards when accessing hydrates near the seabed | 43 |

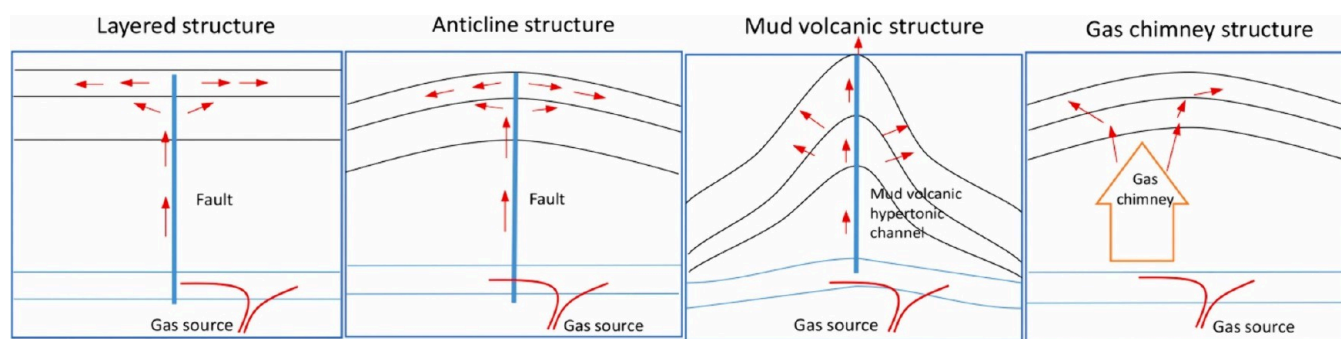


Figure 5. Types of geological structures (faulted systems) on CH_4 hydrate accumulation. Reproduced with permission from ref 30. Copyright 2021 Elsevier.

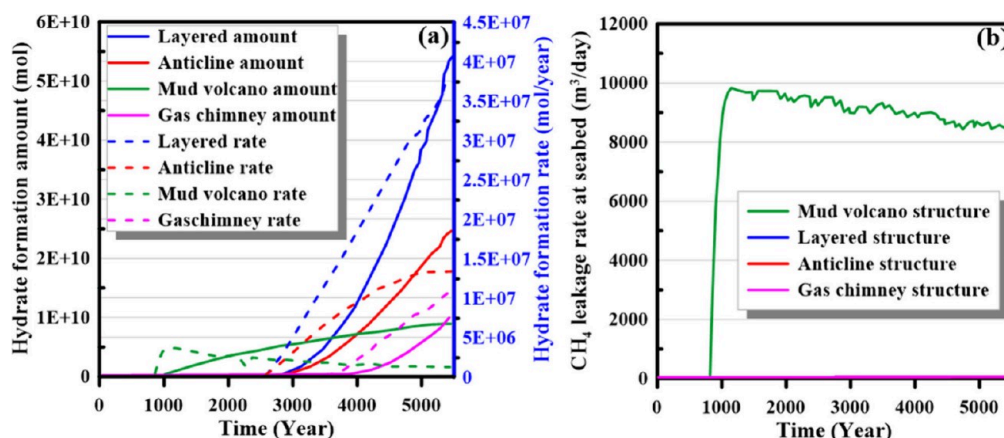


Figure 6. Formation quantity and rate of CH_4 hydrate formation under different geological structures, along with the rate of CH_4 gas leakage: (a) CH_4 hydrate formation amount and formation rate; (b) CH_4 hydrate leakage rate at the seabed.³⁰ Redrawn with permission from ref 30. Copyright 2021 Elsevier.

excellent transport systems such as faults, diapirs, and gas chimneys.³³ Furthermore, the Mohe Basin in Northeast China stands out due to its terrestrial location, unlike many other CH_4 hydrate deposits in marine settings.³⁴ This basin is characterized by gas-prone source rocks, with organic matter having advanced to late oil-generation stages, resulting in condensate and natural gas.³⁴ These conditions render the Mohe Basin one of China's most prolific areas for natural gas hydrate (NGH) accumulation. Such source rocks provide suitable conditions for CH_4 hydrate formation, potentially leading to significant NGH deposits within this basin. Another notable area for CH_4 hydrate potential is the Gulf of Mexico, which has been the subject of several research and exploration projects. This basin is particularly interesting due to its marine settings and the significant presence of gas hydrate occurrences. The Gulf of Mexico exhibits various geological features favorable for hydrate formation, including thick sedimentary deposits and active gas migration pathways such as faults and gas chimneys.^{35,36} These conditions facilitate the formation and stabilization of CH_4 hydrates within the sediment.³⁵ The Gulf also exemplifies the complexity and heterogeneity of hydrate reservoirs with variations in hydrate saturation and distribution observed across different sites.^{35,37} The basin characteristics of Qiongdongnan Basin,³³ Mohe Basin,³⁴ and the Gulf of Mexico³⁵ highlight the diverse nature of CH_4 hydrate reservoirs, indicating that geological and geochemical factors significantly influence the distribution and abundance of CH_4 hydrates. Thus, precise reservoir character-

istics of CH_4 hydrates are crucial for safe and efficient hydrate production.

Furthermore, permafrost regions, such as those in Canada and Alaska, have been identified as significant reservoirs for CH_4 hydrates.^{38,39} These areas are characterized by low-temperature and high-pressure conditions, which are ideal for the formation of CH_4 hydrates. The Alaskan North Slope, for instance, has shown high gas hydrate saturations in sand and coarse silt layers, indicative of promising potential reservoir sediments for gas production.³⁸ Canada's Mallik site in the Northwest Territories has also demonstrated similarly high gas hydrate saturations in sand/sand-gravel layers.³⁹ These findings underscore the critical role that permafrost regions play in the global inventory of CH_4 hydrates and highlight the necessity of including these regions in discussions about CH_4 hydrate reservoirs. Moreover, the Eastern Nankai Trough has been the focus of numerous studies and drilling expeditions aiming to explore and characterize CH_4 hydrate reserves. This area is marked by alternating sandy and muddy layers within submarine sediment strata, where gas hydrate saturations in sandy layers have been reported to be notably higher than in clay-rich layers.^{39,40} These characteristics make the Eastern Nankai Trough a key area for the study of CH_4 hydrates, reflecting the diversity of geological settings that foster CH_4 hydrate formation and stability. In addition, the Krishna-Godavari Basin off Eastern India presents another crucial site for CH_4 hydrate studies. During the National Gas Hydrate Program Expedition 01 (NGHP-01) in 2007, fracture-filling gas hydrates were discovered within this basin.³⁹ Core analyses

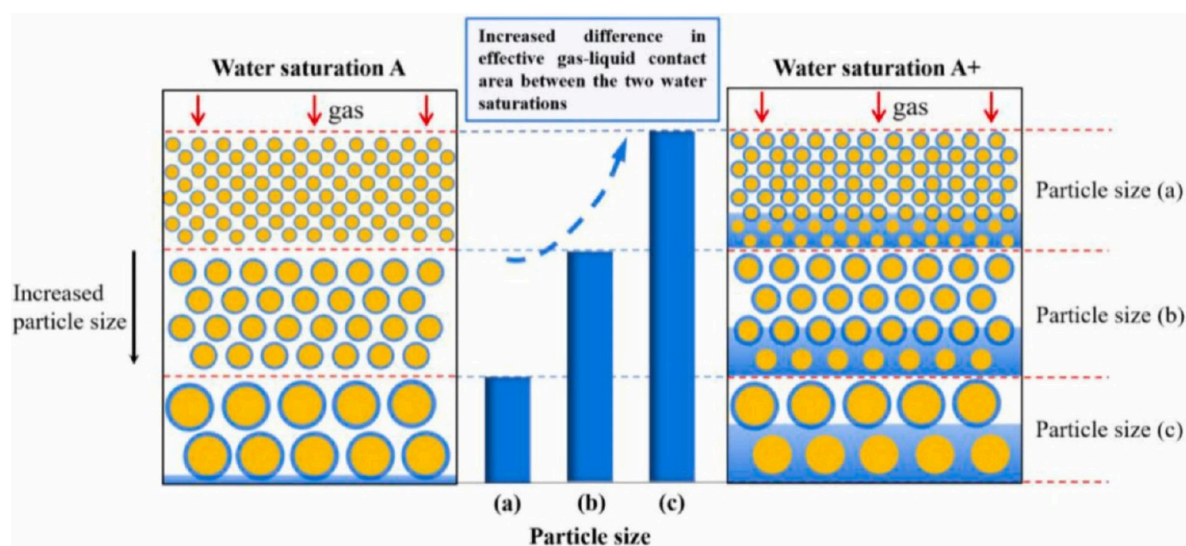


Figure 7. Illustration depicting how the initial water saturation affects the kinetic properties of CH_4 hydrate formation in sediments of varying quartz sand particle sizes. Reproduced with permission from ref 42. Copyright 2024 Elsevier.

indicated the presence of gas hydrate-bearing sediments with notable saturations in clay/silt and silt/sand sediments at different sites.³⁹ This region's significance is highlighted by its contribution to the understanding of gas hydrate behavior in fracture-filling scenarios, further emphasizing the need to cover a wide range of geological settings in discussions on CH_4 hydrate reservoirs. Incorporating detailed discussions on the permafrost regions of Canada and Alaska,³⁹ the Eastern Nankai Trough,^{40,41} and the Krishna–Godavari Basin³⁹ is imperative to provide a comprehensive overview of global CH_4 hydrate resources. These regions encapsulate the vast geochemical and geological diversity influencing CH_4 hydrate formation and stability, thus contributing significantly to the understanding and potential exploitation of these resources for future energy needs.

2.2.2.1. Faulted Systems. Faulted systems, characterized by fractures and displacements within the Earth's crust, significantly impact the accumulation of CH_4 hydrates. These geological structures facilitate the migration of CH_4 -rich fluids, providing conduits for CH_4 to reach zones where conditions are conducive for hydrate formation.^{30,44} These geological discontinuities act as channels, guiding CH_4 from deep sources to shallow sediment layers where pressure and temperature conditions favor hydrate stabilization, as shown in Figure 5. The role of fault systems is further accentuated when considering the interplay between gas source dynamics and the structural complexities of the subsurface. The presence of faults enhances the permeability of sediments, allowing for the accumulation of substantial hydrate deposits in layered and anticline structures.^{30,44,45} The study by Zhang et al.³⁰ revealed that fault-fractured layers and anticlines are identified as the most favorable settings for large hydrate formations, where they enhance CH_4 trapping, thus fostering denser and more extensive hydrate deposits, as diagrammatically illustrated in Figure 6, emphasizing the critical role of fault systems in shaping hydrate reserves.

Moreover, the evaluation of hydrate accumulation characteristics across different geological structures reveals that faulted anticlines and layered formations exhibit distinct accumulation patterns attributed to the differential migration pathways and fluid flow rates enforced by the presence of faults,³⁰ as

illustrated in Figure 6. This highlights the critical influence of fault–fracture systems on the kinetic and thermodynamic processes that govern hydrate formation, underscoring the necessity of integrating geological dynamics into hydrate research methodologies. By delving deeper into the mechanisms through which fault systems influence CH_4 hydrate accumulation, it becomes evident that their role extends beyond mere conduits for CH_4 migration. They actively shape the geochemical and physical landscapes, determining hydrate deposits' locations, concentrations, and viability. This insight enriches the understanding of subsea hydrate formations and illuminates potential pathways for exploring and exploiting hydrate reserves.

2.2.2.2. Porous Sediments. Porous sediments are primary hosts for CH_4 hydrate formations due to their ability to facilitate the formation and stabilization of hydrates.^{29,31} The efficiency of porous media in promoting CH_4 hydrate formation is evaluated based on various kinetic parameters, including induction time, formation rate, water-to-hydrate transition, and gas storage capacity. These parameters help assess the efficacy of different porous media in CH_4 hydrate formation.³¹ The sediments' porosity plays a critical role in the formation and dissociation phases of CH_4 hydrates.²⁹ In environments where high fluid pressures and low temperatures prevail, such as the seafloor, lake-bed sediments, and permafrost, CH_4 hydrate stability is maintained. The initial formation of CH_4 hydrates often occurs in sediments where temperatures are lower, creating nuclei for gradual growth.^{29,31} This phase behavior outlines the crucial interaction between CH_4 's migratory patterns and the sediments' porosity, ultimately influencing hydrate deposits' spatial distribution and density.

The kinetics behavior of CH_4 hydrate formation within saline porous sediments highlights the complex influence exerted by sediment characteristics, including particle size, on the hydrate formation rate.^{42,46} The experimental investigations simulated in situ seafloor conditions, revealing that CH_4 hydrate formation rates do not change in a strictly unidirectional manner with variations in quartz sand particle size.⁴² This indicates that the interaction between CH_4 molecules and sediment particles is nonlinear and influenced by multiple

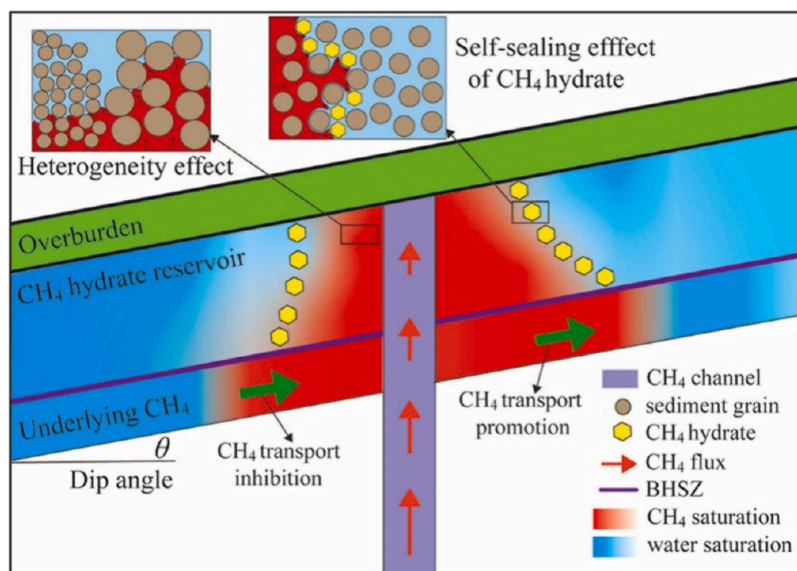


Figure 8. Impact of dip angles (θ) on CH_4 hydrate formation and migration pathways in marine deposits. Reproduced with permission from ref 32. Copyright 2022 Elsevier.

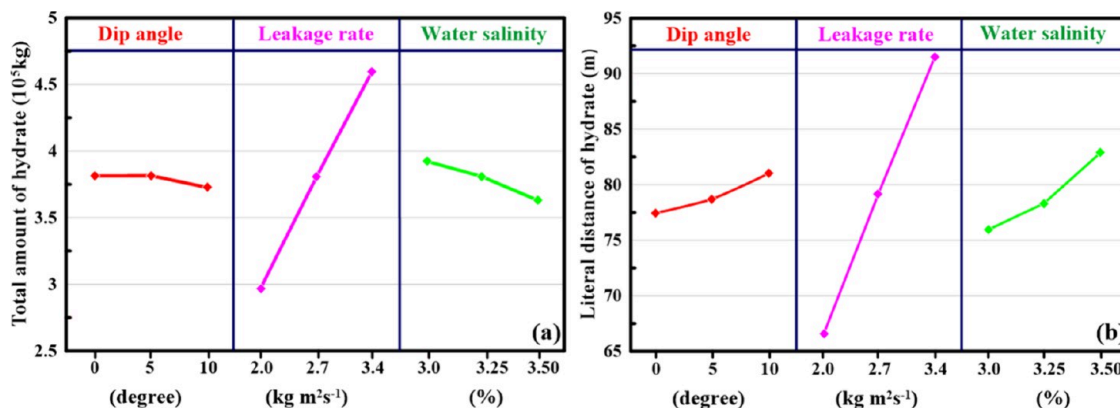


Figure 9. Influence of dip angle, CH_4 leakage rate, and water salinity on CH_4 hydrate formation and longest lateral distance of hydrate: (a) the total amount of methane hydrate (MH) and (b) the longest lateral distance of MH (m).³² Redrawn with permission from ref 32. Copyright 2022 Elsevier.

factors; the hydrate formation rate undergoes simultaneous influence from particle size and the water saturation levels,^{42,46,47} as illustrated in Figure 7. According to the study by Xie et al.,⁴² in quartz sand sediments of varying particle sizes, the formation rate of CH_4 hydrate tends to increase as the initial water saturation decreases. However, the degree of change in the CH_4 hydrate formation rate resulting from shifts in water saturation also depends on the particle size of the quartz sand.⁴² By comprehending the intricate relationship between CH_4 migration, sediment porosity, and environmental conditions, stakeholders can devise more effective strategies for tapping into this unconventional energy resource. The awareness is crucial not only for optimizing CH_4 extraction methods but also for assessing the environmental impacts and sustainability of exploiting CH_4 hydrate deposits.

2.2.2.3. Marine Deposits with Dip Angles. Due to their complex geological structure and diagenesis, marine deposits with dip angles are significant for CH_4 hydrate stability and accumulation.^{30,32} The pressure and temperature conditions, crucial for CH_4 hydrate formation, vary along these angled sediment layers.³² This variability is influenced by the angle of deposition, which can significantly impact the pathways

through which CH_4 migrates, which, in turn, influences hydrate stability zones, as diagrammatically illustrated in Figure 8. As a result, these geological features affect the locations where CH_4 hydrates can accumulate and the quantities formed. The presence of dip angles in geological structures leads to a nonuniform distribution of conditions necessary for CH_4 hydrate formation;³² the migration pathways of CH_4 can become more complex in environments with varied dip angles.^{30,32} This complexity can lead to differences in hydrate saturation levels across different areas, making some regions more prone to hydrate accumulation than others. Bei et al.³² studied the main effect of dip angle, CH_4 leakage rate, and water salinity on the total amount of methane hydrate (MH) (Figure 9a) and the longest lateral distance of MH (m) described as DH (Figure 9b). From this figure, it is evident that the CH_4 leakage rate positively influences both MH and DH, exhibiting the most significant effect among the three variables with the steepest slope. Conversely, the dip angle and water salinity reveal a negative slope for MH and a positive slope for DH. Among these variables, dip angle exhibits the least effect on both MH and DH, as indicated by its smaller slope than the other factors.

The findings suggest that CH₄ hydrate formation and stability are significantly influenced by CH₄ leakage rate, dip angle, and water salinity. Higher CH₄ leakage rates positively impact CH₄ hydrate formation but may also contribute to its destabilization. A shallower dip angle and lower water salinity correlate with enhanced CH₄ hydrate stability. These insights are crucial for understanding CH₄ hydrate dynamics and devising efficient extraction methods, highlighting the need to consider environmental and geological factors for sustainable CH₄ hydrate utilization.

Numerical models and studies have begun to systematically investigate the impact of formation dip on CH₄ migration and associated hydrate formation.^{32,48} These studies employ simplified models to represent marine sediments, allowing for a closer examination of how sediment dip angles affect gas migration and hydrate formation. Despite these efforts, further detailed research is necessary to fully grasp the correlation between dip angles, CH₄ migration pathways, and hydrate accumulation locations and quantities. Such research is crucial for understanding natural CH₄ hydrate formation and considerations related to CH₄ extraction and the potential for hydrate destabilization. This can aid in developing more efficient and safer methods for exploiting CH₄ hydrates as an energy resource while also helping to mitigate potential environmental impacts.

2.2.2.4. Shallow Subsurface and Seafloor. The shallow subsurface and seafloor represent environments where low temperatures and high pressures facilitate the formation of CH₄ hydrates.²¹ These areas are crucial for the stability of near-surface CH₄ hydrate deposits, often found within and beneath permafrost regions and along continental margins. The seafloor and shallow subsurface conditions, including the sediment type and thermal gradients, significantly affect the formation, distribution, and potential for CH₄ hydrate production. The exploration of CH₄ hydrates in these regions poses opportunities and challenges for energy resources given their sensitivity to environmental changes and the technical difficulties associated with their extraction, as described in Table 5.

3. FACTORS INFLUENCING CH₄ HYDRATE STABILITY AND OCCURRENCE

3.1. Effects of Temperature, Pressure, and Salinity on CH₄ Hydrate formation. The stability and occurrence of CH₄ hydrates in natural environments are significantly influenced by a combination of factors, including temperature,^{21,22} pressure,^{21,54} and salinity.^{21,55} These parameters govern the formation kinetics and affect the structural configurations of CH₄ hydrates.²¹ This section provides a discussion on how the temperature, pressure, and salinity affect the formation and stability of CH₄ hydrates.

