

REVIEW ARTICLE

Recent advances in simultaneous saline wastewater treatment and methane storage: A review

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Abstract: Water recovery and reuse are crucial strategies for addressing water scarcity and environmental pollution. Conventional wastewater treatment relies on pollutant removal or degradation; however, it often involves complex unit operations and high energy demand, with limited water recovery. Leveraging the unique structure and physicochemical properties of hydrate crystals, hydrate-based water treatment technologies enable direct extraction and reuse of water molecules through solid-liquid phase transitions, garnering increasing attention. Concurrently, hydrate-based methane storage offers distinctive advantages, including elevated storage capacity, moderate storage and transportation conditions, straightforward release mechanisms, and cost-effectiveness. Building upon this foundation, a dual-purpose strategy emerged, utilizing methane gas to form hydrates with water molecules in saline wastewater. Simple solid-liquid separation then isolates the hydrates from the wastewater. The subsequent decomposition of methane hydrates yields methane gas and pure water, achieving both water purification and recovery, as well as methane storage and release. The nucleation and growth process of hydrates, the exclusion of pollutants via crystal phase transitions, the slow growth kinetics of hydrates, and the difficulties associated with separating solids from liquids after formation have all limited the use of hydrate methods in wastewater treatment. This article provides a comprehensive overview of the application of the hydrate method in gas storage and treatment of saline wastewater, including the utilization of pure methane hydrates, thermodynamic and kinetic promoters, and the key role of porous media in the formation and decomposition of methane hydrates. This review offers valuable insights for practitioners engaged in methane storage and saline wastewater treatment.

Keywords: Saline wastewater; Hydrate; Methane storage; Promoter; Gas storage capacity

1. Introduction

In the contemporary era, which is characterized by unrelenting technological progress and a rapidly accelerating rate of industrialization, energy shortages and environmental pollution represent two significant global challenges. Water scarcity and water pollution, in particular, pose a direct threat to human survival. Traditional biological, chemical, and physical

wastewater treatment methods face challenges such as ineffective treatment of high-concentration or toxic wastewater, the introduction of new pollutants or increased sludge production, and high material costs and energy consumption.¹ Therefore, new wastewater treatment technologies are urgently needed to achieve water resource recovery and reuse from wastewater.

In recent years, hydrate formation-decomposition technology has emerged as a research focus in a range

of disciplines, including, but not limited to, seawater desalination, wastewater treatment, gas storage and transportation, and carbon sequestration. There is an increasing focus on hydrate-based water treatment technologies due to their inherent capacity for resource recovery and reuse. Unlike conventional wastewater treatment methods that focus on destroying pollutants, hydrate technology achieves freshwater extraction by directly binding water molecules with guest molecules to form solid hydrates, thereby extracting water from high-salinity wastewater. Meanwhile, natural gas is considered one of the cleanest fossil fuels. It is found in nature in various forms, including conventional (e.g., natural gas fields) and unconventional sources (e.g., shale gas, natural gas hydrates, and tight gas).

Natural gas constitutes approximately 24% of all fossil fuels. The consumption of natural gas has grown more rapidly than that of oil and coal,^{2,3} and is projected to increase. In addition, the utilization of natural gas has been demonstrated to reduce carbon dioxide (CO₂) emissions by approximately 50% compared with coal and 30% compared with oil.⁴ As a result, natural gas is widely used in industry and manufacturing.

In the context of the imminent transition to a global gas economy, there is an urgent need to develop effective technologies for the storage and transportation of natural gas. The transportation of bulk natural gas (with methane [CH₄] as the primary component) mainly depends on liquefied natural gas (LNG) and pipeline transportation methods, but most of these gas fields are far removed from existing natural gas pipeline networks. It is therefore imperative to develop efficient storage and transportation methods for natural gas at these gas fields. Using energy gases such as CH₄ as the target molecules, the processes of hydrate formation, separation, and decomposition can enable the simultaneous production of pure water and the storage and transportation of CH₄.

Natural gas can be transported and stored in many ways, including pipelines, LNG, compressed natural gas (CNG), adsorbed natural gas (ANG), gas-to-liquids, and natural gas hydrate.^{5,6} CNG is a method of storing natural gas that involves compressing it under high-pressure conditions (typically >20 MPa). However, the cost of manufacturing and maintaining high-pressure vessels, together with the cost of gas compression, results in a large economic burden for CNG, hindering its large-scale commercial application. In addition, CNG cylinders transported by vehicles pose significant safety risks.

Meanwhile, ANG refers to a storage method that adsorbs natural gas onto carbon nanotubes, graphene,

metal-organic frameworks (MOFs), and other adsorbents. The volumetric and gravimetric capacities of these materials are generally low. Even if the volumetric capacity of MOFs is higher when calculated at the single-crystal level, it decreases significantly when calculated at the bulk scale. The utilization of MOFs for natural gas storage is constrained by factors such as mechanical stability, thermal conductivity, and the high cost of the materials.⁷⁻⁹