3.1.1. Effects of Temperature on CH₄ Hydrate Formation. Temperature plays a crucial role in the nucleation and growth processes of CH₄ hydrates. Laboratory experiments have identified specific temperature conditions that favor the formation of CH₄ hydrates, illustrating the dependency of the formation process on temperature. Zhang et al.⁵⁶ revealed that under constant temperature conditions of 1.45, 6.49, and 12.91 °C, CH₄ hydrate formation exhibits distinct stages influenced by changes in pressure, temperature, and gas flow rate, as shown in Figure 10, indicating temperature's significance in hydrate stability and formation mechanisms. Figure 10 shows that the formation process can be segmented

Table 5. Exploring CH₄ Hydrates: Environmental Sensitivities, Technical Challenges, and Energy Opportunities in Shallow Subsurface and Seafloor Environments

| environment | opportunities for energy resources | challenges for energy resource development | sensitivity to environmental changes | technical difficulties for extraction | refs |
|---------------------|--|---|---|--|---------|
| permafrost regions | vast CH ₄ quantities are potentially available for extraction, contributing significantly to energy resources | CH ₄ release during extraction could exacerbate global warming | vulnerable to warming climates, which may destabilize hydrate deposits | requires technologies that can safely extract CH ₄ gas without leading to emissions or seafloor destabilization | 6,7,49 |
| continental margins | the high density of hydrate deposits offers a significant source of natural gas with a minimal environmental footprint | potential seafloor destabilization due to hydrate dissociation poses risks to marine ecosystems | sensitive to changes in ocean temperatures and pressures, which might trigger hydrate breakdown | complexities in accessing deep-sea deposits and managing the risk of ice-like structures dissociating unpredictably | 7,50,51 |
| marine sediments | globally widespread reservoir representing a major pool in the global carbon cycle | risk of CH ₄ venting during extraction processes, contributing to greenhouse gas emissions | influence of subsurface heat, salts, and ocean warming on the limited stability of hydrates | challenges include drilling through sediments and managing the solid nature of hydrates at depth | 7,52 |
| subsea environments | offers a clean fuel source with high energy density that is suitable for future demands | environmental risks related to the release of CH ₄ into the ocean affect marine life and water chemistry | fluctuations in seafloor temperature and pressure could induce hydrate formation or decomposition | necessitates developing methods for in situ conversion or safe extraction to avoid destabilizing the hydrate structures | 7,21,53 |

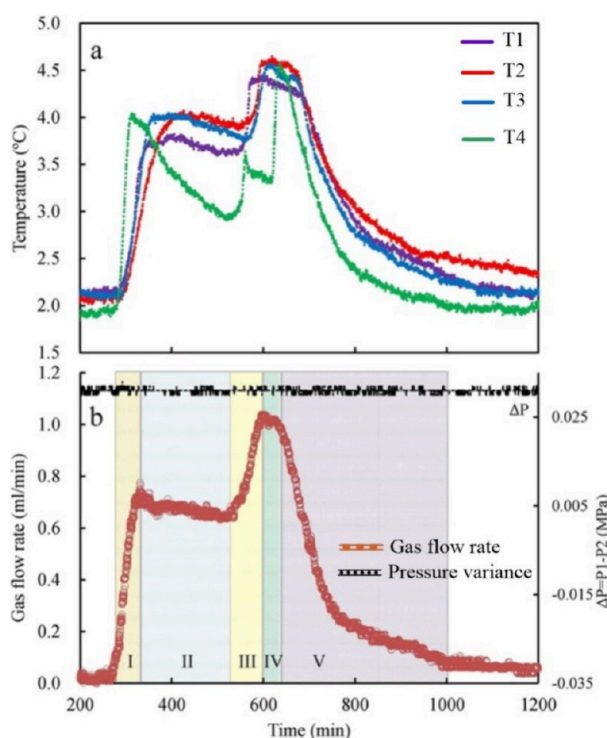


Figure 10. Distinct stages of CH₄ hydrate formation under varying temperatures and gas flow rate conditions: (a) temperatures recorded at points T1 (purple), T2 (red), T3 (blue), and T4 (green), and (b) gas flow rate with the pressure difference between P1 and P2. The black line depicted in b illustrates the pressure variance between points P1 and P2. Reproduced from ref 56. Available under a CC-BY 4.0 license. Copyright 2017 Zhang et al.

into five distinct stages (stages I–V) based on the changing slopes of the temperature and gas flow rate curves. In stage I, temperature and gas flow rate increase rapidly from initial values from 0 to 4.0 °C and 0.025 to 0.716 mL/min, respectively. This suggests the initiation of hydrate nucleation in the solution, accompanied by heat release. Stage II reveals stable temperature and gas flow rate plots, except at the lowest point (T4), indicating continuous hydrate crystal formation and heat release. Stage III exhibits a sudden rise in temperature and gas flow rate, resembling stage I, suggesting secondary

hydrate nucleation. Stage IV mirrors stage II in physical parameter changes but is shorter in duration, representing the secondary growth stage of hydrates. Finally, temperature and gas flow rate decreases rapidly in stage V, indicating the decay stage. Throughout the process, there is a minimal pressure difference between P1 and P2 (0.030–0.032 MPa). Therefore, stage I's rapid temperature increase and rise in gas flow rate signify the initiation of nucleation, suggesting that specific temperature and pressure conditions are requisite for CH₄ hydrate stability. Stable conditions in stages II and IV sustain continuous crystal growth, while the sudden rise in temperature and gas flow rate in stage III indicates secondary nucleation, contributing to hydrate stability. Stage V's rapid temperature and gas flow rate decrease implies hydrate dissociation when stability conditions are no longer met, emphasizing the dynamic nature of CH₄ hydrate occurrence within geological systems.

3.1.2. Effects of Pressure on CH₄ Hydrate Formation.

Pressure is another vital factor influencing CH₄ hydrate stability.^{57,58} The formation and dissociation behaviors of CH₄ hydrates under specific pressure conditions highlight the sensitive nature of hydrates to changes in pressure. Notably, CH₄ hydrates often form under high-pressure conditions, which create a suitable environment for their stability in combination with low temperatures. The equilibrium pressure for CH₄ hydrate formation and stability has been observed in various studies ranging from molecular dynamics simulations to experimental investigations,^{57–59} illustrating how pressure variations directly impact the structural integrity and occurrence of CH₄ hydrates. Luo et al.⁵⁷ reported a machine-learning-derived force field highlighting the mechanism of CH₄ hydrate stability under pressure at the molecular level. The simulation results indicate that pressure exerts a significant influence on the stability of water cages. The investigation of the radial distribution function (RDF) of oxygen–oxygen pairs within water molecules reveals a discernible trend in their spatial arrangement with varying pressure, as depicted in Figure 11a. Notably, all first peak positions shift leftward under increasing pressure, signaling a continuous decrease in the average distance between water molecules. This observation suggests that as pressure rises, the average proximity of water molecules diminishes consistently. Further analysis of the average distance between water

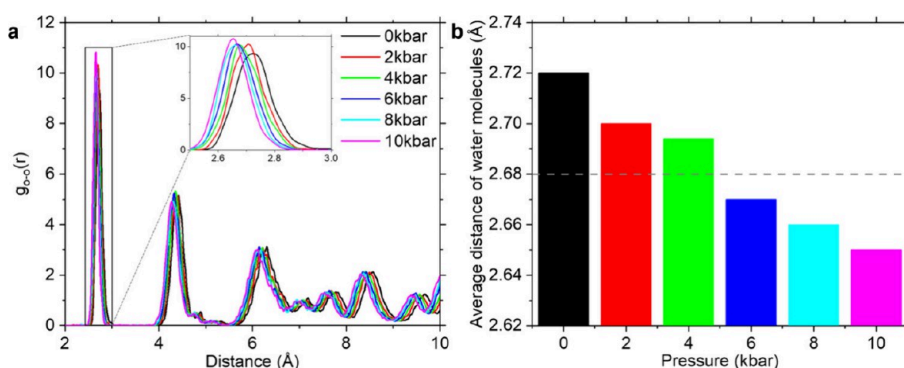


Figure 11. Influence of pressure on water molecule proximity in CH₄ hydrate stability. (a) Radial distribution function (RDF) of oxygen–oxygen pairs within water molecules illustrating spatial arrangement changes under varying pressure conditions. (b) Analysis of the average distance between water molecules in methane hydrate structure I (MhSI) as influenced by pressure, indicating optimal range for stability. The dashed lines depict the distance between water molecules in the ice Ih phase without additional stress within the identical computational framework. Reproduced with permission from ref 57. Copyright 2023 American Chemical Society.

molecules, inferred from the central position of the first peak in the RDF, is presented in Figure 11b. At 0 kbar, water molecules in methane hydrate structure I (MHsI) exhibit an attraction interaction at a distance of 2.72 Å, attributable to the presence of CH₄ guest molecules. This phenomenon implies a tendency for the distance between water molecules to converge toward an optimal value with increasing pressure. However, it is essential to consider the influence of CH₄ molecules. The optimal distance between water molecules in MHsI should exceed that observed in ice under zero pressure (2.68 Å), suggesting an optimal range between 2.68 and 2.72 Å, corresponding to pressures around 2–4 kbar, as shown in Figure 11b. Deviation from this optimal distance range, induced by excessively high or low pressure, disrupts the stable vibration amplitude of water molecules. Consequently, this deviation weakens the structural integrity of the water molecular framework, ending in the decomposition of MHsI. Thus, understanding and controlling pressure conditions are crucial for optimizing extraction processes while mitigating the risk of structural instability in CH₄ hydrates.

Hu et al.⁵⁸ explored the substantial impact of pressure on the stability and dissociation behavior of CH₄ hydrates in a detailed experimental and simulation-based study with implications for extraction strategies, particularly in high-pressure environments where CH₄ hydrates may offer viable energy resources. Findings indicate that contrary to simple linear models, CH₄ hydrate phase equilibria exhibit deviation from linearity at high pressures, which implies that increased pressure leads to higher temperature and lower pressure conditions for hydrate stability, as illustrated in Figure 12.

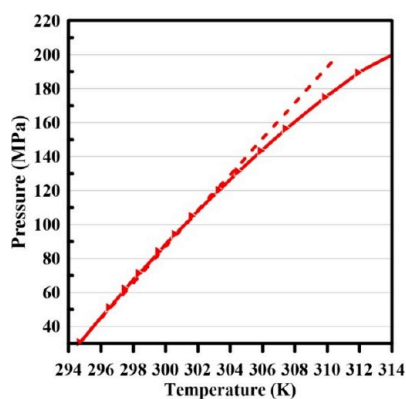


Figure 12. Measured CH₄ hydrate phase equilibria in pure water, presenting the best solid fit line alongside a dashed line to visually indicate linear dependency across the considered temperature range. Redrawn with permission from ref 58. Copyright 2017 Elsevier.

Further, the study revealed that the dissociation enthalpy (ΔH) for CH₄ hydrate increases with pressure, as diagrammatically shown in Figure 13, indicating enhanced stability of CH₄ hydrates under such conditions. This observation suggests that as pressure increases, the system experiences changes at a molecular level, such as tighter packing of water molecules, which facilitates the formation of hydrates and a corresponding rise in CH₄ solubility. Specifically, molecular dynamics simulations revealed shifts in radial distribution functions and increased coordination number and density for CH₄ and water under elevated pressures, as diagrammatically illustrated in Figure 13. These changes likely contribute to the increased enthalpy of hydrate

dissociation, thus underscoring the significant role that pressure plays in affecting the stability and formation of CH₄ hydrates.

References 57 and 58 highlight the intricate relationship between pressure and CH₄ hydrate stability with Luo et al.⁵⁷ focusing on molecular level insights and Hu et al.⁵⁸ providing experimental validation and macroscopic implications for energy extraction strategies. Their combined findings underscore the significant role of pressure in shaping the thermophysical characteristics and stability of CH₄ hydrates, which is essential for optimizing extraction processes and mitigating structural instability risks.

3.1.3. Effects of Salinity on CH₄ Hydrate Formation.

Salinity is crucial in influencing CH₄ hydrate stability, acting as both a stabilizing and a destabilizing agent under different conditions.^{60,61} Salinity affects the CH₄ hydrate phase equilibrium with higher salinity leading to hydrate dissociation and a shift in the hydrate stability zone to shallower depths or lower pressures.^{60–62} This phenomenon occurs because salt ions do not integrate into the CH₄ hydrate structure but remain in the liquid water phase, increasing the local water salinity and inhibiting further hydrate formation.^{60,62} As a result, high-saline water pockets form within the CH₄ hydrate-bearing sediments, equilibrating over time through film flow and ion diffusion in the water phase, wetting the grains.^{60,62} The salinity gradient created causes a broadening of the hydrate stability region, allowing temporary CH₄ hydrate reformation in pores filled with low-salinity water before dissociating again as the salt concentration increases locally.⁶⁰ Furthermore, salinity gradients induce CH₄ hydrate reformation during depressurization, suggested by observations of simultaneous hydrate dissociation and reformation in experiments with saline brine, likely attributed to endothermic hydration effects insufficient to initiate reformation in the absence of salt.⁶⁰ Therefore, salinity intricately affects CH₄ hydrate stability, dissociation, and reformation processes, making it a critical factor in understanding and modeling hydrate behavior in natural and engineered systems. The study by Prasad and Kiran⁶¹ into the effects of salinity, specifically sodium chloride (NaCl) concentration, on the stability and behavior of CH₄ hydrates revealed nuanced interactions between salinity, hydrate stability, and gas uptake kinetics. The findings indicate that lower concentrations of NaCl at 0.0–1.5 wt % facilitate rapid CH₄ hydrate formation, characterized by a single-step process and swift gas uptake. However, as the NaCl concentration increases to 3.0 and 5.0 wt %, hydrate formation becomes notably slower, transitioning into a more complex multistage process, consequently delaying gas uptake, as diagrammatically illustrated in Figure 14. This behavior underscores the dual role of NaCl as both a thermodynamic inhibitor, extending the time required for hydrate conversion, and an agent that modifies the CH₄ hydrate phase, particularly at higher concentrations. Remarkably, the presence of amino acid, particularly methionine (L-met), in the solution emerges as a beneficial promoter for CH₄ hydrate formation, offsetting the inhibitory effects of NaCl and enabling comparable gas uptake across both pure and saline systems.⁶¹ This intricate interplay between NaCl and L-met unveils a strategic avenue to manipulate hydrate formation kinetics and stability for applications in gas storage and transportation.

Furthermore, certain gas hydrates exhibit an unusual level of stability beyond their expected thermodynamic stability zones,

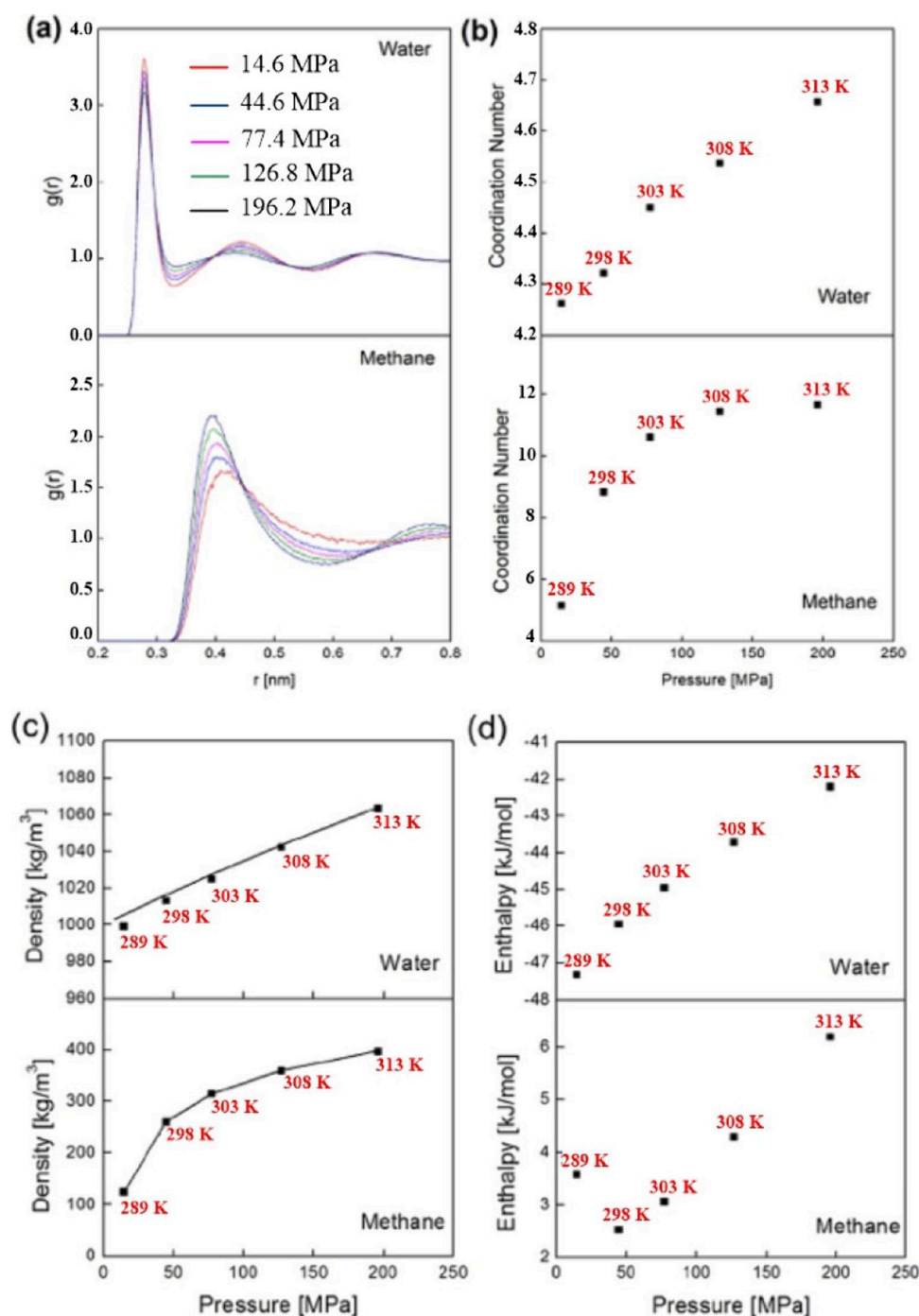


Figure 13. Impact of pressure on liquid water and CH₄ gas thermophysical characteristics under phase equilibrium conditions. (a) Radial distribution function with distinct pressure values represented as follows: (red) 14.6, (blue) 44.6, (pink) 77.4, (green) 126.8, and (black) 196.2 MPa. (b) Coordination number. (c) Density. (d) Enthalpy. Reproduced with permission from ref 58. Copyright 2017 Elsevier.

a characteristic specific to particular systems. This phenomenon, particularly observed in hydrate systems containing guest molecules like methane or carbon dioxide, remains a topic of exploration. Despite the absence of a definitive understanding of this unique stability mechanism, it is noted that these hydrates remain stable for extended durations even under atmospheric pressure provided they are kept at temperatures below freezing. This phenomenon, often called the “self-preservation” or “anomalous preservation” effect, opens up promising avenues for gas storage and transportation applications. The study by Prasad and Kiran⁶¹ also sheds

light on the “self-preservation effect” exhibited by CH₄ hydrates, where hydrates revealed unusual stability outside their general thermodynamic stability regions, as shown in Figure 15, a property markedly influenced by NaCl presence. This elucidation of salt’s impact, particularly NaCl, on CH₄ hydrate behavior enhances understanding essential for optimizing conditions in CH₄ storage and transportation strategies.

3.2. Effects of Sediment Properties on CH₄ Hydrate Formation and Stability. As illustrated in Figure 16, CH₄ hydrate formation is primarily influenced by sediment-specific

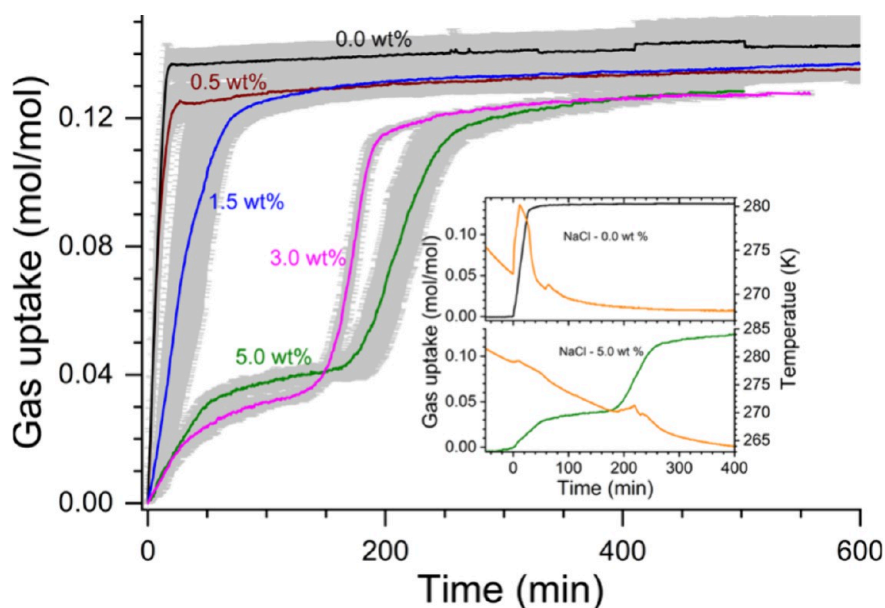


Figure 14. Effect of sodium chloride (NaCl) concentration on methane (CH_4) hydrate formation dynamics. Reproduced from ref 61. Available under a CC-BY 4.0 license. Copyright 2019 Prasad and Kiran.

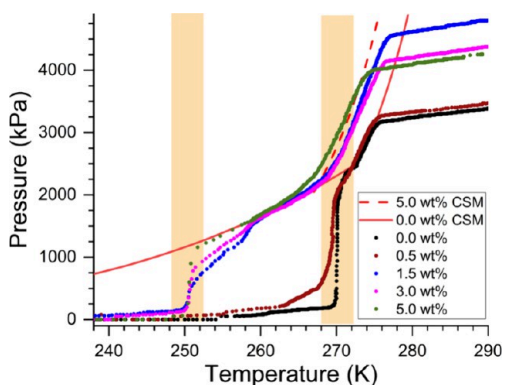


Figure 15. Illustration of the self-preservation effect exhibited by CH_4 hydrates, demonstrating enhanced stability beyond typical thermodynamic zones, influenced by NaCl presence. Reproduced from ref 61. Available under a CC-BY 4.0 license. Copyright 2019 Prasad and Kiran.

factors, including microstructural and chemical composition. These determine the extent of hydrate nucleation and adsorption with potential classified as low, medium, or high based on sediment characteristics. Key aspects like pore size, particle arrangement, and mineral or organic content directly affect the formation process. Sediment modification, whether physical or chemical, can enhance hydrate formation by creating a more favorable environment. This highlights the

importance of sediment analysis and manipulation in CH_4 hydrate studies, particularly for energy extraction and environmental assessments.

3.2.1. Sediment-Specific CH_4 Hydrate Formation Mechanisms. The sediment-specific mechanisms of CH_4 hydrate formation are governed by intricate microstructural interactions, spatial distributions, and the sediment's chemical composition.^{63,64} The microstructural characteristics of sediments play a significant role in CH_4 hydrate formation within porous media. The nucleation sites, particle size, texture of sediment particles, distribution, chemical composition, porous structure of the sediment, and initial water content within the sediment matrix influence the migration and accumulation of CH_4 , which in turn affects the rate and distribution of hydrate formation,^{42,65–67} as described in Table 6. Conditions such as the initial pressure and temperature also control the kinetics of hydrate formation,⁶⁵ highlighting the importance of understanding these microstructural characteristics for effectively exploiting natural gas hydrates as energy resources and ensuring the stability of the reservoir. Chaouachi et al.⁶⁴ reported experimental investigations into the microstructural analysis of sediments during CH_4 hydrate formation, revealing several crucial insights. First, the most favorable sites for gas hydrate nucleation in juvenile water are identified as the interfaces between water and xenon gas, indicating the importance of the gas–water interface in the initial hydrate formation stage. This discovery is critical in understanding the

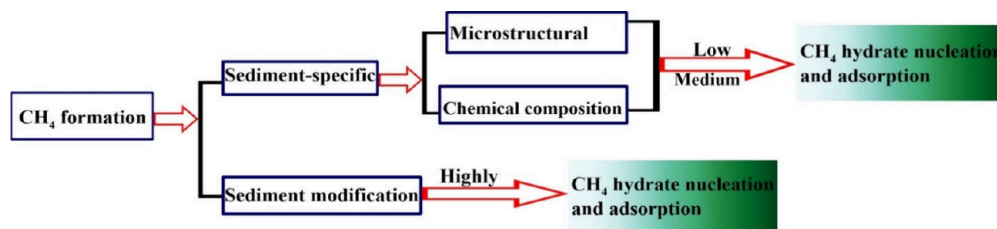


Figure 16. Influence of sediment properties on CH_4 hydrate formation and stability.

Table 6. Microstructural Characteristics of Sediments and Their Influence on CH₄ Hydrate Formation within Porous Media

| microstructural characteristics | influence on CH ₄ hydrate formation | implications for seafloor stability and gas production | remarks and observations | refs |
|---|--|--|--|-------|
| particle size and distribution | affects the rate of CH ₄ hydrate formation | larger grain sizes may enhance gas production | nonunidirectional influence varies with water saturation | 42 |
| porous structure and permeability | determines the migration and accumulation of CH ₄ | critical for evaluating natural gas hydrate reserves | sediments with higher porosity and permeability favor hydrate formation | 66,67 |
| initial pressure and temperature conditions. | controls the kinetics of hydrate formation | high-pressure and low-temperature conditions are favorable | higher initial pressure increases the formation rate | 65 |
| grain surface properties and water saturation | influences the nucleation sites for hydrate | affects the distribution and accumulation of hydrates | hydrates tend to form in the center of pores rather than on grain surfaces | 42 |

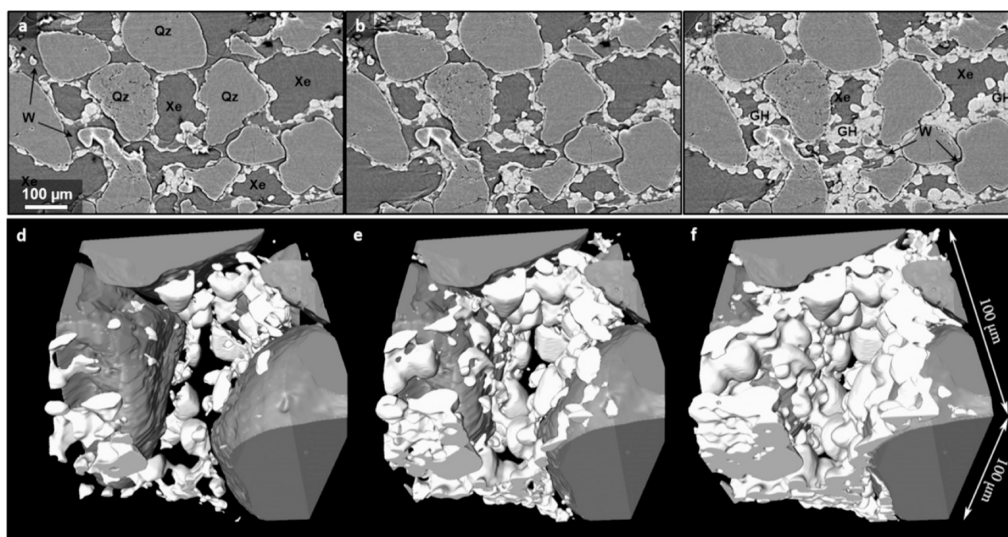


Figure 17. Gas hydrate growth from memory water: (a) initial stage, (b) intermediate stage, and (c) final stage. Initially, large polyhedral crystals form inside the water near the gas–water interface. Subsequently, in the 3-D rendered images (d–f) corresponding to Figures 17a–c, rounded polyhedral gas hydrate crystals (depicted in white) exhibit preferential growth toward the center of the pore space. Notably, these crystals do not adhere to the quartz surface (shown in gray) but are instead covered by a water layer of variable thickness. Reproduced from ref 64. Available under a CC-BY 4.0 license. Copyright 2015 Chaouachi et al.

nucleation process in sediments under varying water saturation levels. The experimental studies further differentiate nucleation and growth patterns based on the source of water used, juvenile water versus xenon-enriched water, with distinct growth behaviors observed between the two, shedding light on the so-called “memory effect” of water enriched with gas molecules from previous hydrate decompositions. The revealed finding on the memory effect indicates that water obtained from the decomposition of crystalline hydrates (memory water) enhances the formation rates of gas hydrates, as shown in Figure 17. This enhancement suggests an enrichment of gases in the liquid phase beyond the equilibrium solubility, either in a hydrophobically hydrated state or as nanometer-sized gas aggregates embedded into the liquid. While the memory effect does not imply the presence of a relic water structure facilitating gas hydrate formation, it does mean an enrichment of guest molecules in the water phase. Experimental evidence supports this effect with observations indicating that gas hydrate nucleation and growth patterns differ between water obtained from juvenile water and water from gas hydrate decomposition scenarios.⁶⁸ Furthermore, indications suggest that liquid water can become metastable and enriched in gas, supported by observations of higher absorption coefficients for small water pockets in gas hydrate-bearing sediments.⁶⁸ This enrichment occurs temporarily and is maintained in micrometer-sized water pockets or water layers before gas molecules are gradually diluted into the bulk

water toward equilibrium solubility. Additionally, the formation of a submicrometer- to micrometer-thick water layer at the quartz–hydrate and glass bead–hydrate interfaces suggests that quartz does not act as a nucleation surface, and the presence of these water layers could significantly influence the distribution and physical properties of gas hydrate within sediments. Remarkably, clay minerals, specifically montmorillonite, revealed an intimate contact with gas hydrate, indicating potential pathways for gas hydrate formation in natural sedimentary environments.

Wang et al.⁶⁶ reported a complex process influenced by various factors, including the pore–throat distribution, surface roughness or wettability, and local capillary force alongside temperature and pressure conditions on the microstructure of sediments in CH₄ hydrate formation. The formation and dissociation of CH₄ hydrates observed through a high-pressure microfluidic chip indicate that CH₄ hydrates initially nucleate rapidly at low and high temperatures, facilitated by sufficient contact between gas and water phases. This is followed by the growth of a thin hydrate film at the gas–water interface, eventually growing into the water phase with variable morphologies, as shown in Figures 18 and 19. Notably, pore-filling-type hydrates are prominently observed within the microfluidic chip, showing different growth patterns, such as the formation of spreading crystal shapes near narrow throats due to mass transfer inhibition, as illustrated in Figure 19. The formation process can cause local water migration, leading to

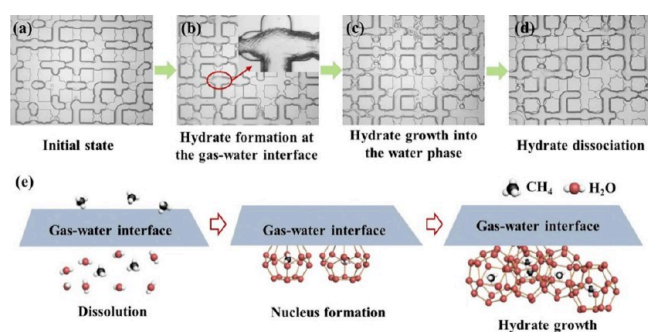


Figure 18. (a–d) CH₄ hydrate phase transitions observed in a microfluidic chip. (e) Schematic representation of the initial hydrate nucleus and the subsequent growth at the interface between CH₄ gas and water. Reproduced with permission from ref 66. Copyright 2021 Elsevier.

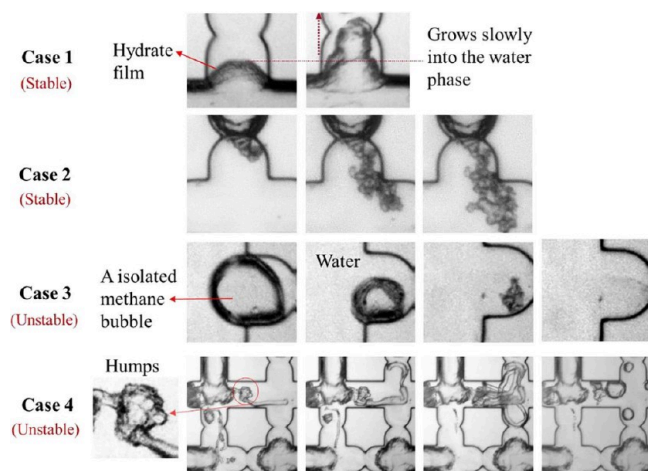


Figure 19. CH₄ hydrate growth morphology in several pores during the CH₄ hydrate formation process. Reproduced with permission from ref 66. Copyright 2021 Elsevier.

transient changes where hydrates form and then dissociate rapidly. Typically, Figure 19 reveals that hydrate formation begins at the gas–water boundary, progressing evenly into the water phase, as illustrated in Figure 19(case 1). As the hydrate expands, its growth rate decelerates and eventually halts due to gas–water contact blockage and hindered mass transfer.^{66,69} In confined spaces like narrow channels, hydrate shapes resemble expanding crystals, Figure 19(case 2), consuming CH₄ gas across a reduced interface area, echoing findings from prior pure solution research.⁷⁰ Initially, disparate small to medium CH₄ bubbles are observed with crystal formations consuming the gas, leading to particle clustering and reshaping, particularly noticeable in medium-sized bubbles, a process paralleling findings by Song et al.⁷¹ at a larger scale. Conversely, small bubbles witness transient crystal formation Figure 19(case 3), inducing local water shifts and subsequent microbubble release from dissolving hydrate. An additional volatile configuration involves CH₄ creating a web-like channel through initial hydrate layers Figure 19(case 4), influenced by gas–water phase pressure differentials. If hydrate forms quicker than gas can flow, the channel becomes obstructed with noticeable surface irregularities. While offering an extensive gas–water interaction surface area, this arrangement is fundamentally unstable due to rapid CH₄ movement, ultimately disintegrating into minor hydrate crystals and gas

bubbles, as depicted. This behavior emphasizes the intricacy of hydrate phase transitions and their impact on the microstructure of sediments, highlighting the necessity to understand these transitions to ensure operational safety and efficiency in CH₄ hydrates exploitation.

In addition, Yang et al.⁶⁷ investigated the microstructure of natural gas hydrate deposits in porous media via microfocus X-ray computed tomography. The study identified that natural gas hydrates primarily occur within the pore spaces of sediments without directly contacting the adjacent grains, suggesting the dominance of the floating model for hydrate occurrence. A water layer coating the grain surfaces was observed, indicating a barrier between the hydrates and the grains. Additionally, the nucleation of natural gas hydrates was heterogeneous, forming lens-shaped clusters at the interface between gas and water. This observation aligns with the theory that hydrates nucleate preferentially at the gas–water interface due to relatively higher supersaturation in the thin water layer.⁷² The low solubility and diffusion of CH₄ gas into pore water and low water saturation in the free gas layer were revealed as factors impacting the formation of natural gas hydrates with high saturation. The study also emphasized the random migration of gas and water during hydrate formation, showing that gas and water exhibit random migration patterns during hydrate formation, contributing to the unpredictable nature of the nucleation and growth of natural gas hydrates. The random migration observed suggests that the movement of gas and water within the sediments is not directed or controlled by specific pathways but instead occurs stochastic. This phenomenon plays a crucial role in shaping the microstructural distribution of natural gas hydrates within the pore spaces, influencing factors such as hydrate saturation and spatial occurrence. Additionally, the random migration of gas and water impacts the mechanical behavior of the sediments, affecting aspects such as solid deformation, multiphase flow dynamics, and phase transformation processes. By characterizing the random migration patterns of gas and water during hydrate formation, researchers can gain deeper insights into the complex mechanisms underlying natural gas hydrate occurrences and their implications for various geological and engineering applications.

Moreover, the sediment's chemical composition, such as the presence of silty and clayey minerals,²³ clay and zeolite,²³ and clay-rich sediments, such as Illite, montmorillonite, smectite, and kaolinite,^{73–75} and the nature of the sediment surfaces⁷⁶ plays a crucial role in CH₄ hydrate nucleation and growth, as described in Table 7. The presence of clays, such as smectite and kaolinite, has been found to enhance CH₄ hydrate stability due to their high specific surface area and cation exchange capacity, which promote the adsorption of CH₄ molecules and inhibit hydrate dissociation.^{75,77} Conversely, carbonate minerals like calcite and dolomite can inhibit hydrate formation by competing for water molecules and reducing the pore space for hydrate crystallization.⁷⁸ Additionally, the presence of sulfate ions in sediments has been observed to catalyze the decomposition of CH₄ hydrates through the formation of high-pressure, low-temperature hydrate phases.⁷⁹ The kinetics of hydrate formation within seabed sediments directly observed nucleation and growth processes, and the impact of sedimentation rates provides essential insights into understanding how chemical composition affects hydrate formation. These factors are vital for assessing global natural gas hydrate reserves and developing efficient exploitation methods. Chen

Table 7. Effects of Sediment Chemical Composition on CH₄ Hydrate Formation Mechanisms and Storage Capacities

| sediment type | impact on CH ₄ hydrate formation rate and capacity | morphological observations | implications for gas storage | refs |
|---------------------------|--|--|--|-------|
| clay-rich sediments | high clay content (e.g., Illite, montmorillonite) enhances the CH ₄ hydrate formation rate and the total amount formed; the mineralogy of the clays present significantly impacts the kinetic behavior and gas storage capacity | formation of CH ₄ hydrates in these sediments tends to create several new cracks, altering the physical structure of the sediment | suggests clay-rich sediments, particularly those high in Illite content, can potentially increase the efficiency of gas hydrate storage systems by accommodating more CH ₄ hydrate | 23,73 |
| silty and clayey minerals | silty and clayey minerals influence the kinetics of CH ₄ hydrate formation; their presence slightly complicates the distribution of CH ₄ hydrates compared to sandy sediments | | indicates that the presence of silty and clayey minerals can result in a more uneven distribution of CH ₄ hydrates, possibly affecting retrieval efficiency | 23 |
| zeolite | the structural properties of sediments, including the presence of clay and zeolite, significantly affect hydrate formation and dissociation | | suggests that adjusting the structural properties of sediments, such as incorporating zeolites, may enhance CH ₄ hydrate storage and recovery by influencing formation and dissociation rates | 23 |
| sediment surfaces | sediment surfaces play a critical role in CH ₄ hydrate formation and dissociation; the type of surface and its interaction with CH ₄ and water can significantly impact the hydrate formation rates and stability | | the specific surface chemistry and physical properties of sediments could be fine tuned to optimize CH ₄ hydrate formation and stability, enhancing gas storage capacity | 76 |

et al.²³ investigated the effects of the sediment's chemical composition, particularly concerning the presence of Illite clay, on CH₄ hydrate formation and stability. The findings revealed that low Illite content in sediments promotes the kinetic growth of CH₄ hydrate, facilitating a more rapid formation process, as diagrammatically illustrated in Figure 20. This

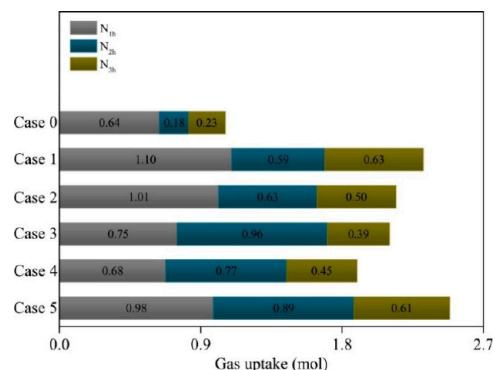


Figure 20. Comparison of gas absorption within 3 h following nucleation across experimental scenarios with varying Illite mass fractions. In Cases 0, 1, 2, 3, 4, and 5, the Illite mass fraction is 0, 10, 20, 30, 40, and 50 wt %, respectively. The N_{1h} increases from 0.64 to 1.10 mol during the first hour in Case 1. With an increase in Illite mass fraction from 10 to 40 wt %, there is a consistent decrease in N_{1h} from 1.10 to 0.68 mol. However, upon reaching an Illite mass fraction of 50 wt %, N_{1h} rises again to 0.98 mol, indicating that lower mass fractions of Illite enhance the CH₄ hydrate formation rate, whereas higher fractions may impede it. Reproduced with permission from ref 23. Copyright 2024 Elsevier.

could be attributed to the physical properties of Illite clay, including its specific surface area, which enhances the contact area between water and CH₄ molecules, thereby providing increased nucleation sites for CH₄ hydrate formation. Conversely, the high content of Illite seems to hinder CH₄ hydrate kinetics, likely due to the increase in bound water content and a consequent decrease in the permeability of the sediment, which impedes the mass transfer rate and inhibits CH₄ hydrate growth kinetics. Additionally, the study revealed that with increased Illite content, CH₄ hydrate particles tend to be smaller and more dispersed, potentially inducing spatial heterogeneity in CH₄ hydrate distribution within the reservoir. Furthermore, the occurrence of cracks in clay-rich CH₄ hydrate reservoirs was noted, suggesting potential implications for gas storage and extractive operations. These findings are essential for understanding the occurrence of CH₄ hydrate in clay-rich sediments and optimizing strategies for the extraction of CH₄ from such hydrate reservoirs.

Generally, the discussion in this section underscores the intricate interplay between sediment microstructure, chemical composition, and gas hydrate behavior, providing essential insights for assessing natural gas hydrate reserves and developing efficient extraction techniques while ensuring seafloor stability and operational safety. The studies collectively reveal the multifaceted nature of CH₄ hydrate formation, indicating that microstructural attributes such as particle size, porous structure, and initial pressure and temperature conditions significantly impact the nucleation, growth, and distribution of hydrates within sediments. Moreover, specific minerals, particularly clays like Illite and montmorillonite, influence the kinetics and stability of CH₄ hydrates with varying compositions either promoting or

Table 8. Comparative Analysis of Sediment Surface Modification Techniques for Optimizing CH₄ Hydrate Formation and Stability

| technique | description | advantages | disadvantages | refs |
|---------------------------|--|---|---|-------|
| surfactant addition | addition of surfactants to sediment surfaces alters the surface properties and enhances CH ₄ adsorption and hydrate formation | enhances CH ₄ adsorption and hydrate stability | surfactant selection is crucial for effectiveness | 82,83 |
| polymer coating | coating sediment particles with polymers increases the surface area and provides sites for CH ₄ adsorption and hydrate nucleation | increased surface area for CH ₄ adsorption | polymer compatibility with sediment is needed | 84 |
| surface functionalization | chemical modification of sediment surfaces with functional groups to improve CH ₄ interaction and stabilize hydrate formation | tailored surface chemistry for CH ₄ adsorption | requires precise control of functionalization | 85,86 |
| nanostructured materials | utilization of nanostructured materials as coatings on sediment surfaces to enhance CH ₄ adsorption and hydrate nucleation properties | high surface area-to-volume ratio | synthesis and application can be challenging | 31 |

Table 9. Summary of the Effect of Different Surfactants in Hydrate Formation, Stability, and Storage Capacities

| guest gases | additives | implication in hydrate formation and stability | storage capacity (v/v) | refs |
|------------------------|------------------------------|---|------------------------|------|
| natural gas | SDS | SDS promotes CH ₄ hydrate formation and stability | 91–159 | 87 |
| | SDS+DPG | the combination of SDS and DPG enhances CH ₄ hydrate storage capacity | 122–137 | |
| methane gas | SDS+CP | SDS with CP exhibits varying effects on CH ₄ hydrate storage capacity | 83–148 | 88 |
| | SDS, LABORATORIES, CTAB, ENP | SDS, LABORATORIES, CTAB, and ENP contribute to increased CH ₄ hydrate storage capacity | 140–170 | |
| ethane and natural gas | SDS | SDS affects the storage capacity of both ethane and natural gas hydrates | 80–160 | 89 |
| methane gas | SDS | SDS exhibits variable effects on CH ₄ hydrate storage capacity | 60–160 | 90 |
| methane gas | SDS | SDS enhances CH ₄ hydrate storage capacity | 152–172 | 91 |
| methane gas | SDS, DPG, CP, MCH | SDS, DPG, CP, and MCH show varying impacts on CH ₄ hydrate storage capacity | 79–163 | 92 |
| natural gas | APG, SDBS, POM | APG, SDBS, and POM influence the storage capacity of natural gas hydrates | 51.7–143.8 | 93 |
| methane gas | THF, NH | THF and NH affect the storage capacity of CH ₄ hydrates | 50–160 | 94 |
| methane gas | SMES | SMES contributes to increased CH ₄ hydrate storage capacity | 149–172 | 83 |

Table 10. Comprehensive Overview of Nanoparticle-Assisted Surfactant and Polymer Formulations on CH₄ Hydrate Formation and Stability

| guest gases | additives | implication in hydrate formation and stability | refs |
|---|---|--|-----------|
| methane (CH ₄) | polymer nanocomposites | increased stability and adequate storage capacity compared to hydrate formed in pure water | 95 |
| CH ₄ , CO ₂ , N ₂ , H ₂ | nanoparticles and surfactants | promote hydrate formation; nanoparticles are incredibly effective when used with surfactants | 96 |
| CH ₄ | graphite nanoparticles | enhanced heat transfer in the liquid phase improves gas consumption and hydrate formation efficiency | 97 |
| CH ₄ | hydrophilic silica nanoparticles | particle size and concentration of nanoparticles influence hydrate formation during CH ₄ gas upward migration | 98 |
| CH ₄ | surfactants@polystyrene nanospheres (Surfactant@PSNS) | fixed surfactants on nanospheres' surfaces notably increase the hydrate formation and dissociation rate | 83,99,100 |
| CH ₄ , CO ₂ | SDS, CTAB, dodecyl alcohol surfactants on polystyrene nanospheres | reduction of energy barrier by surfactant adsorption on hydrate nuclei facilitates enhanced formation | 83,100 |
| CH ₄ | natural and synthetic nanoparticles | CH ₄ hydrate formation shows insensitivity to a wide range of nanoparticles, indicating negligible impact | 101 |

hindering formation rates. Additionally, the interaction between sediment surfaces and CH₄ molecules plays a crucial role, suggesting that tailoring sediment properties could optimize hydrate formation and the stability of CH₄ hydrates.