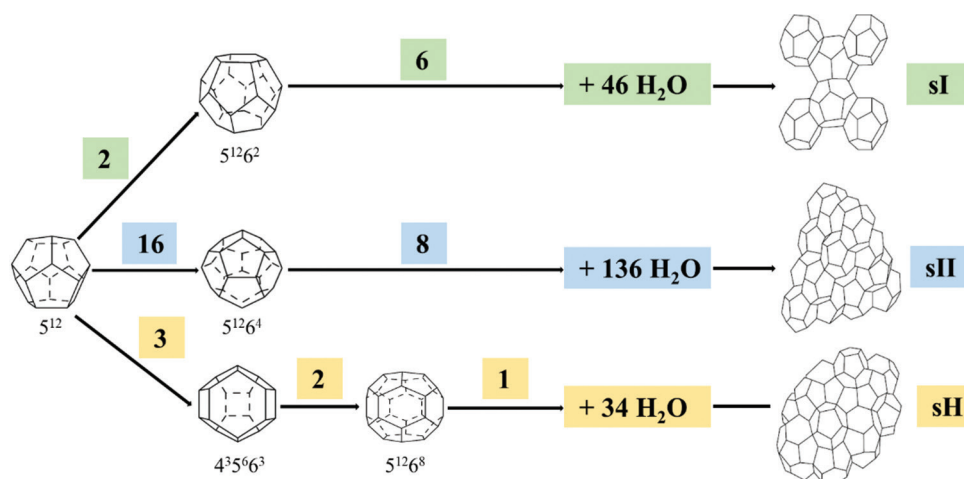
At present, the predominant method for storing and transporting natural gas is LNG, which stores natural gas at a low temperature (−162°C). However, the energy consumption and vaporization losses associated with maintaining this low temperature are the primary drawbacks of LNG. The recent proposal of gas storage and transportation in hydrate form represents a novel methodology with considerable practical application value. This is due to the fact that the pressure required for hydrate storage and transportation is significantly lower than that required for CNG, and hydrates are not prone to explosion. However, the industrial application of hydrate gas storage and transportation technology is hindered by the slow hydrate formation rate and low effective gas storage density. Consequently, the study of hydrate formation enhancement is of great significance for the development of gas storage and transportation in hydrate form.

Natural gas hydrate is a non-stoichiometric, crystal-like compound formed by cage structures (the host), composed of water molecules that interact through hydrogen bonds, encapsulating gas molecules (the guest), which must be of an appropriate size. Gas hydrate, also known as clathrate hydrate, was first identified as causing blockages in oil and gas pipelines.¹⁰ Moreover, natural gas hydrate is widely found in frozen soil and sediments on the continental margin. As an alternative energy source of natural gas,¹¹ it has attracted significant scientific interest and has become an efficient and green energy source.¹² Gas molecules interact with water molecules via van der Waals forces. The gas can only be released by disrupting this weak physical interaction.

There are three main hydrate structures: Type I, Type II, and Type H (Table 1 and Figure 1). Each structure has a specific cage size and shape, as well as a specific number of water molecules.¹³ The type of hydrate formed depends on the size of the gas molecule, as well as the temperature and pressure conditions. Type I hydrate crystals can accommodate small molecules, such as CH₄, ethane (C₂H₆), nitrogen gas, CO₂, hydrogen sulfide, and other non-hydrocarbon molecules. The Type II hydrate crystal structure can

Table 1. Crystal structure parameters of Type I, II, and H hydrates

Cage item	Type I		Type II		Type H		
	Small	Big	Small	Big	Small	Middle	Big
Structure	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Number	2	6	16	8	3	2	1
Diameter (Å)	3.95	4.33	3.91	4.73	3.91	4.06	5.71
Expression	$2(5^{12}) 6(5^{12}6^2) \cdot 46\text{H}_2\text{O}$		$16(5^{12}) 8(5^{12}6^4) \cdot 136\text{H}_2\text{O}$		$3(5^{12}) 2(4^35^66^3) 1(5^{12}6^8) \cdot 34\text{H}_2\text{O}$		

**Figure 1. Schematic illustration of type I, II, and H hydrate crystal structure. Image created by the authors. Created with BioRender.com. Yalong Ding (2025) Microsoft Office.**

accommodate small molecules, such as CH_4 and C_2H_6 , as well as larger molecules, including propane (C_3H_8) and isobutane ($i\text{-C}_4\text{H}_{10}$). The larger cavities of type H hydrate crystals can even accommodate molecules with diameters larger than that of $i\text{-C}_4\text{H}_{10}$.

In the past two decades, the potential applications of natural gas hydrate technology have received extensive attention, such as hydrate cold storage,^{14,15} gas separation,¹⁶⁻¹⁹ CO_2 and hydrogen gas storage and transportation,²⁰⁻²² and seawater desalination.²³⁻²⁵ However, the technology for handling natural gas hydrates remains a significant challenge. The main issue is the thermodynamics and kinetics of their formation. Thermodynamic additives, such as tetrahydrofuran (THF), have been extensively studied to enable the storage of gas hydrates under mild temperature and pressure conditions. At the same time, to overcome the slow rate of hydrate formation, various kinetic promoters, such as surfactants,^{26,27} guest molecules²⁸ or amino acids,²⁹ have been used to accelerate the process.

Compared with LNG and CNG, natural gas hydrate has a higher gas density and can be stored under milder conditions. This makes it one of the leading technologies for the transportation and storage of natural gas.³⁰ The

volume of CH_4 gas contained in CH_4 hydrate at 273 K and 2.6 MPa is about 170 times greater than at standard temperature and pressure.³¹ Storing natural gas in the form of hydrates (i.e., solid natural gas [SNG]) is a promising storage method. It has several advantages: (i) it is environmentally friendly, requiring only water and a small amount of accelerator for generation; (ii) it can be generated and stored at mild temperatures and pressures; (iii) the stored gas can be fully utilized with gas release being a simple step-down or thermal stimulation process; and (iv) it has a high energy density and is non-explosive.