3.2.2. Sediment Surface Modification for Enhanced CH₄ Hydrate Formation and Stability. Enhancing CH₄ hydrate formation and stability through sediment surface modification involves a multifaceted approach considering the type of porous media, the composition and mineralogy of clays within the sediments, and the critical control of sediment parameters.^{31,42,73} Sediment surface modification techniques involve altering the surface properties of sediments to facilitate better interaction with CH₄ molecules and promote stable hydrate formation, offering potential pathways for increased efficiency in CH₄ recovery from hydrate reservoirs.⁷⁶ Among the various methods employed, surface modification through chemical additives,⁷⁶ surface roughening,^{23,80} and pore structure

optimization⁸¹ stand out as key strategies, as described in Table 8. Chemical additives serve as effective agents in modifying sediment surfaces to enhance CH₄ hydrate formation. These additives often include surfactants,^{82,83} polymers,⁸⁴ or other chemical compounds that can alter sediments' surface energy and affinity toward CH₄ molecules. By selectively adsorbing onto sediment surfaces, these additives can create favorable conditions. Additionally, they can inhibit ice formation or other competing phases, thereby promoting the stability of CH₄ hydrates within the sediment matrix.^{82–84} Table 9 summarizes the gas absorption capacity of hydrates revealed from different research investigations. On top of that, surface roughening techniques involve physically altering the texture of sediment surfaces to increase their surface area and provide more nucleation sites for CH₄ hydrate formation.⁸⁵ This can be achieved through abrasion, etching, or mechanical agitation, which creates irregularities and microstructures on

the sediment surface. The increased surface area facilitates greater interaction between CH₄ and sediment, promoting the nucleation and growth of hydrate crystals.⁸⁶ Additionally, roughened surfaces can trap CH₄ molecules more effectively, enhancing the stability of hydrate deposits.^{85,86} In addition, pore structure optimization focuses on modifying the pore size distribution and connectivity within sediments to improve CH₄ hydrate formation and stability.⁸¹ This can be achieved through techniques such as pore plugging, where fine particles or gels are injected into the sediment pores to reduce permeability and create confinement for CH₄ molecules.^{31,81} Altering the pore network can enhance CH₄ retention and hydrate stability, preventing the dissociation of hydrates under changing pressure and temperature conditions. Furthermore, advanced surface modification techniques may involve nano-materials or functional coatings to tailor the surface properties of sediments at the nanoscale. Nanoparticles or thin films deposited onto sediment surfaces can enhance the adsorption capacity, catalyze the hydrate formation kinetics, and provide thermal insulation, thereby improving the overall efficiency and stability of CH₄ hydrate reservoirs.³¹ Table 10 provides a summary of nanoparticles and nanoparticle-assisted surfactant/polymer formulations on CH₄ hydrate formation and stability revealed from different research investigations.

Farhadian et al.⁸² provided a detailed investigation of the oleic acid-based promoter (OAP) surfactant properties, and its impact on CH₄ hydrate formation reveals significant insights into sediment surface modification for enhanced CH₄ hydrate formation and stability. The synthesis of OAP involves the esterification reaction between oleic acid (OA) and *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES), leading to a substance that serves as an anionic surfactant in CH₄ hydrate experiments. The experimental setup for CH₄ hydrate formation utilized pure water or promoter solution in conjunction with CH₄ gas under specific pressures to induce hydrate formation with detailed kinetic parameters calculated to evaluate the efficiency of hydrate formation in the presence of OAP. One of the standout observations from the study was the surfactant properties of OAP, including its ability to significantly reduce the interfacial tension (IFT), form micelles, and enhance the wettability of surfaces. These properties are critical for promoting CH₄ hydrate formation by facilitating the interaction between CH₄ and water phases, thereby increasing hydrate nucleation growth rate and efficiency. In the presence of OAP, the experiments revealed a pronounced decrease in IFT values and a significant increase in CH₄ consumption, storage capacity, and rate of CH₄ uptake, as described in Table 11, indicating enhanced kinetic behavior of CH₄ hydrate formation compared to pure water and sodium dodecyl sulfate (SDS) solutions. Moreover, molecular dynamics (MD) simulations provided additional insights into the OAP CH₄ hydrate growth promotion mechanism. The simulations revealed that OAP molecules tend to self-assemble into micelle structures, which play a crucial role in increasing the solubility of CH₄ in the aqueous phase, as diagrammatically illustrated in Figure 21. This process facilitates the transport of CH₄ molecules to the hydrate–water interface, thereby promoting faster and more efficient hydrate formation. The formation of OAP micelles and their aggregation behavior around CH₄ molecules were crucial in supplying CH₄ for hydrate growth. Additionally, OAP showed significant advantages over SDS in preventing foam formation during hydrate dissociation and gas recovery, as evidenced by

Table 11. Comparison of CH₄ Hydrate Formation Kinetics in the Presence of OAP, Pure Water, and SDS Solutions^{a,82}

| sample | concentration (ppm) | conversion (%) | storage capacity (v/v) | average rate of CH ₄ uptake (mmol/mol·s) |
|------------|---------------------|----------------|------------------------|---|
| pure water | | 15 ± 4.50 | 30 ± 6.00 | 0.0252 ± 0.006 |
| OAP | 500.00 | 34 ± 2.90 | 64 ± 4.90 | 0.0547 ± 0.004 |
| | 1000.00 | 31 ± 3.40 | 57 ± 4.60 | 0.0461 ± 0.003 |
| | 1500.00 | 53 ± 2.60 | 96 ± 1.60 | 0.0930 ± 0.005 |
| | 2000.00 | 60 ± 3.20 | 109 ± 4.10 | 0.1050 ± 0.004 |
| | 2500.00 | 75 ± 3.90 | 126 ± 5.10 | 0.1143 ± 0.002 |
| SDS | 3000.00 | 77 ± 4.00 | 128 ± 5.30 | 0.1241 ± 0.006 |
| | 1000.00 | 81 ± 4.60 | 144 ± 5.20 | 0.1424 ± 0.003 |

^aThe maximum uncertainty observed in the measured storage capacity and average rate of gas uptake was 3.91 v/v and 0.0030 mmol/mol·s, respectively. This table was reproduced with permission from ref 82. Copyright 2024 Elsevier.

experiments conducted with nitrogen gas injection. This property of OAP enhances CH₄ hydrate formation and offers practical benefits in preventing operational issues associated with foam formation.

Song et al.¹⁰² revealed significant findings regarding sediment surface modification for enhanced CH₄ hydrate formation and stability by functionalizing carbon nanotubes (CNTs) with an amphiphilic copolymer, poly(styrene-*co*-sodium styrenesulfonate) (PSCS). First, the modification of sediment surfaces with functionalized CNTs demonstrated improved dispersion and stability of the nanotubes in water. The study utilized an amphiphilic copolymer, PSCS, which facilitated the solubilization of CNTs in water through the electrostatic repulsion of sulfonate groups attached to the nanotube surface. Additionally, the hydrophobic aromatic rings of the copolymer provided stabilization by preventing CNT aggregation through π – π stacking interactions. This modification strategy led to better dispersibility of CNTs in the aqueous phase, reducing their tendency to form aggregates and improving their interaction with CH₄ molecules during hydrate formation. The functionalized CNTs revealed enhanced CH₄ hydrate formation rates and capacities compared to conventional promoters like SDS. The amphiphilic nature of the copolymer-coated CNTs allowed for improved gas–liquid mass transfer, leading to more efficient hydrate formation kinetics, as shown in Figure 22. This was attributed to the ability of individual nanotubes to act as microstirrers, increasing the interfacial area between gas and liquid phases and promoting rapid CH₄ hydrate nucleation and growth. Furthermore, the study revealed the excellent recycling performance of the functionalized CNTs, indicating their potential for repeated use as efficient promoters for CH₄ hydrate formation, as illustrated in Figure 23. This finding contrasts with the gradual depletion of conventional promoters like SDS over repeated hydrate formation–dissociation cycles, highlighting the economic and practical advantages of using functionalized CNTs in hydrate-based applications.

In addition, Liu et al.,¹⁰³ through the utilization of SDS@Fe₃O₄ sol, revealed remarkable improvements in both the induction period and the overall efficiency of CH₄ hydrate formation. SDS@Fe₃O₄ sol, characterized by stable dispersion of Fe₃O₄ nanoparticles coated with SDS molecules, facilitated rapid nucleation of CH₄ hydrates due to the presence of nanointerfaces provided by the SDS-coated Fe₃O₄ nano-

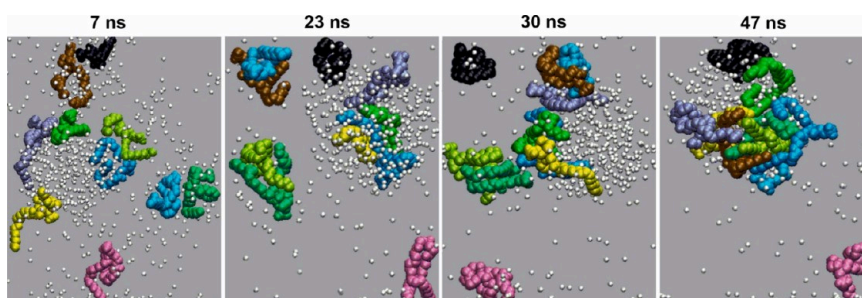


Figure 21. Illustration depicting the promotion mechanism of OAP CH_4 hydrate growth through micelle formation from self-aggregation of OAP molecules, leading to enhanced CH_4 solubility. Each OAP molecule is represented by a distinct color, while CH_4 molecules are depicted as white spheres. Reproduced with permission from ref 82. Copyright 2024 Elsevier.

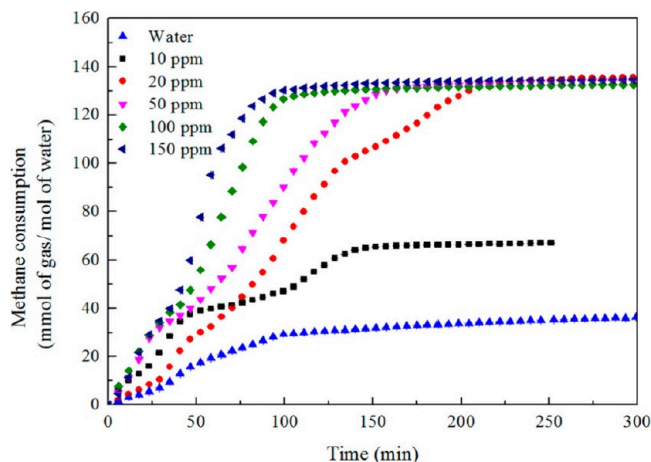


Figure 22. Changes in CH_4 consumption at different concentrations of carbon nanotubes (CNTs). Reproduced with permission from ref 102. Copyright 2017 American Chemical Society.

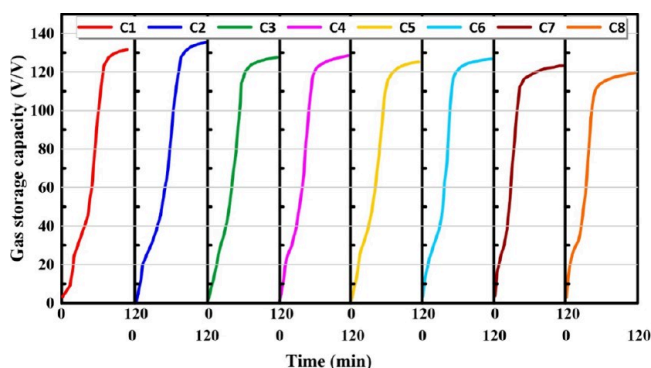


Figure 23. (a) The variations in storage capacity throughout eight cycles of the hydrate formation–dissociation process in a 50 ppm dispersion of CNTs. Here, “ C_i ” denotes the cycle number in the hydrate formation–dissociation process. Reproduced with permission from ref 102. Copyright 2017 American Chemical Society.

particles. This effect led to substantially shorter induction periods compared to conventional SDS solutions, thus accelerating the formation of CH_4 hydrates, as illustrated in Figure 24. Furthermore, the excellent stability of $\text{SDS@Fe}_3\text{O}_4$ sol even after centrifugation suggests its potential for practical applications requiring stable dispersions. Moreover, the study elucidates the influence of $\text{SDS@Fe}_3\text{O}_4$ sol characteristics, such as Fe_3O_4 concentration and particle size on CH_4 hydrate formation kinetics. It was revealed that the particle size of $\text{SDS@Fe}_3\text{O}_4$ sol had a significant impact on the rate of hydrate

formation. Specifically, smaller particle sizes resulted in higher surface free energy, promoting easier adsorption of gas molecules and thus facilitating faster hydrate formation. Additionally, the increase in SDS concentration in $\text{SDS@Fe}_3\text{O}_4$ sol led to a corresponding increase in CH_4 hydrate formation rate, attributed to more free SDS molecules promoting hydrate nucleation, as shown in Figure 25. These findings underscore the importance of careful tuning of sol properties, such as particle size and surfactant concentration, for optimizing CH_4 hydrate formation processes.

In summary, while Farhadian et al.⁸² focused on chemical surfactant additives like OAP, Song et al.¹⁰² explored the use of functionalized CNTs and Liu et al.¹⁰³ investigated the application of $\text{SDS@Fe}_3\text{O}_4$ sol for sediment surface modification. Each study offers unique insights into enhancing CH_4 hydrate formation and stability through different approaches. This implies that tailored sediment surface modification techniques can significantly improve the CH_4 hydrate stability and extraction potential. Chemical surfactant additives like OAP, functionalized carbon nanotubes (CNTs), and $\text{SDS@Fe}_3\text{O}_4$ sol offer distinct advantages in promoting CH_4 hydrate formation and stability by modifying sediment surfaces to improve CH_4 adsorption and hydrate nucleation. By enhancing gas–liquid mass transfer, increasing the surface area for adsorption, and providing stable dispersion of nanoparticles, these approaches offer promising pathways for optimizing hydrate-based natural gas recovery processes. Their diverse strategies underscore the potential for tailored surface modifications to unlock more efficient and reliable CH_4 extraction from hydrate reservoirs.

4. CLASSIFICATION OF METHANE (CH_4) HYDRATES

The classification of CH_4 hydrates is essential in resource assessment and production planning for many reasons. Primarily, it serves as the foundation for evaluating new exploration prospects and formulating accurate production models.¹¹ Precision is indispensable for making optimal development decisions and generating reliable production forecasts. CH_4 hydrates, being a significant potential transitional energy source, require a sophisticated understanding of their classifications to harness this resource efficiently.^{11,104}

The profound impact of CH_4 as the principal ingredient in natural gas necessitates an in-depth classification to manage its production and utilization effectively. The variability in CH_4 content across crude oils underscores the necessity for detailed classification schemes to predict and plan CH_4 extraction and utilization processes.¹⁰⁵ This deep-seated classification supports strategic planning in energy production, ensuring that the

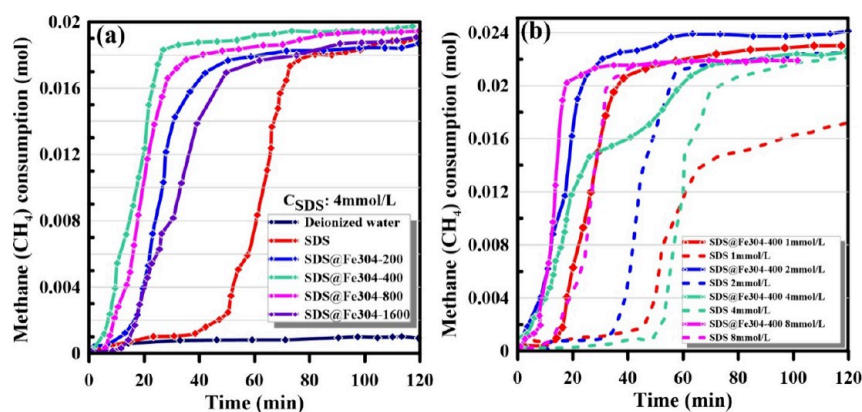


Figure 24. (a) CH_4 consumption during hydrate formation using $\text{SDS}@Fe_3O_4$ sol at a specific SDS concentration and varying Fe_3O_4 concentrations. The SDS concentration remained constant at 4 mmol/L, while the Fe_3O_4 concentrations in the $\text{SDS}@Fe_3O_4$ sol were 200, 400, 800, and 1600 mg/L. (b) CH_4 consumption during hydrate formation using $\text{SDS}@Fe_3O_4$ sol at a fixed Fe_3O_4 concentration and varying SDS concentrations. The Fe_3O_4 concentration remained constant at 400 mg/L, while the SDS concentrations were varied as 1, 2, 4, and 8 mmol/L. Redrawn with permission from ref 103. Copyright 2017 Elsevier.

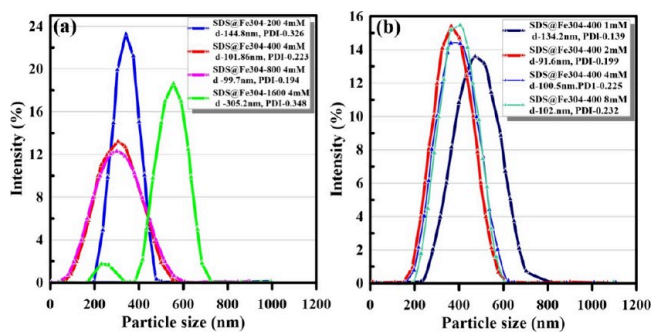


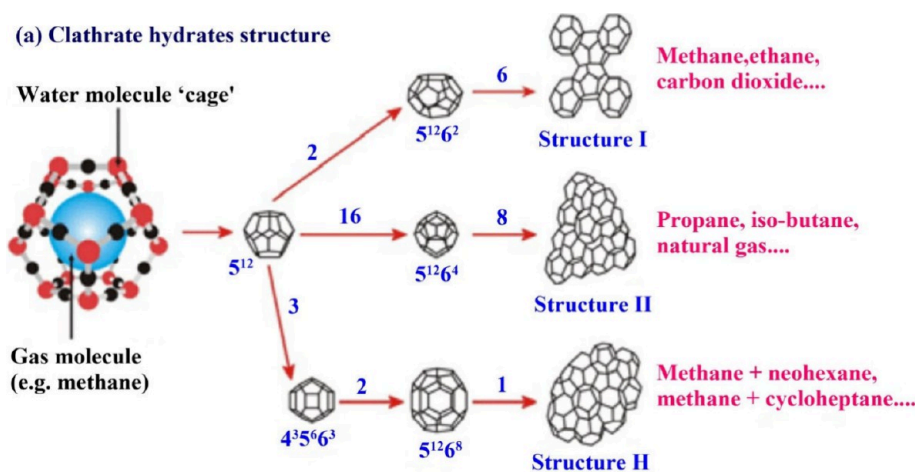
Figure 25. (a) The particle sizes of $\text{SDS}@Fe_3O_4$ sol under specific SDS concentrations and varying Fe_3O_4 concentrations. The SDS concentration was maintained at 4 mmol/L, while the Fe_3O_4 concentrations ranged from 200 to 1600 mg/L in the $\text{SDS}@Fe_3O_4$ sol mixture. (b) The variation in particle sizes of $\text{SDS}@Fe_3O_4$ sol at a fixed Fe_3O_4 concentration and different SDS concentrations. The Fe_3O_4 concentration was maintained at 400 mg/L, while the SDS concentrations varied at 1, 2, 4, and 8 mmol/L in the $\text{SDS}@Fe_3O_4$ sol. Redrawn with permission from ref 103. Copyright 2017 Elsevier.

exploitation of CH_4 hydrates is aligned with socioeconomic gains.^{104,106} The classifications of CH_4 hydrates also aid in the optimization of production schedules.¹⁰⁶ It involves adjusting the production of CH_4 hydrates within a reasonable range to fit the characteristics of the reservoir efficiently. The classifications offer insights into the reservoirs' complexities, allowing for fine tuning production strategies to maximize output while minimizing risks and environmental impacts. Moreover, the classification of CH_4 hydrates plays a critical role in the broader effort to reduce CH_4 emissions, a potent greenhouse gas.¹⁰⁷ By facilitating the targeted management of CH_4 sources, classification aids in developing strategies that significantly reduce emission rates, thereby contributing to global efforts to mitigate climate change effects.