Table 2 shows a comparison of the above natural gas storage methods. Based on the table, SNG's current volumetric capacity is low, and it may only be applied to natural gas supply in fixed locations or to production equipment, such as natural gas supply in remote areas or energy supply for equipment such as automobiles. SNG technology encompasses four main areas: hydrate formation, removal of unreacted water, compaction of natural gas hydrate, and storage at the appropriate temperature and pressure. The main problems at present are the formation stage of gas hydrates (low formation rate and low gas storage capacity) and the

Table 2. Comparison of several natural gas storage methods

Storage state Storage method	Gas		Liquid	Solid	
	Compressed natural gas	Adsorbed natural gas	Liquefied natural gas	Solid natural gas	
				Without promoter	With promoter
Volumetric capacity	230 (v/v)	267 (v/v) ³²	600 (v/v)	170 (v/v)	115 (v/v)
Storage condition	20 MPa, 293.2 K	6.5 MPa, 298.2 K	0.2 MPa, 113.2 K	0.1 MPa, 193 K ³³	0.1 MPa, 277.2 K ³⁴
Advantage	Easy to use	Low-pressure storage, high-weight capacity	High volume capacity, high energy density	Non-explosive, environmentally friendly, high-energy density	Non-explosive, environmentally friendly, high-energy density, mild formation and storage conditions
Disadvantage	Poor security, high-voltage storage, multi-stage compression, and high cost	Low mechanical stability, high adsorbent cost	High vaporization loss, cooling energy consumption	Low volume capacity	Low volume capacity

storage stage (at around -20°C). The primary methods for overcoming the low formation rate and gas storage limitations include developing new, effective reactors to increase the gas-liquid contact area during formation and utilizing kinetic accelerators to enhance hydrate formation kinetics without compromising storage.

2. Hydrate method for saline wastewater treatment

Around 1940, Parker³² first proposed a water treatment strategy based on the hydrate method, which utilizes the phase transition process of hydrates to extract freshwater from seawater. The principle of hydrate-based treatment for saline wastewater is similar to seawater desalination technology. At specific temperatures and pressures, guest molecules (such as CH_4) interact with saline wastewater, causing water molecules to form cage-like structures. These cages encapsulate guest molecules, forming solid hydrates, while excluding salts and other impurities from the crystal structure of the hydrate. Following hydrate formation, the process of solid-liquid separation yields pure hydrates and residual liquid. The hydrates subsequently decompose into desalinated water and guest molecules, which are then recovered and recycled for reuse.

The primary barrier to commercializing hydrate desalination lies in the challenges associated with separating the hydrate phase from brine. Several researchers have compared the effects of different

solid-liquid separation methods on desalination efficiency and water recovery rates.³³⁻³⁵ Montazeri and Kolliopoulos³⁶ conducted a detailed analysis of the energy consumption in hydrate-based seawater desalination. Their findings demonstrated that this method achieves higher water recovery rates with lower energy input. They indicated that the hydrate method represents a promising and sustainable approach for seawater desalination.

For high-concentration heavy-metal wastewater that cannot be effectively treated by conventional methods, Dong *et al.*³⁷ first proposed the treatment of high-concentration heavy metal ions using the hydrate method. They found that, within the range of 100–1,000 mg/L of heavy metal ions in wastewater, the removal efficiency reached 96.63%, with a water recovery rate exceeding 70%. This demonstrates the significant importance of recovering heavy metals from wastewater. Truong-Lam *et al.*³⁸ further confirmed that hydrate technology could remove 80.8% and 81.0% of ionic compounds from brine and wastewater, respectively. Geo Lim *et al.*³⁹ employed the hydrate method to recover freshwater from nuclear wastewater containing cesium, strontium, and iodine. They found that SNG hydrates contained no radioactive chemicals.

Furthermore, the proposed hydrate process can be applied to radioactive wastewater with extremely high initial concentrations. Babu *et al.*³⁴ discovered that water molecules can migrate from the bottom to the top of porous media, where they convert into solid hydrates.

This suggests the potential of hydrate technology for improving the separation of contaminants. Wu *et al.*⁴⁰ conducted dehydration experiments on high-water-content sludge using *in situ* propane hydrates. The hydrate decomposition water met discharge standards, demonstrating the excellent separation performance of the hydrate method and indicating that the resulting water can be discharged directly without further treatment.⁴¹

Cha *et al.*⁴² measured phase equilibrium data for CH₄ hydrate in mixed salt solutions of sodium chloride (NaCl), potassium chloride (KCl), and ammonium chloride (NH₄Cl) at concentrations of up to 10 wt.%, investigating the inhibitory effect of cations on hydrate formation. Hu *et al.*⁴³⁻⁴⁵ reported on the phase behavior and kinetics of CH₄ hydrate in high-salinity brines under ultra-high pressure. They found that, at elevated pressures, the phase equilibrium conditions for CH₄ hydrate shifted toward lower temperatures and higher pressures as the salt concentration increased.

In addition, Cha and Seol⁴⁶ employed water-insoluble cyclopentane (CP) and cyclohexane as host molecules to form hydrates with CO₂ for desalination of hypersaline wastewater. They observed desalination efficiencies exceeding 90% at 3.1 MPa and elevated temperatures (7°C, 16°C). Fakharian *et al.*⁴⁷ employed CNG hydrates for desalination of oilfield-produced water. They demonstrated that CNG hydrates could reduce salinity by approximately 82%, with a maximum brine's total dissolved solids of 160,000 mg/L. Seo *et al.*⁴⁸ measured thermodynamic conditions for hydrate formation in 30 wt.% NaCl solutions using CH₄, sulfur hexafluoride, and 1,1,1,2-tetrafluoroethane as guest molecules, demonstrating the potential of hydrate methods for seawater desalination, particularly for treating saturated brines. According to Mallek *et al.*,⁴⁹ the formation kinetics of CP hydrates were significantly enhanced at a salinity of 16 wt.% NaCl when porous activated carbon particles were used to assist the process.

Despite the increasing use of novel guest molecules in hydrate-based methods for treating saline wastewater in recent years, challenges such as stringent thermodynamic requirements for formation and slow growth kinetics continue to hinder the advancement of hydrate-based wastewater treatment technologies. Certain host molecules, such as CP and some chlorofluorocarbons, exhibit lower formation pressures or higher formation temperatures. However, due to their significant ozone-depleting potential, they are unsuitable for large-scale application in hydrate-based water treatment. The hydrate method for treating saline

wastewater has become a research hotspot, relying on the participation of guest gas molecules. At the same time, the hydrate method for storing CH₄ also forms a solid through the interaction between CH₄ molecules and water molecules, which is then separated and decomposed to obtain gas and pure water. The coupling of these two technologies can achieve CH₄ gas storage and transportation while simultaneously treating saline wastewater. However, these two technologies face the same problem: the conditions for hydrate formation are too harsh, the formation rate is low, and the final gas storage capacity is limited. Therefore, many researchers have invested in studying hydrate formation promoters.

In addition to the experimental research mentioned above, the techno-economic analysis of the hydrate method for treating saline wastewater is also essential. Many researchers have made significant contributions to this field. Javanmardi and Moshfeghian⁵⁰ developed a computer program that simulates the process of treating saline wastewater using the hydrate method. The program estimates total capital investment, operating and maintenance costs, and total product costs. By investigating the impact of hydrate formation promoters on the energy consumption and economic parameters of the process, as well as the cost of treating saline wastewater using different methods, the researchers concluded that treating saline wastewater using the hydrate method without a promoter is not economically beneficial. However, when the appropriate accelerators are selected, the cost of treating saline wastewater using the hydrate method reduces significantly. This makes the process attractive, as it is comparable to other methods such as multi-stage flash distillation, multi-effect distillation, and reverse osmosis. Choi *et al.*⁵¹ evaluated the energy demand, costs, environmental impact, and water quality of a wide range of desalination technologies. They also highlighted the advantages and disadvantages of using the hydrate method to treat saline wastewater, as well as its potential for integration with other technologies.

3. Methane storage in pure methane hydrate

Pure CH₄ molecules form structure I hydrate, and its unit cell includes six 5¹²6² cavities and two 5¹² cavities. Assuming that all the cavities are completely occupied by CH₄ molecules and that one cavity contains only one CH₄ molecule, the maximum ideal mass fraction of CH₄ in 8CH₄·46H₂O hydrate is 13.39 wt.%. In our previous studies on CH₄ hydrate formation, we used different methods of CH₄ gas injection.¹⁹ For example, we injected

CH₄ gas into the container from both the gas phase area at the top and the liquid phase area at the bottom. When CH₄ gas was injected into the gas phase area at the top of the reactor, CH₄ hydrate first formed at the gas-liquid interface. It then gradually extended downwards from this interface into the liquid phase. However, the thickness of the CH₄ hydrate layer increased slowly before ultimately stabilizing at approximately 1.0 cm. Figure 2A-D depicts the state of the reactor interior on days 1, 3, 6, and 9 of the experiment, respectively.

When CH₄ gas was injected from the liquid phase area at the bottom of the container, CH₄ hydrate was initially generated at the gas-liquid interface. The difference is that the CH₄ hydrate layer extended into the gas phase region above the gas-liquid interface and became compressed, changing from a loose state to a relatively dense state. After 9 days, all the water in the reactor had been converted into CH₄ hydrate. Figure 2E-H depicts the state inside the reaction reactor on days 1, 3, 6, and 9 of the experiment, respectively. It can be concluded that gas bubbling from the bottom

of the reactor can convert a greater amount of CH₄ gas into CH₄ hydrates, whereas gas injection from the top of the reactor results in a limited amount of CH₄ gas being converted into CH₄ hydrates. The main reason is that CH₄ gas has sufficient time to come into contact with the water when entering the reactor from the bottom, increasing the contact area between the gas and the water and promoting the formation of CH₄ hydrates. However, when CH₄ gas enters the reactor from the top gas phase, CH₄ hydrate forms at the gas-liquid interface and maintains a certain thickness. Ultimately, further contact between the gas and water is restricted.

Even outside the thermodynamically stable region, CH₄ hydrate can be preserved at atmospheric pressure and below 273 K due to its “self-preservation” effect. “Self-preservation” is a dynamic anomaly. Under mild temperature and pressure conditions, a large amount of gas can be kept away from the thermodynamic stability field of natural gas hydrate for days, weeks, or even months by maintaining a temperature below the melting point of ice. Khokhar *et al.*⁵² first reported the feasibility