4.1. Traditional Classification of (CH_4) Based on the Crystal Structure. The structure of gas hydrate is divided into three groups based on the configuration of their component water cavities, as described in Figure 26, such as cubic structures I and II and structure H, which possesses a hexagonal configuration.¹⁰⁸ Each crystalline structure commonly accepts a distinct structural water cage. Structure I is the most widely occurring natural gas hydrate structure, charac-

terized by a crystalline lattice that can encapsulate relatively small guest molecules. The sI structure consists of a unit cell comprising 46 water molecules, forming two types of cages: small and large. The smaller cages accommodate guest molecules like methane (CH_4) and ethane (C_2H_6), while occasionally, this structure can also harbor binary mixtures involving carbon dioxide (CO_2) and hydrogen sulfide (H_2S) alongside CH_4 and C_2H_6 .¹⁰⁹ Structure II is designed to encapsulate larger guest molecules than sI. The sII lattice comprises 136 water molecules within its unit cell, arranged into 16 small cages and 8 large ones. This structure type is ideal for containing larger guest molecules such as propane (C_3H_8), nitrogen (N_2), and isobutane, offering a versatile accommodation capacity beyond that of sI.^{109,110} Structure H is less prevalent and hardly originates in nature.^{110,111} Distinct from sI and sII, structure H showcases a hexagonal configuration with a unit cell holding 34 water molecules. This structure forms through the cooperative stabilization provided by two guest molecules, usually one larger and one smaller. The uniqueness of sH lies in its ability to accommodate larger guest molecules in combination, such as a mix of methane (CH_4) and cycloheptane, owing to its specific cage sizes that include one "huge" cavity sufficient for large molecules.¹¹²

The diverse structures of gas hydrates significantly influence their formation, stability, and potential for extraction as an energy resource. Table 12 provides a comparative analysis summarizing the characteristics of the three main structures—structure I (sI), structure II (sII), and structure H (sH). This table highlights the differences in their configurations, guest molecule capacities, and stability characteristics. By focusing on the specific advantages of each structure, such as the prevalence of sI in natural environments and the unique stability of sH, this work provides a fresh perspective that can contribute to ongoing research in gas hydrate extraction methods. This comparative approach can help clarify the potential for utilizing these structures as energy resources, which is a critical area of interest in current energy research. Structure I, the most prevalent, exhibits stability under moderate conditions and is commonly found in natural environments, making it a primary target for extraction research.²⁴ With larger cages, structure II accommodates larger gas molecules, expanding the range of extractable gases but



(b) Cage types of clathrate hydrates

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

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

Figure 26. Gas hydrate structure based on the configuration of water cavities. Adapted with permission from ref 113. Copyright 2023 American Chemical Society.

Table 12. Comparative Analysis of Gas Hydrate Structures and Their Guest Molecule Accommodations

| structure | water molecules per unit cell | cage types | guest molecules | stability conditions | novelty/advantages | refs |
|-----------|-------------------------------|-------------------|--|--|---|---------|
| I (sI) | 46 | 2 small, 1 large | CH ₄ , C ₂ H ₆ , CO ₂ , H ₂ S | moderate pressure and temperature | most prevalent in nature; primary target for extraction due to stability under moderate conditions | 108 |
| II (sII) | 136 | 16 small, 8 large | C ₃ H ₈ , N ₂ , isobutane | higher pressure and lower temperature than sI | accommodates larger guest molecules, expanding the range of extractable gases, though with technical challenges | 109,110 |
| H (sH) | 34 | 1 huge, 2 small | CH ₄ with larger molecules (e.g., cycloheptane) | unique stability properties; requires specific combinations of guest molecules | less common but offers unique extraction opportunities due to its ability to stabilize larger guest molecules | 112 |

posing technical challenges due to its stability characteristics.^{24,109,110} Structure H, though less common, offers unique stability properties, allowing for the accommodation of a combination of larger and smaller gas molecules, which may present additional extraction opportunities.^{24,112}

4.2. CH₄ Classification Based on Deposits, Composition, and Formation Mechanisms. CH₄ hydrate deposits are categorized into four main classes, Class 1, Class 2, Class 3, and Class 4, as diagrammatically illustrated in Figure 27. These classifications are based on fundamental geological characteristics and the initial reservoir conditions, providing a framework for assessing their potential as an energy resource.^{104,114} Each class presents unique characteristics and challenges for extraction and exploitation. While some classes offer higher saturation and the presence of free gas, making them more appealing for energy production, others require more advanced technologies and methods for efficient utilization. These classifications are crucial for the future

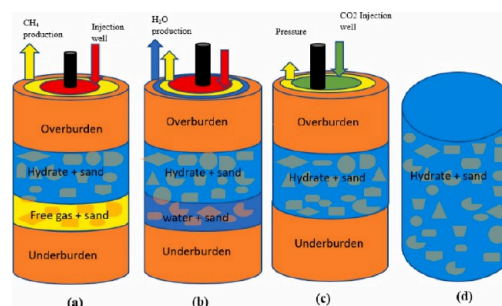


Figure 27. Classification of CH₄ hydrate deposits based on geological characteristics and initial reservoir conditions: (a) Class 1, (b) Class 2, (c) Class 3, and (d) Class 4. Reproduced with permission from ref 11. Copyright 2022 Elsevier.

exploration and development of gas hydrates as a significant energy resource.

4.2.1. Class 1: High-Potential Reservoirs. Class 1 hydrate reservoirs, such as the Mallik field in Canada's Mackenzie

Table 13. Overview of Novel Approaches to CH₄ Hydrate Classification: Stability, Accessibility, and Extraction Potential

| approach | stability characteristics | accessibility features | extraction potential | refs |
|---|---------------------------------|------------------------|--------------------------------------|------|
| empirical correlations | moderate to high | high | variable | 123 |
| van der Waals Platteeuw (VdW-P) Thermodynamic Model | high | moderate | high | 123 |
| classification and regression tree (CART) methodology | detailed stability conditions | high | | 124 |
| semianalytical approaches | focus on multiphysics coupling | high | high | 125 |
| machine learning for methane–hydrate equilibrium prediction | high accuracy predictions | high | enhances understanding of extraction | 126 |
| mechanical properties and recovery issues | insight on exploitable hydrates | under investigation | seen as a potential energy source | 127 |

Delta and the Eileen field in Alaska, United States,^{104,106} are characterized by the presence of two zones: a hydrate-bearing zone and an underlying two-phase fluid zone containing both mobile gas and liquid water. This class of reservoirs generally offers promising potential due to their high saturations of gas hydrates at the base of the gas hydrate stability zone, immediately above a free gas layer.¹⁰⁶ These types of reservoirs are typically found in sediments with high reservoir quality, such as sand-rich formations.^{104,106}

4.2.2. Class 2: Water-Associated Reservoirs. Reservoirs of Class 2, as described in Figure 27, entail a hydrate-bearing layer that overlies a zone containing mobile water.^{115,116} Unlike Class 1, an underlying free gas zone is not typical of this class. These reservoirs are also located in sand-rich sedimentary formations and represent different challenges and opportunities for gas extraction due to the water zone below the hydrate-bearing layer. This class notably includes formations with fractures or vugs, common in sandstones and carbonate rocks.^{115,116}

4.2.3. Class 3: Hydrate and Underburden. Class 3's defining characteristic is the absence of either a free gas zone or a mobile water zone beneath the hydrate-bearing strata. Like the other classes, these reservoirs are located within high-quality, sand-rich sediments.¹¹⁶ This class is primarily found in sandstone and carbonate rocks, exemplified by the Qilian Mountains permafrost in China.^{106,116} The absence of underlying zones distinguishes Class 3, focusing the potential extraction processes on the hydrate-bearing sediments.

4.2.4. Class 4: Dispersed Low-Saturation Hydrates. Although explicit details in manuscripts directly examining Class 4 CH₄ reservoirs are minimal, Class 4 reservoirs are markedly different from Classes 1, 2, and 3 in that they are generally associated with gas hydrates found within marine muds rather than in sand-rich sediments.^{117,118} The hydrates in Class 4 contain scattered, low-saturation hydrate formations (SH < 10%) within the host rock without specific stratification.¹¹⁷ The dispersed nature and low saturation levels pose additional challenges for commercial extraction.^{117,119} Developing a sustainable extraction method for CH₄ hydrates, especially for complex reservoirs like class 4, is challenging and requires careful consideration of environmental and economic factors. Methods like depressurization and thermal stimulation carry the risk of causing seabed instability, which could have catastrophic consequences.⁵ Therefore, more research and field-scale testing are needed to ensure the methods are viable and safe for large-scale implementation. The CO₂ replacement technique emerges as a promising method for CH₄ extraction from Class 4 CH₄ hydrate reservoirs, offering a balance between efficiency and environmental responsibility.⁵ By swapping CH₄ molecules with CO₂, this approach not only facilitates CH₄ extraction but also enables CO₂ sequestration, addressing both energy

production and environmental concerns. With inferred benefits, including reduced seabed disturbance and potential CO₂ emission reduction, the method underscores its potential for sustainable CH₄ extraction. Further research and development are vital to refine and scale up this technique for commercial application while assessing its efficacy and environmental impact comprehensively.

4.2.5. CH₄ Hydrate Reservoirs with Varying Classifications. The classification of CH₄ hydrate deposits can vary based on updated geological findings and advancements in understanding these complex systems. The Eastern Nankai Trough has been widely studied, and recent research may suggest characteristics that align it with both Class 2 and Class 3 hydrate reservoirs.¹²⁰ Class 3 reservoirs, unlike Class 2, do not have a mobile water zone beneath the hydrate-bearing sediments but may be present above a free gas zone or none at all, which might be applicable in certain areas of the Eastern Nankai Trough. This dual characterization emphasizes the need for nuanced descriptions based on the latest geological data and interpretations. On top of that, the Krishna–Godavari Basin, located on the eastern coast of India, is renowned for its significant gas hydrate deposits. This basin is primarily characterized by Class 1 and Class 2 hydrate reservoirs.¹²¹ The presence of high-quality sandstone layers with high hydrate saturations makes it a prime example of areas where efficient gas extraction methods can be employed. While Class 1 reservoirs feature a hydrate-bearing layer above a free gas zone, Class 2 reservoirs, as described, have a hydrate-bearing layer above a zone of mobile water without a free gas zone underneath. Given the diversity in sedimentary environments and hydrate saturations, the Krishna–Godavari Basin encompasses both classifications depending on the specific location and geological structure.¹²¹ In addition, the Gulf of Mexico is another critical area with abundant CH₄ hydrate resources. This region is predominantly classified as Class 2 and Class 3 hydrate reservoirs owing to its complex sedimentary structures, including thick sand layers with high degrees of hydrate saturation.¹²² The presence of sandy layers interspersed with hydrate-bearing sediments allows for the distinction of these classes. Class 3 reservoirs, as previously discussed, feature hydrate occurrence within the water-saturated zone without an overlying gas zone, which differentiates them from Class 1 and 2. Thus, in the Gulf of Mexico, the classification is nuanced and depends on the specific characteristics of the sediment and hydrate distributions.

4.3. Novel Approaches for CH₄ Hydrate Classification Considering Stability, Accessibility, and Extraction Potential. Various models and methodologies, such as the VdW-P model, were assessed for their accuracy in predicting and maintaining stable conditions for CH₄ hydrates.¹²³ Accessibility features of these approaches, including analytical, semianalytical, and empirical methods, were evaluated for their

effectiveness in identifying and accessing CH₄ hydrate deposits. The extraction potential examines how these methodologies contribute to or predict the viability of CH₄ hydrate extraction, crucial for future resource management amidst increasing energy demand. Table 13 outlines an overview of novel approaches to CH₄ hydrate classification, evaluating the stability, accessibility, and extraction potential.

5. PRODUCTION METHODS FOR METHANE (CH₄) EXTRACTION

5.1. Conventional Production Methods for CH₄ Extraction.

Conventional methods for CH₄ extraction from CH₄ hydrates include four primary techniques that have proven effective: depressurization, thermal stimulation, inhibitor injection, and CO₂ swapping. These methods are essential for gas production from hydrate reservoirs and are based on destabilizing the phase equilibrium of gas hydrates. Table 14 outlines the comparative analysis of these conventional production methods for CH₄ extraction, evaluating the efficiency, environmental impact, economic viability, and scalability. Implementing cost-saving measures requires a thorough understanding of each method's operational and technical aspects and continuous research and development to enhance the efficiency and economic viability, as described in Table 15. Integrating renewable energy technologies, such as solar and wind, into the energy mix can influence the economic attractiveness of CH₄ hydrates. For instance, the cost of renewable energy has been decreasing significantly, making it a more competitive option than traditional fossil fuels. This shift could lower the demand for CH₄ extracted from hydrates as energy systems rely more on renewables.¹ Furthermore, advancements in carbon capture and storage (CCS) technologies can enhance the environmental viability of CH₄ production, making it a more appealing option in a market increasingly focused on sustainability. While conventional methods for CH₄ extraction, such as depressurization and thermal stimulation, have established economic viability, the rising costs associated with these methods must be weighed against the benefits of renewable energy advancements. For example, utilizing waste heat from industrial processes for thermal stimulation can reduce operational costs, promoting a more sustainable approach to CH₄ extraction.^{1,20} Additionally, CO₂ swapping not only aids in CH₄ recovery but also addresses carbon emissions, aligning with global climate goals and potentially improving the economic outlook for CH₄ hydrates.

Depressurization is the most widespread technique employed for mining natural gas hydrates. It involves lowering the reservoir's initial pressure by circulating low-density drilling fluid or extracting the free fluid under the hydrate layer.^{134,135} When the pressure reduces to the critical phase equilibrium value, the hydrates dissociate, releasing significant amounts of gas.¹³⁴ This method's efficiency in extracting CH₄ from hydrate formations has been validated through both practical applications and theoretical studies, highlighting its role as a cornerstone in hydrate exploitation strategies.^{134,135} Thermal stimulation introduces heat to the reservoir to destabilize the CH₄ hydrate equilibrium, thereby facilitating gas production.¹³⁶ The process typically results in higher gas outputs than depressurization.^{136,137} Thermal stimulation is deemed a viable method for gas recovery from hydrates, indicating its significant potential in enhancing CH₄ extraction from such reserves.¹³⁶ Furthermore, the chemical inhibitor injection method presents a promising avenue for CH₄ hydrate recovery by introducing substances that induce instability in hydrate formations. Despite its limited implementation in laboratory-scale experiments and field tests thus far, this approach holds significant potential as a novel technique. The principle behind inhibitor injection revolves around creating conditions where hydrates lose their stability, thus facilitating gas release.¹³⁸ Potential substances for injection include salts like calcium chloride or sodium chloride,¹³⁹ alcohols such as methanol or ethanol,¹⁴⁰ glycols like ethylene glycol or propylene glycol,¹⁴¹ surfactants,¹⁴² and polymeric additives.¹⁴³ These substances disrupt the hydrate structure, alter the water chemistry, or

Table 14. Comparative Analysis of Conventional CH₄ Extraction Techniques: Assessing Efficiency, Environmental Impact, Economic Viability, and Scalability

| method | efficiency | environmental impact | economic viability | scalability | refs |
|--------------------------|---|---|---|--|---------|
| depressurization | relatively economical and mature choice | limited information is generally considered to have a moderate impact | considered economically viable due to its more established nature | good scalability due to established technology | 128,129 |
| thermal stimulation | high energy requirements may reduce efficiency | potential for moderate environmental impact due to energy use | high operational costs could affect viability | scalability might be limited by energy and cost efficiency | 130 |
| inhibitor injection | efficiency may be impacted by the specific inhibitors used | could have varying environmental impacts based on the chemicals used | costs of inhibitors can affect economic viability | depends on the availability and cost of suitable inhibitors | 129 |
| CO ₂ swapping | kinetics and replacement efficiency are current bottlenecks | promising for CO ₂ emission reduction and safe sequestration | kinetic enhancement is needed for economic viability | the need for improved kinetics and efficiency challenges scalability | 131 |

Table 15. Summary of Potential Cost-Saving Measures in Conventional Methods for CH₄ Extraction

| method | potential cost-saving measures | description | refs |
|--------------------------|--|--|------|
| depressurization | optimization of depressurization rates to maximize gas production while minimizing energy costs | effective management of depressurization rates can lead to significant cost reductions by minimizing the energy input required while ensuring maximum methane production from hydrate dissociation; adjusting the depressurization rates according to real-time reservoir conditions can optimize production rates and costs | 20 |
| thermal stimulation | utilizing waste heat from adjacent industrial processes can reduce the energy required for heating | leveraging thermal energy from nearby industrial operations as a heat source for thermal stimulation can significantly lower the costs of generating the required temperatures for CH ₄ extraction from hydrates; this method promotes sustainability by recycling waste heat that would otherwise be lost to the environment | 20 |
| inhibitor injection | developing multifunctional inhibitors could reduce the amount and cost of chemicals required | developing and using advanced, multifunctional chemical inhibitors can minimize the required volume and frequency of injections, consequently reducing the overall costs associated with chemical procurement, handling, and injection systems; innovative chemical formulations could also enhance the inhibitor's effectiveness, lowering the needed amount | 132 |
| CO ₂ swapping | direct flue gas injection from power stations avoids the cost of CO ₂ separation, making it more economical | injecting a mixture of CO ₂ and N ₂ directly into CH ₄ hydrate formations presents a cost-effective alternative due to avoiding CO ₂ separation processes; this method reduces operational costs and simultaneously addresses CH ₄ recovery and CO ₂ sequestration objectives, offering a dual environmental benefit | 133 |

modify the thermal properties within the formation. By selectively targeting hydrate stability, inhibitor injection can enhance CH₄ recovery.¹³⁸ However, further research and optimization are necessary to fully understand this emerging method's applicability and effectiveness in practical scenarios. In addition, CO₂ swapping offers a dual-purpose solution that combines carbon capture and storage (CCS) technology with CH₄ recovery from subsurface reservoirs, particularly CH₄ hydrates.¹⁴⁴ This technique involves injecting CO₂ into underground geological formations, displacing CH₄ from pore spaces in the rock as the CO₂ migrates through the formation. The displaced CH₄ is then extracted alongside the CO₂, providing an opportunity to utilize CH₄ as an energy resource while simultaneously sequestering CO₂,^{144,145} a potent greenhouse gas. CO₂ swapping leverages existing infrastructure and knowledge from the oil and gas industry, making it a feasible option for large-scale implementation. However, the success of CO₂ swapping hinges on various factors, including geological characteristics, such as porosity and permeability, as well as economic considerations related to CO₂ capture, transport, and injection costs.¹⁴⁵ Moreover, stringent monitoring and risk assessment protocols are imperative to ensure the long-term safety and environmental integrity of stored CO₂.^{145,146} Despite these challenges, CO₂ swapping holds promise as an environmentally sustainable method for CH₄ extraction from hydrate formations, contributing to both energy production and climate change mitigation efforts.

Moreover, another ground-breaking extraction method employs lasers for extracting CH₄ from CH₄ hydrates. The utilization of a chemically pumped oxygen–iodine energy transfer laser (COIL) has been proposed, highlighting its superiority over other methods for this purpose.¹⁴⁷ The specific type of laser identified for CH₄ extraction, the COIL, exemplifies the innovative approach toward efficient and potentially less environmentally impactful methods of CH₄ extraction from hydrates.¹⁴⁷ Recent studies have revealed the feasibility of using lasers for CH₄ extraction from hydrates. The research by Kadobayashi¹⁴⁸ involving laser-heated diamond anvil cell (LHDAC) experiments has shown promising results in manipulating CH₄ hydrates under controlled conditions. These experiments indicate that lasers can effectively induce phase changes in hydrates, increasing gas production rates while maintaining structural integrity.¹⁴⁸ In addition, recent pilot projects have revealed the promising potential of laser-assisted extraction techniques for CH₄ hydrate recovery. The Alaska North Slope Test is a significant ongoing project that has explored various extraction methods, including the integration of laser technology. This innovative approach enhances CH₄ recovery efficiency while managing hydrate stability and reservoir pressure challenges effectively. Using lasers allows for precise control over the dissociation of CH₄ hydrates, potentially leading to improved production rates and reduced environmental impact.¹⁴⁹ Similarly, the Shenhu Area in the South China Sea has seen successful continuous production tests, which have allowed for the incorporation of advanced technologies like laser-assisted extraction.¹⁵⁰ The focus on innovative extraction methods in this region aligns with its vast potential for large-scale CH₄ production, making it an ideal candidate for further exploration of laser technology applications. Therefore, the future of laser-assisted extraction looks promising as it offers a more controlled and efficient means of dissociating CH₄ hydrates. As research progresses, combining laser technology with traditional extraction methods could significantly advance the economic viability and environmental sustainability of CH₄ hydrate production. Continued experimental studies and pilot projects will be crucial in validating these techniques and addressing the technical challenges associated with their implementation, paving the way for more effective and sustainable CH₄ recovery strategies in the coming decade.¹⁵¹

5.2. Experimental and Numerical Simulation Approaches for CH₄ Production. **5.2.1. Experimental Approaches for CH₄ Production.** Numerous research efforts have focused on the laboratory-scale production of CH₄ from CH₄ hydrate reservoirs, revealing important insights into the process.^{152–156} It has been observed that fine marine sediments can obstruct CH₄ synthesis,

Table 16. Comparative Analysis of Simulators for CH₄ Production from Class 1 CH₄ Hydrate Reservoirs

| simulator | source | methodologies | application focus | performance and prediction | refs |
|---------------|---------------------------------------|--|--|-----------------------------|------|
| HydrateResSim | Lawrence Berkeley National Laboratory | simulates gas production from various hydrate reservoirs | general CH ₄ production from hydrate reservoirs | | 164 |
| CMG STARS | comparative studies | advanced modeling and simulation capabilities | predictive results for CH ₄ production rates | better prediction results | 165 |
| TOUGH+HYDRATE | comparative studies | multiphase, nonisothermal chemical reactions simulation | hydrate formation and dissociation; CH ₄ production rates | highly accurate predictions | 165 |
| STOMP-HYD | National Energy Technology Laboratory | CO ₂ injection and hydrate dissociation | CH ₄ production via CO ₂ injection | | 166 |
| EOSHYDR2 | a module for the TOUGH2 simulator | nonisothermal gas release, phase behavior, and flow | simulation of gas production from CH ₄ hydrates | | 167 |

causing unregulated decreases in pressure and gas emissions, as discovered through various studies on the efficiency of CH₄ production from CH₄ hydrate reservoirs sediments using depressurization. Liang et al.¹⁵⁶ revealed that a gradual reduction in pressure not only cools the reservoir but also promotes the formation of rehydration. Liang et al.¹⁵⁶ also explored the hydrate formation reaction rate constant through X-ray techniques, noting an increase in the reaction constant from 5.3×10^7 to 1.65×10^6 m/s as temperatures escalated. Furthermore, Ruan and Li¹⁵³ reported how variances in temperature, particularly from 274 to 284 K and pressure from 3 to 10 MPa, can influence the equilibrium curve of hydrates; the research investigated the surface area of CH₄ hydrate during dissociation in porous media. It was found that these conditions crucially influence the kinetics of hydrate dissociation, which in turn affects gas production efficiency. The study underscored the importance of understanding the interaction between temperature and pressure variances and their effects on the CH₄ hydrate surface area for optimizing gas extraction from hydrate-bearing sediments. Two models were emphasized: the grain-coating model, which performs better at lower hydrate saturation, and the pore-filling model, which is more effective at higher hydrate saturations. This articulation provides a better understanding of the parameters controlling CH₄ hydrate dissociation and their implications for improving hydrocarbon recovery processes. Moreover, Nakayama et al.¹⁵⁴ evaluated both experimental and computational findings regarding the role of CH₄ hydrate surface area on porous surfaces in CH₄ dissociation induced by depressurization. The study indicated that the hydrate surface area can be denoted as a function of porosity, hydrate saturation, and the average diameter of sediment particles. Additionally, Lee et al.¹⁵⁵ have reported a recovery rate of 64% of CH₄ from class 3 CH₄ hydrate reservoirs through CO₂ injection. Despite these advancements, future investigations should focus on enhancing reservoir permeability, mitigating sand production in alliance with CH₄, managing bottom well pressure, and overseeing gas hydrate reformation near the wellbore.

5.2.2. Simulation Approaches for CH₄ Production. Numerical simulation represents a computational method that employs a program to create a mathematical representation of a physical system. These simulations are crucial for nonlinear systems whose complex mathematical models elude simple, analytical solutions, making it essential to use numerical approaches for understanding their dynamics.¹⁵⁷ In particular, reservoir simulation employs computer algorithms to mimic the movement of fluids within porous materials over time, focusing explicitly on fluid dynamics and heat transfer under the assumption that the solid component remains stationary. This technique draws upon various scientific principles to accurately model petrophysical properties within a geological deposit. Different simulators use diverse methodologies to capture the intricate process of gas hydrate dissociation.¹⁵⁸ Research into the CH₄ hydrate reservoir production simulation further investigates this by solving a complex set of interlinked equations governing fluid movement, heat exchange, and mass transport alongside the potential emergence or dissolution of various solid phases within the system.^{158,159}

The success of numerical simulations hinges on three pillars: the availability of sophisticated simulators that accurately describe

dominant processes, understanding the interplay of parameters that define the physical and thermophysical properties of the system, and the collection of field and laboratory data to validate the numerical models.^{159,160} Furthermore, Ruan et al.¹⁶¹ introduced five distinct models—equilibrium, thermal conductivity, kinetic, permeability, and mechanical—each incorporating equilibrium and kinetic approaches for analyzing hydrate production and dissociation. These models, while diverse, operate under defined assumptions and parameters. For example, the equilibrium hydration model accounts for heat transfer and four mass components, such as H₂O, CH₄, and water-soluble inhibitors like salts or alcohols, with the kinetic model introducing a fifth element, CH₄ hydrate, treating it as a distinct component instead of a state within the H₂O–CH₄ system.¹⁶² The process of hydrate dissociation is modeled to occur at equilibrium in these simulations. Further, the effectiveness of hydrate production across different reservoirs is assessed through simulations that evaluate various characteristics, such as permeability, porosity, and temperature, among others, to establish a comprehensive understanding of reservoir behavior and potential output.¹⁶²

5.2.2.1. Simulation Approaches for CH₄ Production from Class 1 CH₄ Hydrate Reservoirs. A three-dimensional, compositional, multiphase flow simulator has been developed and utilized to examine the production characteristics of Class 1 reservoirs, analyzing the effects of various production parameters such as well-completion location, well spacing, and production schedule on gas production efficiency.¹⁶³ This high level of detail allows researchers to optimize extraction methodologies by altering simulation inputs according to the reservoir's specific characteristics. Simulating the behavior of CH₄ within Class 1 hydrate reservoirs under various extraction methods, as described in Table 16, is a crucial step toward efficiently exploiting these energy resources. As simulation technologies advance, the accuracy and efficiency of CH₄ extraction from these complex reservoirs are expected to improve, contributing significantly to the field of energy production. HydrateResSim is noted for its generalized application across various hydrate reservoirs, including Class 1 CH₄ hydrates.¹⁶⁴ Both CMG STARS and TOUGH+HYDRATE are recognized for their enhanced predictive capabilities, making them valuable tools for assessing production rates and reservoir behavior under different operational conditions.¹⁶⁵ STOMP-HYD focuses particularly on CO₂ injection methods for CH₄ production, which represents an intriguing approach toward more sustainable hydrate exploitation.¹⁶⁶ Further, EOSHYDR2 provides capabilities for detailed modeling of gas and heat flow within hydrate-bearing sediments, making it a valuable tool for investigating the dynamics around hydrate dissolution and CH₄ recovery.¹⁶⁷ Each simulator offers unique strengths contributing to a comprehensive understanding of CH₄ hydrate production processes.

Wu et al.¹⁶⁵ investigated CH₄ production from Class 1 hydrate reservoirs; two primary simulation models were developed: the oil-phase hydrate and solid-phase hydrate models. The commercial reservoir simulator STARS, developed by Computer Modeling Group Ltd., was used, which, despite lacking a specific hydrate module, allowed for the simulation of gas hydrate dissociation and reformation through self-created kinetic reactions. The simulation involved numerical models incorporating geological data, hydrate reaction

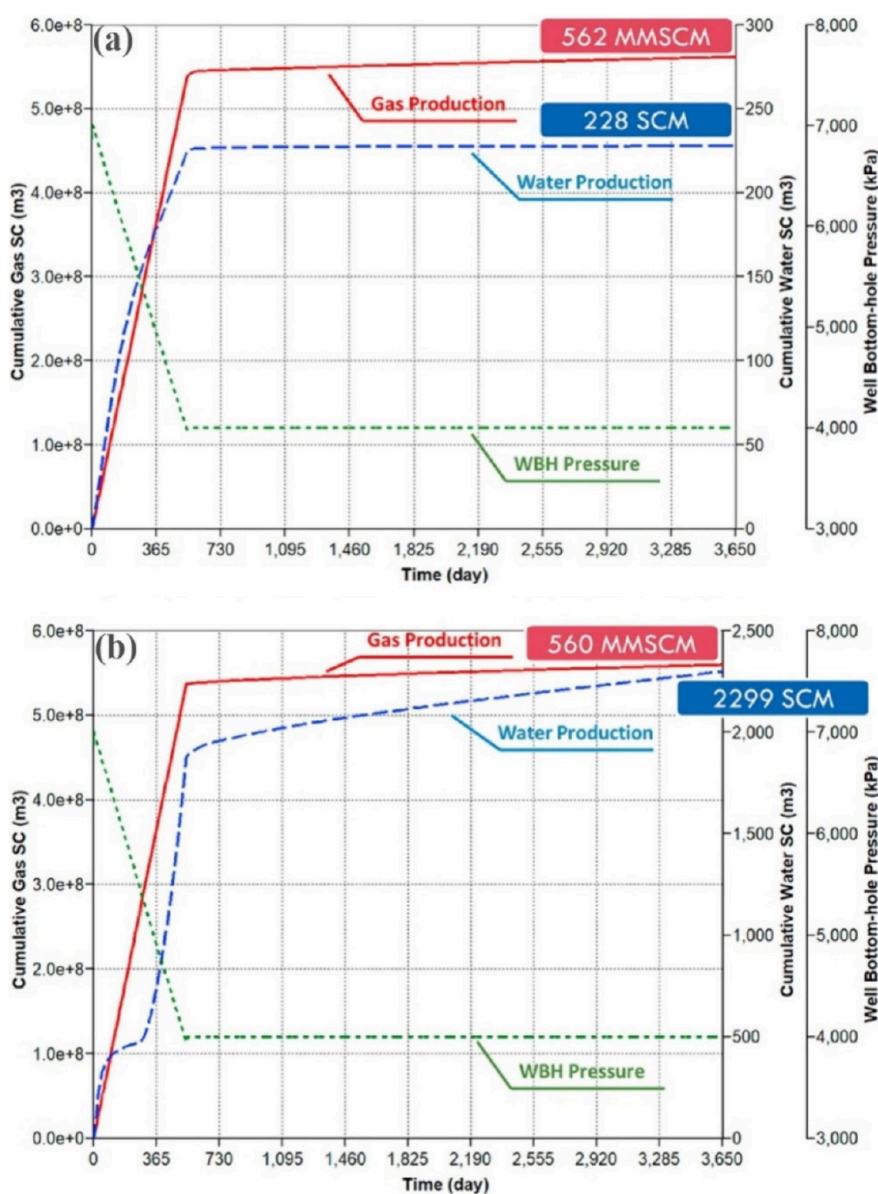


Figure 28. Cumulative gas and water production profiles: (a) oil-phase hydrate model; (b) solid-phase hydrate model. Reproduced with permission from ref 165. Copyright 2020 Elsevier.

Table 17. Comparison of Cumulative Gas and Water Production between Solid-Phase and Oil-Phase Hydrate Models for All Simulated Cases^{165a}

| model | cumulative gas production (MMSCM) | cumulative water production (SCM) | dissociation rate (%) | recovery factor (%) | seabed subsidence (m) |
|------------------------------------|-----------------------------------|-----------------------------------|-----------------------|---------------------|-----------------------|
| oil-phase hydrate model | 562 | 228 | 11.14 | 23.04 | |
| solid-phase hydrate model | 560 | 2299 | 10.84 | 22.96 | |
| modified solid-phase hydrate model | 575 | 236 | 11.94 | 23.58 | |
| coupled oil-phase hydrate model | 863 | 1102 | 29.90 | 35.27 | 0.492 |
| coupled solid-phase hydrate model | 880 | 363 | 31.69 | 35.99 | 0.423 |

^aThis table was reproduced with permission from ref 165. Copyright 2020 Elsevier.

modules, and initial formation conditions to produce a natural-state model. Crucially, these models differed in their treatment of hydrates—either an oil component with high viscosity or a solid component—to simulate the characteristic behavior of gas hydrates within the reservoir. The initial step was to compare the performance and accuracy of these models based on cumulative water and gas

production. The study revealed several critical findings regarding the production of CH₄ from Class 1 hydrate reservoirs. Initially, the oil-phase and solid-phase hydrate models generated comparable gas production results. However, they differed significantly in water production; the solid-phase model predicted a much higher water output, as illustrated in Figure 28. This discrepancy was addressed by

Table 18. Maximum Cumulative Gas Production through Depressurization in Class 1 CH₄ Hydrate Reservoirs Using Various Simulators

| simulator | parameter | approach | maximum cumulative | refs |
|---------------|--|------------------|--|------|
| CMG STAR | porosity, permeability, pressure, temperature, saturation, wellbore, CO ₂ injection rate, and well bottom hole pressure | depressurization | 70.00% | 171 |
| TOUGH+HYDRATE | porosity, absolute permeability, initial gas saturation, relative permeability, capillary pressure, thickness, gas production rate, water saturation, and irreducible water saturation | depressurization | 75.00% | 169 |
| STOMP-HYD | permeabilities, capillary pressure, porosity, liquid CO ₂ adequate saturation, gas effective saturation, and aqueous effective saturation | depressurization | add 10.00% cumulative after depressurization | 173 |
| MH-21 HYDRES | pressure, temperature, absolute permeability, effective permeability, porosity, well type, thickness saturation, and clay content | depressurization | 74.80% | 174 |

Table 19. Maximum Cumulative Gas Production through Depressurization and Thermal Methods in Class 2 CH₄ Hydrate Reservoirs Using Various Simulators

| simulator | parameters | approach | maximum cumulative | refs |
|---------------|--|--|--------------------|---------|
| CMG STAR | porosity, permeability, pressure, temperature, saturation, wellbore, CO ₂ injection rate, well bottom hole pressure | depressurization and thermal method | 87.80% | 179,180 |
| TOUGH+HYDRATE | porosity, absolute permeability, initial hydrate saturation, relative permeability, capillary pressure, thickness, and gas production rate | thermal and depressurization technique | 72.40%, 49.06% | 137 |
| HydarteResSim | porosity, permeability, temperature, saturation, relative permeability, capillary pressure, thickness of hydrate | depressurization | 61.99%, 74.87% | 181 |
| MH-21 HYDRES | pressure, temperature, absolute permeability, effective permeability, porosity, well type, thickness saturation, and clay content | depressurization | 10.00% | 116 |
| | | | >36% | |

adjusting the relative permeability curves in the solid-phase model to more accurately represent water and gas saturations. This resulted in a modified solid-phase hydrate model that more closely matched the oil-phase model regarding gas and water production rates. Coupling these models with a geomechanical module showed that the coupled solid-phase model produced slightly higher cumulative gas production than the oil-phase model, as described in Table 17. This was attributed to the added geomechanical support from solid hydrates, which lessened formation deformation and induced a lower reservoir average pressure, encouraging further hydrate dissociation. Another critical observation was that the seabed subsidence was more significant in the coupled oil-phase model than in the coupled solid-phase model. This finding underscores the impact of the geomechanical characteristics of solid hydrates and their role in supporting formation strength, thereby mitigating subsidence near production wells. These insights are vital for future hydrate exploitation strategies, offering a path toward more efficient and controlled gas production from Class 1 CH₄ hydrate deposits.

Grove et al.¹⁶⁸ used the TOUGH+HYDRATE model to forecast CH₄ production at the Messoyakha Field, a Class 1 hydrate reservoir, attributing depressurization as the key recovery strategy. The study examined porosity, absolute and relative permeability, initial gas and water saturation, capillary pressure, reservoir thickness, and gas production rates. The findings revealed that maintaining constant sedimentary conditions while increasing the permeability and heat flow could enhance CH₄ production. The study reported that about 36% of the CH₄ could be extracted from hydrates over two decades. This approach mirrors the methodology of other research efforts, such as those in refs 169 and 170, that used the same simulation tool to assess factors such as the porous medium, porosity, relative permeability, capillary pressure, gas hydrate saturation, gravity equilibrium, and thermal conditions on CH₄ extraction from Class 1 hydrate reservoirs. They identified that permeability manages the gas flow, the capillary pressure indicates pressure variations disturbing hydrate stability, and thermal flux affecting hydrate reformation significantly influences CH₄ recovery. Additionally, Ruan and Li¹⁵³ integrated practical and theoretical insights on surface area effects

underscored significant impacts on CH₄ yield under depressurization, notably at varying hydrate saturations. The finding concluded that depressurization is highly suitable for Class 1 deposits because it is straightforward, cost-effective, and rapidly responsive. These findings align with the study by refs 169 and 171–174, which revealed similar insights, as described in Table 18.

The comparative analysis of simulation studies on CH₄ production from Class 1 CH₄ hydrate reservoirs highlights the significance of advanced simulation methodologies in optimizing extraction processes. Models like TOUGH+HYDRATE (T+H) and CMG STARS offer high predictive accuracy, enabling the assessment of various production parameters such as well spacing, porosity, and pressure for maximizing CH₄ recovery. Depressurization emerges as a preferred strategy with studies indicating potential extraction rates of up to 75% over two decades. Additionally, the coupling of simulation models with geomechanical modules reveals insights into the role of solid hydrates in supporting formation strength and enhancing cumulative gas production. The models discussed made assumptions based on nonsalinity in all of the case studies due to uncertainties and early pressure conditions at the hydrate–gas interface and temperature equilibrium. Although there is a promising recovery factor through depressurization in Class 1 CH₄ hydrate reservoirs, the remaining gas content in the reservoir suggests the need to consider combined methods with other techniques, such as thermal treatments and inhibitors, to maximize production. Further investigation regarding applying dual vertical wells, horizontal wells, and fracking techniques, which increase the permeability and improve the gas flow to enhance CH₄ production from CH₄ hydrate reservoirs, is vital.

5.2.2.2. Simulation Approaches for CH₄ Production from Class 2 CH₄ Hydrate Reservoirs. CH₄ production from Class 2 gas hydrate reservoirs presents challenges due to their inherent low permeability and insufficient thermal properties.¹⁷⁵ Consequently, the most viable technological solutions for CH₄ extraction from these reservoirs encompass depressurization and thermal methods,¹⁷⁵ as described in Table 19. These reservoirs have high hydrate saturation and substantial thermal inputs, necessitating applying enhanced fracking procedures to improve permeability, thus facilitating the gas flow.^{11,175}

Table 20. Maximum Cumulative Gas Production through Depressurization, Thermal, and Hydraulic Fracturing Methods in Class 3 CH₄ Hydrate Reservoirs Using Various Simulators

| simulator | parameter | approach | maximum cumulative | refs |
|---------------|--|---|---|------|
| CMG STAR | porosity, permeability, saturation, pressure, temperature | depressurization | 35.00% | 188 |
| TOUGH+HYDRATE | porosity, absolute permeability, initial gas saturation, relative permeability, capillary pressure, thickness, gas production rate, water saturation, and irreducible water saturation | depressurization, thermal, and hydraulic fracturing | 61.60% with no fracture 80.60% with fracture | 189 |
| HydarteResSim | porosity, permeability, temperature, saturation, relative permeability capillary pressure, the thickness of hydrate, and horizontal well | depressurization, thermal | >65.00% | 185 |
| H-21 HYDRES | pressure, temperature, absolute permeability, effective permeability, porosity, well type, thickness saturation, and clay content | depressurization | 60.00% | 116 |

Furthermore, heat infusion, a critical factor for CH₄ dissociation, subsequently augments gas release within these Class 2 hydrates. The TOUGH+HYDRATE model has been instrumental in replicating CH₄ production dynamics from Class 2 hydrates, integrating both equilibrium and kinetic modeling approaches.¹⁷⁶ The use of the original porous medium (OPM) model, leveraging assumptions like unaltered medium porosity and intrinsic permeability during production and the optimization of relative permeability, provides a fundamental framework for comprehending fluid dynamics within the pore structure during the gas extraction process.¹⁷⁷ Notably, the strategic deployment of horizontal wells has been pinpointed as a significant factor that could considerably elevate gas output from such challenging reservoir deposits.¹⁷⁷ Complementary to depressurization and thermal techniques, CO₂ injection emerges as a promising alternative with potential benefits for CH₄ recovery from Class 2 reservoirs. This approach leverages the favorable thermodynamic stability and the swift diffusion dynamics of CO₂ compared to CH₄, facilitated by its greater molecular mass and smaller kinetic diameter, potentially enhancing CH₄ displacement through a mix of chemisorption and physisorption processes.^{166,178} This method highlights the thermodynamic benefit of CO₂ over CH₄ in hydrate formations, suggesting a novel avenue for enhancing CH₄ extraction efficiency while potentially ensuring the structural integrity of hydrate-bearing formations through CO₂–hydrate substitution.¹⁶⁶

The comparative analysis of the discussed studies of CH₄ production from Class 2 CH₄ hydrate reservoirs reveals a range of methodologies and techniques employed to enhance recovery. Researchers have predominantly focused on combination methods such as depressurization/thermal or CO₂ swamping/depressurization, highlighting the importance of leveraging multiple mechanisms to maximize production efficiency. Simulation models like CMG STAR, TOUGH+HYDRATE, HydrateResSim, and MH-21 HYDRES have been used to predict CH₄ recovery, considering porosity, permeability, pressure, temperature, and saturation parameters. These studies emphasize the significance of reservoir characteristics, geomechanical stability, and the impact of operational variables on CH₄ production. While results vary, with maximum cumulative recovery ranging from approximately 10% to over 87%, they collectively underscore the complexity of CH₄ production from Class 2 CH₄ hydrate reservoirs and the need for integrated approaches combining thermal, pressure-based, and chemical techniques for efficient recovery. Further research avenues include exploring reservoir fracturing, geomechanical stability, and optimization of operational parameters to enhance reservoir permeability and overall CH₄ recovery. Additionally, the interaction between salinity and depressurization techniques highlights the complexity of reservoir management in hydrate-bearing formations.^{182,183} Research investigating the effect of salinity in CH₄ production from Class 2 gas hydrate reservoirs is scant. Salinity within a reservoir influences hydrate stability and can alter the thermodynamic conditions necessary to safely and efficiently extract natural gas from CH₄ hydrates.¹⁸² Salt, acting as a hydrate inhibitor, necessitates careful observation of salinity levels to ensure an optimal balance between hydrate formation and dissolution processes.¹⁸⁴ Monitoring salinity levels in reservoirs is essential as it impacts the effectiveness of inhibitors when used alongside depressurization methods.^{182–184} This

is due to precipitate formation compromising the gas's permeability.¹⁸² Moreover, it is crucial to investigate further methods to manage sand production and enhance rehydration processes during CH₄ extraction from CH₄ hydrates. The dynamics of these factors are critical for minimizing operational challenges and improving recovery rates. Innovative approaches to manage these aspects can significantly increase the exploitation of CH₄ hydrates as an energy resource.