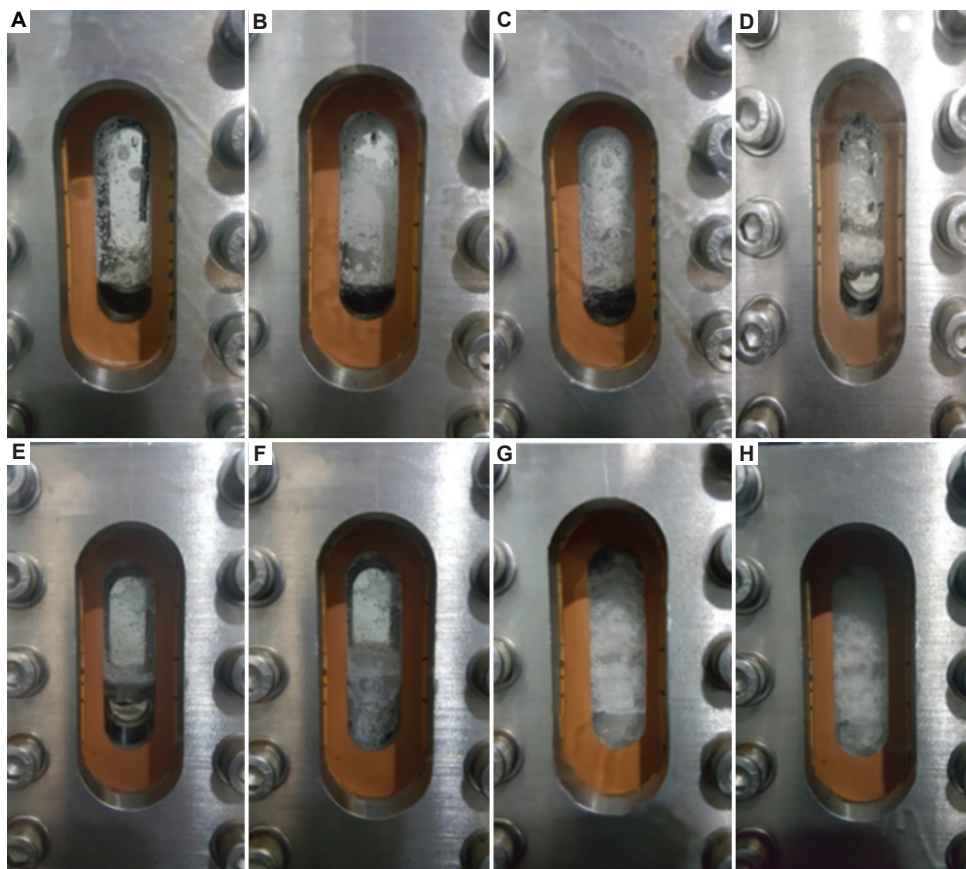


Figure 2. Captured images on the 1st, 3rd, 6th, and 9th days during the experiment (conducted at 275.13 K and 5.0 MPa). Methane gas was injected from the gas-phase region at the top of the reactor (A-D) and from the liquid-phase region at the bottom of the container (E-H). Reprinted with permission from Li *et al.*¹⁹ Copyright © 2017, American Chemical Society.

of using natural gas hydrate for the transport of natural gas at atmospheric pressure and below the ice melting point (<273 K).

Stern *et al.*⁵³ found that dissociation of CH₄ hydrate was significantly inhibited at temperatures between 242 K and 271 K in an atmosphere containing CH₄, which is consistent with the “self-preservation” phenomenon. Some researchers believe that when CH₄ forms a mixed hydrate with other molecules, there is no “self-preservation” phenomenon,⁵⁴ but some other researchers believe that the “self-preservation” phenomenon still exists. In general, the “self-preservation” phenomenon of gas hydrates is related to various factors, including the thickness of the ice layer formed by hydrate dissociation, the size and specific surface area of hydrate particles, the ice structure, the gas composition, and the hydrate structure.⁵⁵

Mimachi *et al.*⁵⁶ employed a continuous process with a daily output of 0.24 tons, utilizing simulated natural gas (91.5% CH₄ + 6.7% C₂H₆ + 1.8% C₃H₈) as the raw material for forming hydrate microspheres at 278 K and 5.5 MPa, as depicted in Figure 3A. The mass fraction of natural gas exceeded 70%, and it remained stable at atmospheric pressure and 253 K for over 3 months. Takeya *et al.*⁵⁷ produced 33 mm-diameter CH₄ hydrate pellets in a 2.7 wt.% NaCl aqueous solution at temperatures between 273 K and 277 K and pressures of 5.5 MPa (Figure 3B). The results demonstrated that the stability of CH₄ hydrate formed in the NaCl solution is due to the presence of ice and NaCl·2H₂O crystals at the hydrate grain boundary. Once the NaCl·2H₂O melts, the boundary between hydrate and ice acts as a diffusion path for CH₄ generated by the dissociation of the hydrate. Takeya *et al.*⁵⁷ demonstrated the potential of CH₄ hydrate spheres formed using a NaCl solution or seawater for storing and transporting CH₄ gas.

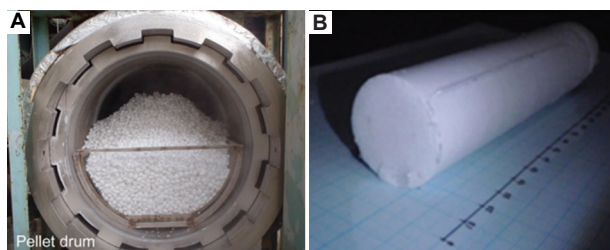


Figure 3. Schematic diagram of large-scale production of natural gas hydrate. (A) Natural gas hydrate microspheres. Reprinted with permission from Mimachi *et al.*⁵⁶. Copyright © 2015, American Chemical Society. (B) Typical methane hydrate pellet. Reprinted with permission from Takeya *et al.*⁵⁷ Copyright © 2018, Elsevier Ltd.

Falenty *et al.*⁵⁵ used an *ex situ* low-temperature scanning electron microscope to observe the morphology of ice covering hydrate surfaces at various stages, as shown in Figure 4. They also studied the kinetics of CH₄ hydrate decomposition into ice and CH₄ gas at various temperatures and pressures. Studies have shown that “self-preservation” is related to the microstructure of ice (i.e., the shape, arrangement, and size of ice crystals) and the melting rate of the ice layer, which acts as a gas diffusion barrier. The optimal temperature for CH₄ hydrate storage and transportation under ambient pressure is 250 K.

Researchers have studied the “self-preservation” phenomenon of CH₄ hydrate from both the micro level^{58–60} and the macro levels.⁶¹ Below 273 K and at atmospheric pressure, the temperature can effectively hinder the decomposition rate of CH₄ hydrate. The gas storage of pure CH₄ hydrate can be effectively improved by physical enhancement. The vertical reciprocating method employed by Xiao *et al.*⁶² and the reactor with the top spray device used by Rossi *et al.*⁶³ can both significantly increase the rate at which CH₄ hydrate forms and the capacity for CH₄ storage. Wang *et al.*⁶⁴ reported that the storage capacity of CH₄ in the hydrate formed by mixing dry water and hydrophobic silica nanoparticles reached 175 v/v within 1,500 min.

Although the CH₄ contained in gas hydrate is approximately one-third of the CH₄ contained in the same volume of LNG, the initial cost of gas hydrate is low, and it can be used in conjunction with LNG receiving stations in undeveloped small- and medium-sized gas fields. Since LNG is transported at atmospheric pressure and 110 K, whereas gas hydrates are better preserved at atmospheric pressure and at 273 K due to the “self-preservation” phenomenon, this method is more energy-efficient. Therefore, the “self-preservation” phenomenon of natural gas hydrate is essential for the storage and transportation of CH₄.

4. Application of chemical promoters

4.1. Thermodynamic promoters

Although the theoretical gas storage capacity of pure CH₄ hydrate is 176 v/v, the actual value obtained in the laboratory is usually much smaller. The primary function of hydrate chemical promoters is to reduce the thermodynamic conditions required for hydrate formation or to enhance the gas transfer process, thereby promoting the formation of hydrates. Some chemical substances, including THF,^{65,66} tetrahydropyran,⁶⁷ CP,^{68,69} tetrabutylammonium bromide (TBAB),^{70,71} and

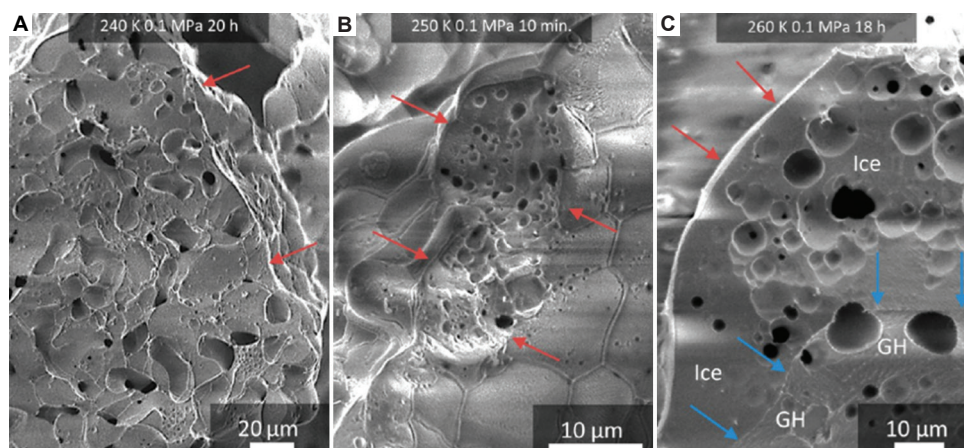


Figure 4. SEM images of surfaces accidentally exposed during methane hydrate preparation. (A) Microstructures of ice films after 20 h when methane hydrate was formed at 240 K, 0.1 MPa (scale bar = 20 μm). (B) Microstructures of ice films after 10 min when methane hydrate was formed at 250 K, 0.1 MPa (scale bar = 10 μm). (C) A plane cutting through the ice film (scale bar = 10 μm). Blue arrows indicate the hydrate/ice interface, and red arrows indicate edges between the original and broken-off surfaces. Reprinted with permission from Falenty *et al.*⁵⁵ Copyright © 2014, American Chemical Society.

acetone⁶⁷ have been found to effectively reduce hydrate formation pressure and promote hydrate formation. These chemical additives are known as thermodynamic accelerators.

The mechanism of action of a thermodynamic promoter involves its molecules participating in the hydration process of gas molecules and occupying some hydrate cavities during hydrate formation, thereby assisting gas molecules in stabilizing hydrate cavities under milder thermodynamic conditions. However, the gas storage capacity decreases rapidly, precisely because thermodynamic promoter molecules occupy hydrate cavities.

In the absence of a thermodynamic promoter, the theoretical gas storage capacity of CH_4 hydrate is 216 v/v. However, in the presence of a thermodynamic promoter, the CH_4 molecules generally form Type II hydrate, occupying only small cages within it. In addition, the theoretical gas storage capacity of Type II CH_4 hydrate is only 118 v/v. However, using a thermodynamic accelerator enables CH_4 hydrate to be formed at significantly lower pressures and at near-ambient conditions, which greatly offsets the reduction in gas storage capacity. Identifying more ideal thermodynamic accelerators to obtain the maximum gas storage is a key research direction in this field.

At present, the most extensively studied thermodynamic accelerator is THF. Using THF as an accelerator significantly shifts the hydrate phase equilibrium line toward the low-pressure, high-temperature region. The experiments by Luo *et al.*⁷² and

Ning *et al.*,⁷³ which used a $\text{CH}_4 + 6 \text{ mol\% THF} + \text{water}$ system to form hydrates, confirmed the advantages of using THF as a thermodynamic accelerator (i.e., hydrates can be formed at low pressure and high temperature). However, the CH_4 storage capacity was not reported in either of these experiments. The maximum CH_4 storage capacity achieved was $88 \pm 2.6 \text{ mmol/mol}$ of water. Veluswamy *et al.*²⁸ generated hydrates in the $\text{CH}_4 + \text{THF} + \text{water}$ system and obtained a CH_4 storage capacity of 63 mmol/mol water in 2 h at 3.0 MPa and 283.2 K. At 7.2 MPa and 293.2 K, a higher CH_4 storage capacity was achieved at a lower kinetic rate, making SNG technology more commercially viable.