5.2.2.3. Simulation Approaches for CH₄ Production from Class 3 CH₄ Hydrate Reservoirs. Class 3 hydrate reservoirs are characterized by a unique structure with an impermeable top cover layer, an impermeable bottom layer, and a hydrate-bearing layer sandwiched between them.¹⁸⁵ These reservoirs pose specific challenges for gas production due to their structural and physical properties. High hydrate saturation in Class 3 reserves leads to limited flow without inducing fractures due to the low permeability of these fractures, presenting significant extraction challenges.^{180,185} Among various techniques, depressurization is the most practical and effective,^{167,172} as described in Table 20. Boosting the temperature of the hydrate plays a critical role in maintaining stability under specific pressures and enhancing gas production by impacting permeability. However, the depressurization technique can extract only a portion, about 7–36%, of the total gas available, leading to the belief that Class 3 deposits are not economically viable for development.^{118,180} Fracturing operations can improve permeability, thus facilitating gas liberation and enhancing CH₄ production.¹⁸⁶ This is primarily due to increased surface area coming into contact with hot water and creating more pathways for gas release.¹⁸⁶ Gas production rates are closely tied to hydration levels with lower hydration resulting in faster decompression and dissociation of hydrates and hence higher production rates early in the extraction process. Hydraulic fracturing, or fracking, introduces high-pressure fluid into the subsurface to create fissures, enhancing permeability and facilitating the extraction of trapped CH₄ from hydrate formations. This method significantly impacts the productivity of Class 3 CH₄ hydrates by altering initial reservoir conditions such as temperature and porosity, which are critical in determining the effectiveness of CH₄ recovery.¹⁸⁶ The process's success hinges on meticulously controlling the brine's temperature and the cycle duration to maximize the CH₄ production rate while maintaining the structural integrity of the hydrate reserves.^{186,187}

Yang et al.¹⁸⁵ used a numerical simulation approach to investigate CH₄ production from Class 3 CH₄ hydrate reservoirs, exploring various aspects of reservoir properties, well design, and production strategies to optimize gas extraction. The simulation used the HydrateResSim code to model the gas–water system in dissociating CH₄ hydrate reservoirs. This includes applying different production pressures to understand the gas production response better. The study's approach consists of a detailed reservoir discretization, ensuring the model incorporates a realistic representation based on China's Shenhua area hydrate reservoirs, including considerations such as thickness, porosity, salinity, and intrinsic permeability. The well design within these simulations adopts an “L” shape, optimizing the layout for effective depressurization and thermal stimulation to induce hydrate dissociation. The production strategy involves setting constant well temperatures and varying well pressures to evaluate the most efficient parameters for gas release rates and overall natural

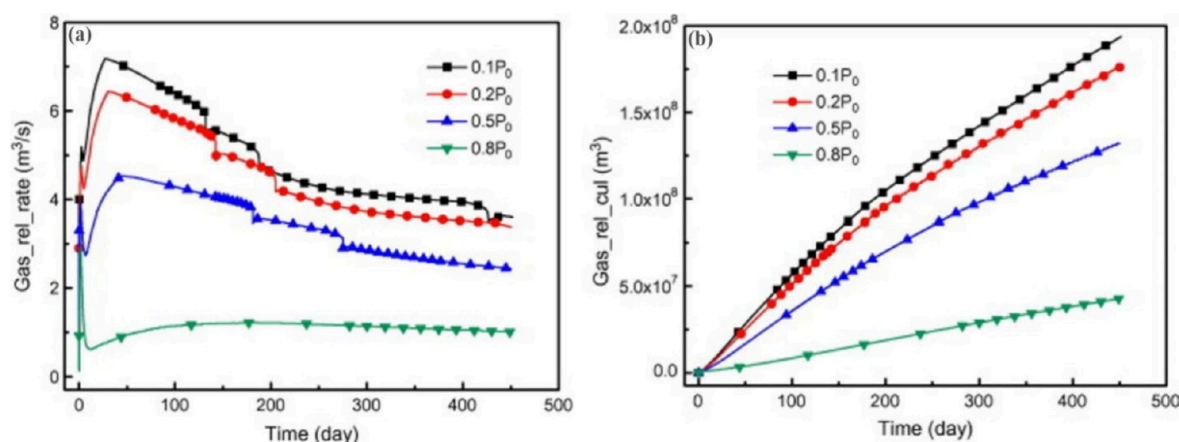


Figure 29. Impact of well pressure on gas release rates and cumulative gas production from Class 3 hydrate reservoirs. (a) Variation of gas release rate with different well pressure conditions over 450 days. (b) Gas accumulation over 450 days under varying pressures. Reproduced with permission from ref 185. Copyright 2014 Elsevier.

Table 21. Physical Properties and Conditions of a Class 3 Hydrate Reservoir at the SH2 Site Shenhu Area on the North Slope of the South China Sea^{a,189}

| parameters | value | parameters | value |
|---|---|--------------------------------|---|
| overburden thickness | 30 m | grain density (all deposits) | 2600 kg/m ³ |
| underburden thickness | 30 m | intrinsic permeability (wells) | 1.0 × 10 ⁻⁹ m ² (1000 D) |
| HBL thickness | 40 m | fracture width | 6 mm |
| intrinsic permeability (overburden, HBL, and underburden) | 1.0 × 10 ⁻¹⁴ m ² (=10 mD) | relative permeability model | $k_{rA} = (S_A^*)^n$ $k_{rG} = (S_G^*)^{nG}$ $S_A^* = \frac{S_A - S_{irA}}{1 - S_{irA}}$ $S_G^* = \frac{S_G - S_{irG}}{1 - S_{irG}}$ |
| initial saturation | SH = 0.4, SA = 0.6 | <i>n</i> | 3.572 |
| porosity (wells) | 1.0 | <i>n_G</i> | 3.572 |
| geothermal gradient | 0.047 | <i>S_{ir}</i> | 0.30 |
| gas composition | CH ₄ 100% | <i>S_{ir}</i> | 0.03 |
| porosity (overburden, HBL, underburden) | 0.38 | capillary pressure model | $P_{cap} = -P_0[(S^*)^{-1/\lambda} - 1]$ |
| porosity (fracture) | 0.80 | <i>S_{ir}</i> | 0.29 |
| dry thermal conductivity (all deposits) | 1.0 W/m/K | λ | 0.45 |
| wet thermal conductivity (all deposits) | 3.1 W/m/K | <i>P₀</i> | 105 Pa |

^aThis table was reproduced with permission from ref 189. Copyright 2020 Elsevier.

gas production. The findings from the simulations reveal that depressurization and thermal driving forces are crucial for inducing hydrate dissociation with the effects potentially extending over 10–30 years, enabling significant gas and water production if appropriate strategies are employed. The depressurization's driving force heavily influences the productivity of Class 3 hydrate reservoirs, as illustrated in Figure 29. Lower well pressures (e.g., 0.1P₀ and 0.2P₀) resulted in higher gas release rates and cumulative gas production than higher pressures (e.g., 0.8P₀), where gas release rates were insufficient for commercial-level production. The heterogeneous nature of the hydrate distribution within the reservoir significantly affects production behavior, underlying the importance of understanding reservoir heterogeneity for accurate prediction of gas production performance.

In addition, Zhong et al.¹⁸⁹ reported numerical simulation approaches to enhance CH₄ production from Class 3 CH₄ hydrate reservoirs, specifically in the Shenhu area on the north slope of the South China Sea. The methods include examining the geological background from detailed logging data, highlighting the potential for exploitation based on properties such as porosity, layer thickness, hydrate saturation levels, well and fracture design, model establish-

ment, and various simulation parameters, such as hydrate reservoir's physical properties and conditions, as described in Tables 21 and 22. The primary objectives were to evaluate the impact of varying fracture permeabilities and well spacings on CH₄ production, understand the hydrate dissociation behaviors, and assess the production efficiency through simulations. Simulations used the T+H numerical code, favoring the equilibrium reaction model's accuracy in large-scale natural gas hydrate (NGH) productions. The initial and boundary conditions were meticulously set to reflect the hydrate-bearing sediments' real thermal and pressure environments, facilitating a comprehensive assessment. The simulations revealed that modifying fracture parameters significantly affects CH₄ production in Class 3 hydrate reservoirs. Increasing fracture permeability and optimizing well spacing enhanced gas production efficiency by facilitating pressure drop transmission and hydrate decomposition rate, as illustrated in Figure 30. Introducing fractures and the strategic setting of well spacings accelerated the hydrate dissociation process, which is crucial for effective CH₄ production. Well-designed fracturing and spacing setups led to larger hydrate decomposition areas, suggesting an accelerated gas release from hydrates. Furthermore, fracturing positively influenced CH₄ production rates by providing favorable

Table 22. Simulation Schemes (Fracture Permeability and Well Spacing) at the SH2 Site Shenhua Area on the North Slope of the South China Sea^{a,189}

| | fracture permeability (D) | well spacing (m) |
|-----------|---------------------------|------------------|
| Case 1-1 | no fracture | 50.00 |
| Case 1-2 | 1.00 | 50.00 |
| Case 1-3 | 1.50 | 50.00 |
| Case 1-4 | 2.00 | 50.00 |
| Case 2-1n | no fracture | 40.00 |
| Case 2-2n | no fracture | 50.00 |
| Case 2-3n | no fracture | 60.00 |
| Case 2-1 | 2.00 | 40.00 |
| Case 2-2 | 2.00 | 50.00 |
| Case 2-3 | 2.00 | 60.00 |

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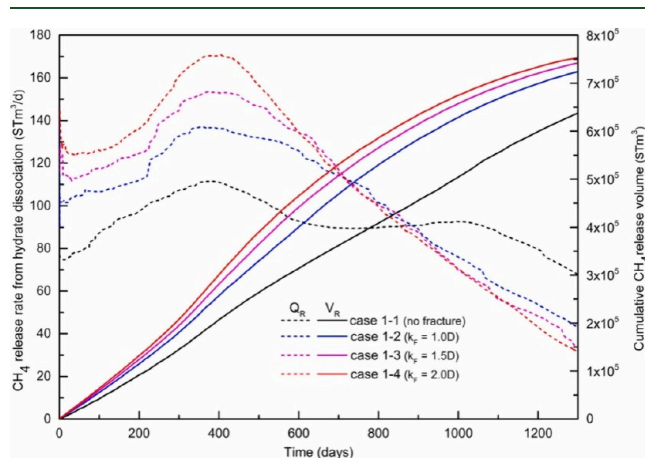


Figure 30. Effect of fracture parameters on CH₄ production efficiency in Class 3 hydrate reservoirs, evaluating the CH₄ release rate (Q_R) and cumulative CH₄ release volume (V_R) in varied fracture permeability. Reproduced with permission from ref 189. Copyright 2020 Elsevier.

channels for gas migration. However, the stimulation also revealed increased water production, as diagrammatically shown in Figure 31, indicating a need for careful consideration of fracture designs to balance gas-to-water ratios effectively. Moreover, the study emphasized that the energy ratio (ER), a crucial economic index, improves with the application of fractures, especially under large well spacing, as shown in Figure 32. This suggests that fracturing enhances gas recovery and contributes to more energy-efficient CH₄ production from hydrate reservoirs.

The comparative analysis of the discussed studies highlights several key findings regarding CH₄ production from Class 3 hydrate reservoirs. Both studies emphasize the importance of simulation approaches in understanding the reservoir properties, well design, and production strategies to optimize gas extraction. They underscore the significance of depressurization, thermal stimulation, and hydraulic fracturing in enhancing CH₄ production rates from these challenging reservoirs. While depressurization remains a practical and effective method, hydraulic fracturing emerges as a promising technique to improve permeability and facilitate gas release, although with careful consideration of water production. The studies emphasize the need for comprehensive assessments considering reservoir heterogeneity and varying fracture parameters to achieve efficient CH₄ recovery. These studies signify the potential of simulation-driven approaches in addressing the complex challenges associated with Class 3 CH₄ hydrate reservoirs, offering insights into effective strategies for maximizing CH₄ production while balancing economic viability and environmental considerations.

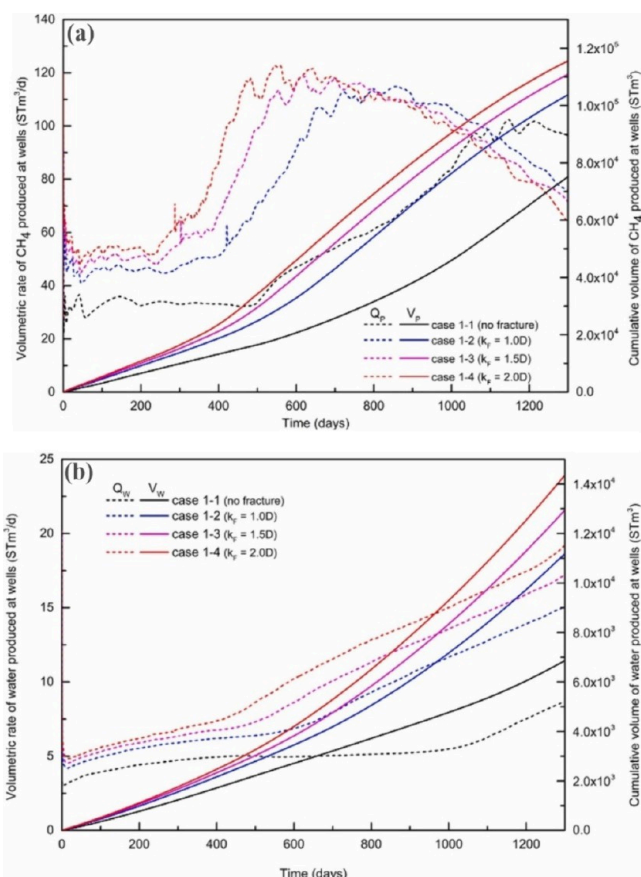


Figure 31. Effect of fracturing on CH₄ and water production rates in Class 3 hydrate reservoirs. (a) CH₄ production rate (Q_P) and cumulative CH₄ production volume (V_P) in varied fracture permeability. (b) Water production rate (Q_W) and cumulative water production volume (V_W) in varied fracture permeability. Reproduced with permission from ref 189. Copyright 2020 Elsevier.

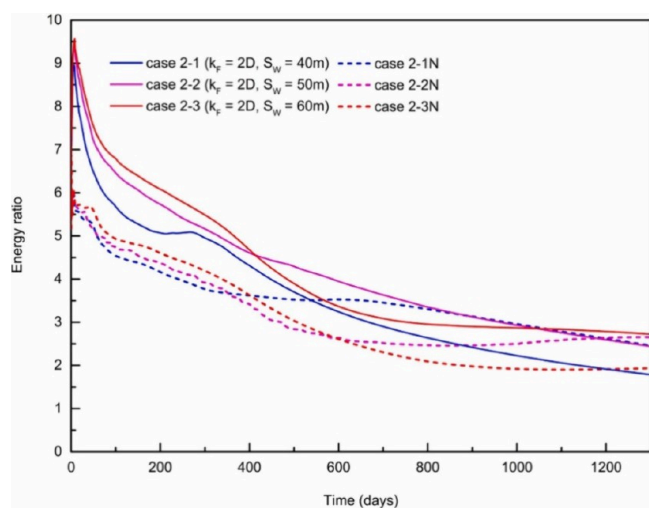


Figure 32. Effect of fracturing on the energy ratio (ER) in Class 3 hydrate reservoirs with varied well spacing. Reproduced with permission from ref 189. Copyright 2020 Elsevier.

5.2.2.4. Significance of Comparative Analysis in CH₄ Hydrate Reservoir Simulation. The comparative analysis of simulators is a fundamental aspect of advancing the understanding and management of CH₄ hydrate reservoirs. This comparison not only benchmarks the accuracy and reliability of different simulation tools but also aids in

optimizing production strategies, driving technological advancements, and ensuring economic and environmental sustainability in hydrate exploitation. Simulators like HydrateResSim,^{172,181,185} CMG STARS,^{171,179,188} TOUGH+HYDRATE,^{137,189} STOMP-HYD,¹⁷³ and MH-21 HYDRES^{116,173} each bring unique strengths to the table, catering to different aspects of hydrate simulation. From handling multiphase flows and chemical reactions to specializing in CO₂ injection methods and detailed gas and heat flow modeling, the choice of simulator hinges on the specific requirements of the reservoir under study. This tailored approach ensures that the predictive models align more closely with actual reservoir behaviors, significantly aiding in the decision-making processes related to hydrate reservoir management and gas extraction strategies. The need for accuracy and reliability in simulation outputs cannot be overstated. Distinct simulators, relying on different methodological frameworks, physical models, and assumptions, offer diverse perspectives on reservoir dynamics. This variety is particularly crucial in the realm of gas hydrate dissociation—a complex phenomenon where each simulator's ability to capture and predict the nuances of physical processes varies. The comparison of simulation outcomes, therefore, serves as a litmus test for delineating the most reliable and accurate tools suited for specific reservoir types or operational conditions.

Optimizing production strategies emerges as a critical area that benefited from comparative simulation analyses. With a myriad of possible extraction methods available, the ability to predict how different simulators respond to identical conditions allows for an evidence-based selection of the optimal approach. This optimization touches on aspects like well placement, production scheduling, and the design of secondary recovery operations, all of which have substantial implications for both the efficacy and the efficiency of hydrate production. Furthermore, the iterative process of comparing and contrasting simulator predictions fuels the progression of simulation technologies. Identifying the front runners in simulation accuracy and reliability prompts a concentrated effort toward advancing these models, enhancing their predictive capabilities. Such advancements not only refine existing simulation tools but also pave the way for the invention of new methodologies that could offer more insightful forecasts of reservoir behavior. Moreover, accurate predictions are the cornerstone of economically viable and environmentally sustainable gas hydrate exploitation. A simulator that offers precise forecasts facilitates more efficient approaches to reservoir development, mitigating risks of overexploitation and minimizing environmental disturbances. Thus, the role of simulation in guiding environmentally responsible and economically feasible hydrate production strategies is indispensable.

5.3. Impact of Wellbore Type on CH₄ Production. Chong et al.^{190,191} investigated the effects of wellbore type on the efficiency of CH₄ production from hydrate formations. The study underscores the significance of wellbore architecture in enhancing gas recovery rates, comparing horizontal, vertical, and deviated well configurations. The findings reveal that horizontal wells, due to their extended contact with the hydrate-bearing layer, offer higher CH₄ recovery rates compared to vertical and deviated wells. This is attributed to the increased surface area for heat and mass transfer, facilitating more efficient hydrate dissociation. Moreover, horizontal wells allow for the application of hydraulic fracturing techniques, further improving permeability and CH₄ flow toward the wellbore. These insights stress the importance of wellbore design as a key factor in optimizing CH₄ hydrate reservoir exploitation strategies.

5.4. Reservoir Pressure Regulation and Control. Investigations by Gao et al.,¹⁹² Yin et al.,¹⁹³ and Gao et al.¹⁹⁴ explore methodologies for reservoir pressure regulation and control to enhance CH₄ recovery from hydrate formations. These studies present techniques such as the injection of warm brine, depressurization strategies, and controlled CO₂ injection to maintain or adjust reservoir pressure levels conducive to efficient hydrate dissociation. Gao et al.^{192,194} highlight the potential of warm brine injection to supplement thermal stimulation efforts, thereby increasing the rate of hydrate decomposition. Additionally, Yin et al.¹⁹³ propose an adaptive

pressure regulation system that dynamically adjusts depressurization rates based on real-time feedback from reservoir conditions, maximizing CH₄ production while minimizing energy input. These advancements in reservoir pressure management are essential for sustaining high levels of CH₄ recovery, indicating the necessity for incorporating pressure control mechanisms into production strategies.

6. CASE STUDIES AND FIELD APPLICATIONS

Notable projects have revealed the feasibility and potential of extracting CH₄ from hydrate reservoirs, highlighting progress in the Nankai Trough Test, Japan,¹⁹⁵ Messoyakha, Russia,¹⁹⁶ Shenhu, South China Sea,¹⁹⁷ the United States,¹⁹⁸ the Alaska North Slope Production Test (Ongoing), the Ignik Sikumi field test, Alaska,^{6,199} and Mallik, Canada,²⁰⁰ as described in Table 23. In the North Slope of Alaska, an unprecedented test utilized a mixture of carbon dioxide (CO₂) and nitrogen to extract natural gas from CH₄ hydrates.^{199,201} This method, involving in situ CO₂ exchange with CH₄ molecules within the hydrate structure, marked a significant advancement by extending the depressurization phase to over 30 days, significantly longer than previous trials.²⁰¹ Japan led a ground-breaking project off the Atsumi and Shima Peninsula coasts, achieving the first offshore production test of CH₄ hydrate worldwide.¹⁹⁵ This venture produced approximately 120 000 m³ of gas over 6 days, pioneering offshore CH₄ hydrate extraction.¹⁹⁵ These case studies have contributed valuable insights into CH₄ extraction from hydrates, such as the following. (1) The importance of CO₂ utilization: the successful use of CO₂ in the Alaskan test project underlined the dual benefit of CH₄ recovery and potential CO₂ storage, emphasizing this approach's environmental and efficiency advantages. (2) Challenges in offshore extractions: the Japanese project illustrated the feasibility of offshore CH₄ hydrate extraction and highlighted the technical and environmental challenges associated with operations in marine environments. Achieving such extraction sustainably and economically remains critical for future research and technological development. (3) Extended production trials: extending the duration of production trials, as seen in Alaska, provides a more comprehensive understanding of the reservoir responses, technological efficacy, and potential environmental impacts. These longer trial periods are invaluable for developing more effective and efficient extraction methodologies. (4) Global resource potential: both projects underscore the vast potential of CH₄ hydrates as a future energy source, indicating the importance of continued investment in research, technology development, and environmental analysis to unlock this resource sustainably. The exploration and pilot testing of CH₄ hydrate extraction are developing, yet they offer promising prospects for future energy supplies. Continuing research, technological innovation, and international collaboration will be essential in overcoming the existing challenges and harnessing this resource commercially.