When TBAB forms semi-clathrate hydrates near ambient pressure and near room temperature, anions participate in the formation of cage-type lattices, and cations enter cage-type cavities. The semi-cage hydrate formed by TBAB and water molecules consists of three types of cavities: Two $5^{12}6^2$ cavities, two $5^{12}6^3$ cavities, and several 5^{12} cavities. The Br^- ion is a part of the cage structure lattice. The tetrabutylammonium cation (TBA^+) is located at the center of four larger cavities, and the remaining smaller cavities can encapsulate small molecules such as CH_4 and H_2 . Shimada *et al.*⁷⁴ reported that the $\text{TBAB} \cdot 38\text{H}_2\text{O}$ unit cell contains two 5^{12} cavities for encapsulating small molecules, as illustrated in Figure 5. Therefore, the ideal maximum mass fraction of CH_4 for $2\text{CH}_4 \cdot \text{TBAB} \cdot 38\text{H}_2\text{O}$ semi-clathrate hydrate is 3.08 wt.%.

In the temperature and pressure range of 273.64–278.23 K and 2.01–7.07 MPa, Yang *et al.*⁷⁵ measured

the CH_4 storage data for the CH_4 -TBAB- H_2O ternary system in solutions containing 20.8 and 43.3 wt.% of TBAB. The results showed that CH_4 -TBAB semi-clathrate hydrate and pure CH_4 hydrate formed simultaneously in a 20.8 wt.% TBAB solution at 273.64 K and 5.05 MPa. In a 43.3 wt.% TBAB solution, the maximum mass fraction of CH_4 in the CH_4 -TBAB- H_2O clathrate hydrate was only 1.64 wt.% at the same experimental temperature and pressure, which is lower than the ideal value of 3.08 wt.%. They found that at 5.05 MPa and 273 K, some TBAB molecules could not be replaced by CH_4 molecules. This resulted in a lower CH_4 mass fraction, which was possibly due to under-pressurization of the CH_4 gas.

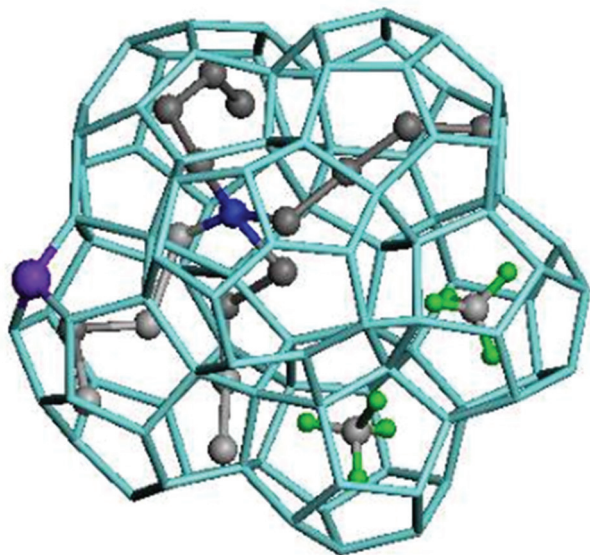


Figure 5. Structure of methane-tetrabutylammonium bromide semi-clathrate hydrate unit. Reprinted from Shimada *et al.*⁷⁴.

Liu *et al.*⁷⁶ investigated the formation of CH_4 hydrate in water/diesel emulsions in the presence of the thermodynamic additives TBAB, THF, and CP. It was found that neither TBAB nor THF could promote CH_4 hydrate formation in the water/diesel emulsion. However, CP significantly reduced the formation pressure of CH_4 hydrate in the water/diesel emulsion. The resulting hydrate/diesel slurry had good fluidity, as shown in Figure 6. At a temperature of 276.15 K and a pressure of 6 MPa, the CH_4 storage capacity of the water/diesel/CP emulsion containing 30 wt.% water was $152.32 \text{ m}^3/\text{m}^3$, which was significantly higher than that of pure water, the water/CP solution, and the water/diesel emulsion. Xu *et al.*⁷⁷ compared the effects of TBAB, THF, and CP on the formation and storage of CH_4 from gas hydrates. They reported that strong polar ion promoters were not helpful in achieving optimal gas absorption, as the formation of the hydrate layer hindered the diffusion of gas from the gas phase to the bulk solution. Veluswamy *et al.*^{28,78} used a 2 mL THF aqueous solution to form CH_4 hydrate and found that the gas storage capacity of the hydrate was 104.3 v/v at 283.15 K and 7.2 MPa. Kumar *et al.*,⁷⁹ who were also part of the same research team as Veluswamy *et al.*,⁷⁸ found that the hydration process could be completed in about 15 min when the medium was changed to a THF-seawater solution, and that the gas absorption of hydrate was about 89.2 v/v.

Park *et al.*⁸⁰ discovered a new type of hydrate former—cyclobutanemethanol—and investigated the crystal structure and guest behaviors of the binary hydrate (cyclobutanemethanol + CH_4). The results showed that cyclobutanemethanol molecules could be enclathrated in the large cages of sII hydrates, while

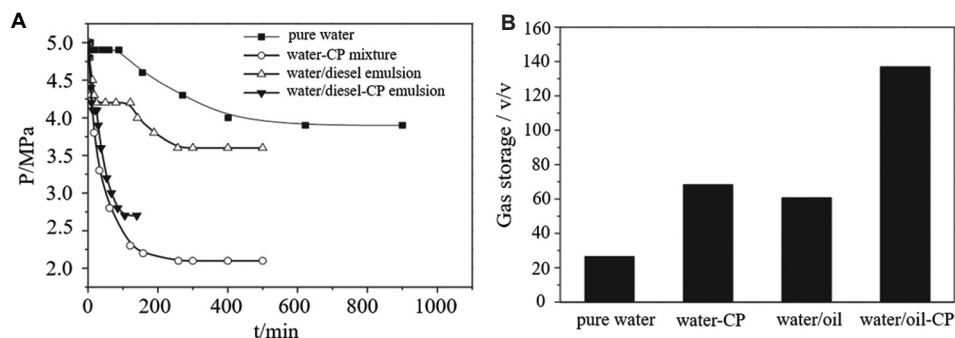


Figure 6. Methane hydrate formation kinetics and methane storage volume in different system. (A) Methane hydrate formation kinetics and (B) methane storage volume per unit volume of water in pure water, a water-cyclopentane (CP) mixture, a water/oil emulsion, and a water/oil-CP (17 wt.% relative to water) emulsion at 276.15 K, with an initial pressure of 5.0 MPa. Reprinted with permission from Liu *et al.*⁷⁶ Copyright © 2020, Elsevier B.V.