6.1. Shenhu, South China Sea. The exploration and extraction of CH₄ from the Shenhu Area, South China Sea, represent significant milestones in the commercial utilization of this energy resource. The Shenhu Area has been identified as one of the most promising fields for CH₄ hydrate exploration due to its vast potential and proximity to major cities like Hong Kong and Guangzhou.¹⁹⁷ Several rounds of exploration and testing culminating in successful production trials in 2017 have marked the area as a key focus for CH₄ hydrate research and development.¹⁹⁷ This journey from initial geophysical surveys

Table 23. Comparative Analysis of CH₄ Extraction Techniques and Challenges Across Global Field Cases

| field applications | methods used | CH ₄ hydrate produced | challenges | refs | remarks |
|---------------------------------|--|---|---|------|---|
| Messoyakha, Russia | depressurization, thermal, and chemical injection | prod. rate: 18 000.00–98 000.00 m ³ /day | increase in reservoir pressure | 196 | incorporates a multifaceted approach to enhance CH ₄ production despite the challenge of managing reservoir pressure, which is a critical factor for sustainable extraction |
| Mallik, Canada | depressurization and thermal | production: 2000.00–3000.00 m ³ /day over 6 days | sand production and CH ₄ hydrate reformation | 200 | employs a combination of methods to mitigate sand production and prevent the reformation of CH ₄ hydrates, highlighting the delicate balance required in CH ₄ extraction processes |
| Ignik Sikumi field test, Alaska | depressurization with CO ₂ and N ₂ injection | improved rates: 566.41–1274.43 m ³ /day over 30 days | fine sand and water production | 199 | demonstrates an innovative approach by using CO ₂ and N ₂ injection to displace CH ₄ , effectively managing the production of fine sand and water, which are common operational challenges |
| Nankai Trough test, Japan | depressurization with sand-proof designs | 2.0 × 10 ⁴ m ³ /day over 6 days | sand formation, potential increase in bottom well pressure, and CH ₄ hydrate reformation | 195 | the field case illustrates using sand-proof designs to combat sand formation, focusing on preventing an increase in bottom well pressure and CH ₄ hydrate reformation, thus showcasing innovative engineering solutions to common extraction issues |
| Shenhu, South China Sea | combination of depressurization and thermal | max 3.5 × 10 ⁴ m ³ /day, declines to 2.2 × 10 ³ m ³ /day over 60 days | reformation effects of CH ₄ hydrate and the inflow of hot water | 197 | despite their low permeability and high clay content, the Shenhu field reveals the technical viability of gas production from clayey silt NGH reservoirs; successful production tests indicate scalability for future exploitation; challenges include CH ₄ hydrate reformation and the inflow of hot water affecting reservoir temperatures, emphasizing the importance of balancing thermal stimulation with hydrate decomposition |

aboard the “Struggle No. 5” vessel in 1999 to the declaration of successful continuous production tests in 2017 reveals the potential and the challenges inherent in CH₄ hydrate extraction on an industrial scale.¹⁹⁷ The 2017 production test in the Shenhu Area was ground-breaking in several ways. It was the first to achieve continuous gas production from CH₄ hydrates at a large scale for as long as 60 days, setting a precedent for future exploration and extraction projects. More than 300 000 m³ of gas were produced during this test, far exceeding initial expectations. The test was designed to exploit a CH₄ hydrate reservoir below a water depth of 1266 m with the H₄ hydrate layer ranging from 203 to 277 m below the seabed. Achieving continuous large-scale production was a testament to the advancements in extraction technology and understanding of geological conditions conducive to stable CH₄ hydrate disassociation and gas production.¹⁹⁷

6.1.1. Lessons Learned from the Shenhu Field Project and Future Implications. One of the primary lessons learned from Shenhu Area exploration is the criticality of managing production rates for both short-term peaks and long-term sustainability. High production rates tend to decrease over time, presenting a need for strategies to maintain or enhance production levels. The fluctuating production rates observed call for further research into cyclic depressurization, thermal stimulation, and other innovative techniques that could stabilize and extend productive periods.¹⁹⁷ Another critical lesson revolves around understanding geomechanical responses to CH₄ hydrate recovery processes. The Shenhu tests highlighted the necessity of comprehensive models incorporating thermal, mechanical, and flow dynamics to predict how reservoirs respond to various extraction methods. Future enhancement strategies must consider the holistic management of reservoir layers, including manipulating water flows and thermal gradients, to optimize gas production.¹⁹⁷ The journey toward commercial exploitation of CH₄ hydrates underscores the need for collaboration among research institutions, industry, and government bodies. The Shenhu tests revealed technical feasibility and opened policy development and investment avenues in CH₄ hydrate exploration and extraction technologies.

6.2. Ignik Sikumi Field Test, Alaska. The Ignik Sikumi field experiment, conducted on the Alaska North Slope, was a pioneering venture investigating the viability of CO₂–CH₄ exchange in gas hydrate reservoirs.^{199,202} This experiment holds substantial lessons for future endeavors in CH₄ production from gas hydrates, which are crucial for advancing the capabilities in this field. The Ignik Sikumi field trial delivered insightful findings on CH₄ production. The experiment was designed as a huff-and-puff operation involving CO₂ and N₂ gas injection followed by pressure reduction to induce gas production. This approach resulted in specific observations: First, the initial stages revealed increased gas hydrate saturation near the wellbore, potentially due to the formation of secondary hydrates.¹⁹⁹ Toward the end of the injection period, a slight decrease in saturation suggested partial-pressure-induced hydrate dissociation because of the unsaturated nature of the injected gas mix concerning CH₄.¹⁹⁹ Second, postinjection operations revealed a preferential retention of CO₂ within the reservoir with 70% of the injected N₂ recovered, while only 40% of the injected CO₂ was retrieved.¹⁹⁹ This indicates effective CO₂ retention, possibly due to the bulk exchange between CO₂ and CH₄. Moreover, the latter phase of the test highlighted the reservoir's

responsive nature to depressurization, showcasing a direct correlation between pressure reduction and an uptick in production rate.¹⁹⁹ This phase provided a unique viewpoint into the reservoir's behavior postalteration by the chemical injection.

6.2.1. Lessons Learned from the Ignik Sikumi Field Test Field Project. The Ignik Sikumi experiment has underscored several key lessons for future CH₄ production projects from gas hydrate reservoirs: The test reinforced the significance of controlled depressurization in managing and enhancing CH₄ production. Variations in pressure impact gas production rates and the reservoir's geomechanical stability. Maintaining a stable depressurization process is key to maximizing production while minimizing risks. Furthermore, the experiment highlighted how the chosen injectant composition affects near-wellbore geochemistry and, consequently, injectivity and gas production.¹⁹⁹ Future endeavors should optimize injectant mixes to balance the formation of secondary hydrates against maintaining or enhancing reservoir injectivity. In addition, managing sand production emerged as a significant challenge, emphasizing the need for robust well design and completion tactics. Future projects must prioritize geomechanical stability to ensure the integrity of the well and the surrounding reservoir.

6.3. Messoyakha, Russia. The Messoyakha gas hydrate deposit, discovered in 1967 and located in the Arctic eastern border of West Siberia, represents a pioneering field in gas hydrate production. Despite initial oversight of the hydrates' presence, the deposit rapidly transitioned to the production phase by December 1969, employing a depressurization method across 57 drilled wells.¹⁹⁶ This innovative approach facilitated gas transformation from a solid to a free state, marking a significant milestone in exploiting gas hydrates as an energy source.¹⁹⁶ The production of CH₄ from the Messoyakha field proved to be successful, yielding an average production rate between 18 000 and 98 000 m³/day across operational wells.¹⁹⁶ The initial estimates of gas in place (IGIP) did not consider hydrate presence, leading to an adjusted understanding of reserves postproduction assessments.¹⁹⁶ Various methods, including volumetric calculations, *p/z* plots, and hydrodynamic models, have provided diverse IGIP estimates, highlighting the complexity of accurately gauging reserves in gas hydrate fields.¹⁹⁶

6.3.1. Lessons Learned from the Messoyakha Field Project. One significant lesson from the Messoyakha field project is the importance of hydrate consideration; ignoring hydrates during the initial drilling and development phases can lead to inaccurate reserve estimates and potential production challenges. Future projects should incorporate hydrate presence to optimize reserve assessments and production strategies. Furthermore, the successful use of the depressurization method in Messoyakha offers a viable technique for hydrate reservoir exploitation. This method, complemented with comprehensive field data, allows for tailored approaches to enhancing the production efficiency.¹⁹⁶ Additionally, integrating data from 57 wells into field-scale models streamlined production and pressure behavior analyses, ensuring alignment with actual development parameters.¹⁹⁶ Continuous monitoring and modeling adjustments are crucial for managing hydrate dynamics and ensuring sustained production. Moreover, the temperature behavior and aquifer activity reveal the intricate dynamics within hydrate fields. Recognizing these subtleties aids in navigating challenges such

as pressure fluctuations and water production management, which is essential for efficient field operations. The Messoyakha experience has catalyzed worldwide natural gas hydrate research. Its lessons extend beyond production techniques, encouraging a global discourse on hydrate exploitation's environmental and economic implications.

6.4. Alaska North Slope Production Test (Ongoing).

The Alaska North Slope natural gas production test is an ongoing project led by Arctic Slope Regional Corporation (ASRC) Energy and involving collaborators including the U.S. Geological Survey (USGS), the Department of Energy (DOE), and the Japan Oil, Gas and Metals National Corporation (JOGMEC)²⁰³ and marks a significant step forward in understanding the technical and economic feasibility of hydrate-derived natural gas production, a crucial alternative energy resource. Given the underexplored nature of Alaska compared to most basins,^{203,204} this test represents an essential step forward in harnessing the vast untapped energy reserves present in CH₄ hydrates. Key insights from the project include the successful drilling of a test well in 2018, confirming the presence of highly saturated gas hydrate-bearing reservoirs and validating the potential of gas hydrate as an energy source.²⁰⁴ The project's focus on characterizing the response of these reservoirs to controlled depressurization strategies through a meticulously planned three-well program²⁰⁴ highlights the importance of ongoing research, innovation, and international collaboration in commercializing CH₄ hydrate as a sustainable energy source. The project, closely watched by industry stakeholders, integrates advanced extraction techniques and environmental considerations, promising to offer valuable data and perspectives on the challenges, methodologies used, and quantity of CH₄ hydrate produced. This ongoing exploration is of immense importance not only for understanding the technical and environmental dynamics of CH₄ hydrate extraction but also for advancing global energy sustainability and security.

7. CHALLENGES, RESEARCH GAPS, AND FUTURE PERSPECTIVES

7.1. Challenges. CH₄ hydrate formation and extraction present challenges, including stability and formation conditions, slow kinetics, safety concerns, environmental impact, and economic viability. Addressing these requires a thorough understanding of thermodynamics and kinetics, utilization of advanced technologies, rigorous risk assessment, and stakeholder collaboration. Continuous research and technological advancements are essential to ensure reliability and efficiency in CH₄ hydrate formation and extraction strategies. This study outlines some of these critical challenges as follows.

The production and classification of CH₄ from CH₄ hydrates reservoirs are profoundly influenced by environmental conditions such as temperature, pressure, and salinity, each contributing complex challenges to hydrate formation. The temperature and pressure directly impact the CH₄ uptake and hydrate formation rates with optimal CH₄ uptake observed at specific conditions and a notable increase in formation time under certain temperatures and pressures.^{205,206} Additionally, salinity presents a dual effect: while increasing salinity can shift the CH₄ hydrate phase boundary toward higher pressures or lower temperatures, thereby potentially facilitating hydrate formation under certain conditions, it can also retard the hydrate formation kinetics in systems with higher salinity levels.²⁰⁶ These factors significantly affect the mass transfer and

phase separation of CH₄ molecules within marine environments,^{205,206} highlighting the nuanced balance required between these conditions to manage CH₄ hydrate production efficiently. The interplay of these environmental variables complicates the extraction and production processes, requiring tailored strategies to optimize CH₄ recovery from hydrate reservoirs under varying geological and environmental settings.

The formation of CH₄ hydrates within sedimentary matrices is a process critically influenced by the physical and chemical properties of the sediments themselves, including the particle size, water saturation levels, and specific surface areas of porous clay media. Studies have shown that the kinetics of CH₄ hydrate formation are significantly impacted by these sediment-specific factors, underlining a nonunidirectional influence of such variables on hydrate formation kinetics.⁴² This complexity is further compounded when sediment surface modifications by chemical additives or CO₂ swapping are considered, which can drastically alter the hydration dynamics and stability conditions necessary for CH₄ hydrate formation.^{31,42,73} Moreover, the potential for utilizing CO₂ injection for CH₄ extraction and CO₂ sequestration introduces additional variables to this complex system. The interaction between the injected CO₂, CH₄ hydrates, and the sedimentary environment offers a unique opportunity to recover energy resources and mitigate climate change impacts. However, this approach requires a detailed understanding of the pore-scale changes in electrical resistance and relative stiffness during CH₄ hydrate formation and CO₂ replacement processes.²⁰⁷

Extracting CH₄ from CH₄ hydrate reservoirs, categorized into Classes 1, 2, 3, and 4 via depressurization, thermal stimulation, inhibitor injection, and CO₂ swapping methods, poses distinct challenges that significantly impact the CH₄ production processes' efficiency and environmental viability. Class 1 reservoirs offer a more straightforward extraction process due to their structure, which facilitates hydrate dissociation with minor changes in pressure and temperature, potentially allowing for a more manageable extraction process.²⁰⁸ However, the extraction from Class 2 and Class 3 reservoirs is entangled with technological and efficiency constraints, chiefly due to their complex structural compositions that hinder straightforward CH₄ recovery.²⁰⁹ Moreover, across all CH₄ hydrate reservoir classes, the CH₄–CO₂ replacement technique, signaled for its dual benefit of CH₄ extraction and CO₂ sequestration, is vulnerable to low replacement efficiency, slow kinetics, and the formation of impermeable CO₂ hydrate layers that act as mass transfer barriers.^{131,210,211} Additionally, the immature state of current technologies aggravates these challenges, limiting the application spectrum of this promising technique.²¹⁰

The exploration and extraction of CH₄ from hydrate reservoirs, as evidenced by case studies in locations such as the Nankai Trough test, Japan,¹⁹⁵ Messoyakha, Russia,¹⁹⁶ Shenhu, South China Sea,¹⁹⁷ the Iġnik Sikumi field test, Alaska,^{6,199} and Mallik, Canada,²⁰⁰ show a potential pathway toward a new energy source yet highlight pronounced challenges including managing the reservoir pressure, mitigating the environmental impact, and addressing technical and operational hurdles like sand production and CH₄ hydrate reformation. The innovative use of CO₂ and N₂ injection in the Iġnik Sikumi field test in Alaska for CH₄ recovery introduces an environmentally beneficial method, leveraging the dual advantage of CH₄ recovery and potential CO₂ storage, but also underscores the need for robust well design and

completion strategies to manage common operational challenges such as fine sand and water production.^{6,199}

7.2. Research Gaps and Future Perspectives. Despite extensive research on CH₄ hydrate formation, significant gaps remain regarding the intricate interplay between temperature, pressure, and salinity and their collective impact on CH₄ hydrate formation and extraction strategies. Although studies have delineated the general influence of temperature on CH₄ hydrates' nucleation and growth processes, delineating clear stages of hydrate formation under constant temperature conditions,⁵⁶ the detailed mechanisms of these processes at various temperatures, pressures, and salinity levels remain inadequately understood. Furthermore, while the dissolution rate of CH₄ hydrates in seawater is heavily dependent on environmental conditions,⁵³ comprehensive models that predict the hydrate behavior under varying salinity, pressure, and temperature conditions are scarce. Similarly, efforts to elucidate the effects of these environmental factors on hydrate exploitation in wellbores have highlighted the critical roles of salinity, temperature, and pressure.²¹² Yet, the specific responses of CH₄ hydrates to these variables during extraction operations demand further exploration. Thus, a profound research gap exists in developing a unified, comprehensive model that accurately predicts the CH₄ hydrate behavior under many environmental conditions. This necessitates further investigation into the detailed physiochemical interactions during hydrate formation and decomposition. Bridging these gaps is essential for optimizing extraction strategies and advancing CH₄ hydrate dynamics.

Although significant progress has been made in understanding the CH₄ dynamics within sedimentary environments, substantial research gaps remain concerning the interactions between sediment characteristics and CH₄ hydrate stability and extraction strategies. Specifically, the influence of sediment particle size on the mechanical properties of hydrate-bearing sediments highlights a complex interplay that directly impacts the effectiveness and safety of exploitation technologies.²¹³ Furthermore, although studies have begun to elucidate the nonunidirectional influence of sediment particle size and porous media's specific surface areas on hydrate formation kinetics, the precise mechanisms by which these factors impact hydrate stability and formation rates remain insufficiently understood.⁴² This is compounded by the need for a deeper investigation into the role of sedimentation and sediment type in natural occurrences of CH₄ hydrates, particularly regarding seabed and subseabed stability and gas venting patterns.²¹⁴ Therefore, a profound gap exists in the comprehensive assessment of the effects of sediment-specific and surface modifications on hydrate stability, necessitating targeted research that can inform more effective and environmentally sustainable extraction strategies. Addressing these gaps will advance significantly impact practical approaches to hydrate exploitation, potentially unlocking new avenues for energy extraction from CH₄ hydrate reserves.

Despite significant advancements in CH₄ extraction techniques from CH₄ hydrate reservoirs, existing research reveals substantial gaps in adapting these techniques across different hydrate reservoirs—Class 1, Class 2, Class 3, and Class 4. Most research has focused on depressurization, thermal injection, chemical injection, and CH₄–CO₂ replacement methods with varying success and efficiency across these classes.¹⁶⁴ Class-specific challenges include the slower decomposition rate of CH₄ hydrates in Class 1 samples

under specific conditions compared to Class 3, indicating a need for more tailored depressurization strategies or alternative methods that could enhance CH₄ recovery rates effectively across all classes.²¹⁵ Furthermore, with Class 4 reservoirs constituting a significant 75% of natural occurrences, the absence of exploration into specific extraction techniques applicable to this class signifies a critical research void.¹⁶⁴ Enhanced techniques, like hydraulic fracturing, have shown potential to improve the gas production efficiency; however, details on their effectiveness, sustainability, and environmental impact across the hydrate classes, particularly implications on reservoir stability and the potential for induced seismicity, necessitate deeper investigation.^{50,216} This elucidates a poignant research gap in developing, testing, and validating production methods that are both class specific and environmentally sustainable, underscoring the immediate need for interdisciplinary research to bridge these gaps and advance the realm of CH₄ hydrate extraction.

Even though notable advancements in understanding CH₄ hydrate reservoirs and their potential role as a future energy resource have been made, significant research gaps persist, particularly in case studies and field applications for CH₄ production from CH₄ hydrate reservoirs. While various production methods such as thermal stimulation, depressurization, and inhibitor injection have been proposed and partially tested, there is a notable lack of comprehensive field-scale applications that validate these approaches under diverse geological and environmental conditions.²¹⁷ Moreover, the economic viability, environmental sustainability, and technological challenges of scaling these methods from the laboratory to the field remain largely unresolved. In addition, the impact of gas production from hydrate reservoirs on surrounding ecosystems and climate change implications due to potential CH₄ release require further empirical data and modeling efforts.¹¹⁵ Integrating numerical simulations with real-world field production tests has been suggested to bridge some of these gaps; however, detailed case studies documenting such integrative approaches are scarce and often limited in scope.¹¹ Lastly, despite the promising results from a few flow tests in oceanic and arctic environments, the comprehensive assessment of gas hydrate reservoir behavior under production scenarios, particularly concerning CH₄ recovery rates and reservoir stability, is inadequately represented in the current literature, impeding the path toward commercial exploitation of CH₄ hydrates.²¹⁸

8. CONCLUSION

This work presents a detailed review of CH₄ classifications and production methods from CH₄ hydrates. CH₄ hydrates were observed to represent a promising yet intricate future energy source. The distinct and varied geological settings—from faulted systems and porous sediments to marine deposits with dip angles and shallow subsurface areas—illustrate the potential and challenges of hydrate exploration and production. Critical factors such as the kinetic behavior of CH₄ hydrate formation, the impact of geological structures on CH₄ migration and accumulation, and the environmental and technical challenges underscore the necessity of a comprehensive understanding of these reservoirs for their safe and efficient exploitation. The following conclusions were made from this study.

- (1) A profound factor influencing the stability and occurrence of CH₄ hydrates is the interplay between temperature, pressure, and salinity. These environmental parameters significantly dictate the kinetics and thermodynamic stability of CH₄ hydrates within geological settings. Temperature affects hydrates' nucleation and growth rates with specific conditions facilitating or inhibiting the formation process. Pressure plays a key role in stabilizing the hydrate structure, drastically affecting its formation and dissociation behaviors. High-pressure conditions are generally conducive to hydrate formation, emphasizing the material's sensitivity to pressure changes. Salinity stabilizes and destabilizes CH₄ hydrates by affecting the hydrate phase equilibrium and altering the hydrate stability zone. This triad of factors governs the complex dynamics of CH₄ hydrate formation, stabilization, and potential for energy extraction. Understanding their synergistic effects is crucial for developing efficient methods for CH₄ recovery from hydrate reserves and optimizing conditions for hydrate storage and transport technologies.
- (2) The extraction of CH₄ from hydrate reservoirs encompasses various methodologies tailored to the unique characteristics of Class 1, Class 2, and Class 3 reservoirs. Depressurization is widely recognized across all class types for its effectiveness due to the low economic cost and feasibility of implementation, particularly highlighted in Class 1 and Class 3 reservoirs, where it facilitates the dissociation of CH₄ hydrates for CH₄ recovery up to 75% over two decades. Thermal stimulation and CO₂ swapping also stand out, especially for Class 1 reservoirs, as viable methods to contribute to CH₄ extraction by directly heating the reservoir to destabilize hydrates or injecting CO₂ to replace CH₄ in the hydrate structure, simultaneously sequestering CO₂. Class 2 reservoirs, characterized by low permeability, often require combining depressurization with thermal methods or innovative approaches like CO₂ injection to enhance the CH₄ extraction efficiency up to 87.80%. Furthermore, hydraulic fracturing emerges as essential for Class 3 reservoirs by improving the permeability and facilitating gas flow, thus enhancing CH₄ extraction up to 80.60%.
- (3) The exploration and pilot testing across various significant global sites, such as the Nankai Trough in Japan, Messoyakha in Russia, Shenhu in the South China Sea, and, notably, the Igñik Sikumi field test in Alaska, have shown the immense potential and challenges of CH₄ hydrate extraction. These cases have offered insights into extraction methods, notably the CO₂–CH₄ exchange technique in Alaska, which allows for CH₄ recovery and potential CO₂ sequestration. Challenges in sustainable offshore extraction, like fine sand production, CH₄ hydrate reformation, water production, and a possible increase in the bottom well pressure due to sand formation, highlight the need for ongoing research. Extended production trials, especially in Alaska by extending the depressurization phase to over 30 days, provide an understanding of reservoir responses and environmental impacts, which are essential for refining extraction methods. These efforts underscore the promise of CH₄ hydrates as a future energy source and emphasize the importance of

continued investment in research, innovation, and international collaboration to overcome challenges and commercialize this resource.

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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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