CH_4 molecules were captured in both the large and small cages. The average CH_4 storage capacity in the binary hydrate (cyclobutanemethanol + CH_4) is approximately 104 mmol of CH_4 per mol of water.

Seol⁸¹ synthesized a new CH_4 hydrate containing four nitroalkanes: Nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane. They investigated the structure and guest behavior of this hydrate, as well as its thermodynamic stability and CH_4 capacity, using high-resolution powder diffraction, carbon-13 nuclear magnetic resonance, and high-resolution Raman spectroscopy. The results showed that all nitroalkane + CH_4 hydrates are of the sII type, as shown in Figure 7, and the large and small cages of these hydrates are mainly occupied by nitroalkanes and CH_4 , respectively. It was also found that nitroalkanes act as effective thermodynamic promoters, significantly reducing the CH_4 storage pressure by 4–6 MPa at 283 K. In addition, these hydrates exhibit a high energy density, containing a large amount of CH_4 as the main fuel, approximately 105 mmol/mol H_2O , equivalent to 90% of the theoretical maximum capacity, alongside high-energy nitroalkanes as an additional fuel and oxidant. Seol⁸² also investigated the formation of CH_4 hydrates of the sH type by using nitrocyclopentane and nitrocyclohexane as thermodynamic promoters.

4.2. Kinetic promoters

Kinetic promoters can increase the rate of hydrate formation without altering the temperature, pressure

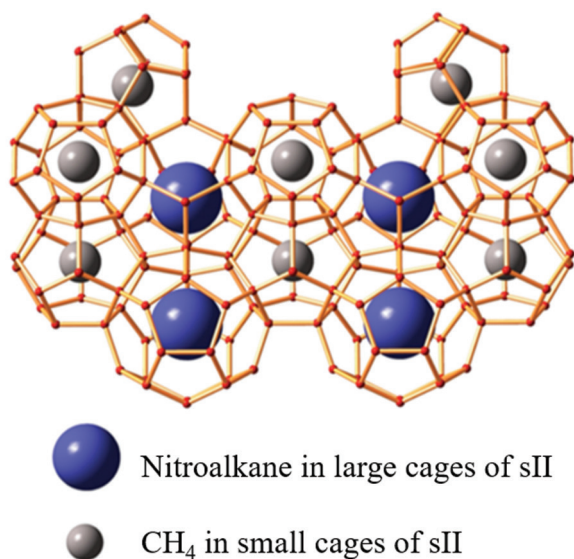


Figure 7. The microstructure and guest distribution of the nitroalkane + methane (CH_4) hydrates. Reprinted with permission from Seol.⁸¹ Copyright © 2022, American Chemical Society.

conditions, or the structure of the hydrate, thus retaining the theoretical gas storage capacity of the hydrate. A wide range of kinetic promoters has been investigated to promote the formation of CH_4 hydrates. Among these, surfactants are the most widely used. The addition of surfactants usually reduces the surface tension of water, thereby increasing gas uptake during hydrate formation. Karaaslan and Parlaktuna⁸³ investigated the impact of various surfactants on hydrate formation. The results showed that surfactants did not alter the thermodynamic conditions of hydrate formation. Anionic surfactants promoted hydrate formation at all concentrations tested, while cationic surfactants only promoted hydrate formation at low concentrations. The promotional effect of non-ionic surfactants was lower than that of anionic and cationic surfactants.

Sodium dodecyl sulfate (SDS) is the most widely used kinetic promoter.^{84,85} Liu *et al.*⁸⁵ reported that during hydrate formation in an SDS solution, the transparent liquid film moved forward while the hydrate formed behind it. Zhong and Rogers⁸⁶ were the first to use SDS to promote the formation of natural gas hydrates, achieving a gas storage capacity of hydrates close to the theoretical value. Link *et al.*⁸⁷ found that the gas storage capacity reached 97% of the theoretical value when SDS was used to promote CH_4 hydrate formation. Lin *et al.*⁸⁸ also used SDS to achieve a similar CH_4 storage capacity. In addition to surfactants, amino acids have also been shown to effectively promote the formation of hydrates.

Liu *et al.*⁸⁹ used leucine to promote the formation of CH_4 hydrates, achieving a good gas storage effect. Veluswamy *et al.*⁹⁰ obtained a similar gas storage capacity to that of Liu *et al.*⁸⁹ using leucine combined with intermittent stirring. In addition, Veluswamy *et al.*⁹¹ investigated the morphology of the hydrate in the presence of leucine. Their results showed that at a leucine concentration of 0.3 wt.%, obvious CH_4 bubbles appeared at the gas-liquid interface. These bubbles then gradually moved into the liquid phase during hydrate growth, enhancing the gas mass transfer process. Furthermore, hydrates formed with the assistance of amino acids are relatively loose, which increases the gas mass transfer rate of gas through the hydrate layer. Although surfactants can greatly improve the kinetics of hydrate formation, there are also practical issues with their use:

- (i) Hydrates formed with the aid of a surfactant are relatively loose, which decreases the apparent gas storage density of the hydrate.
- (ii) When the hydrate forms in the surfactant solution, it grows upwards along the reactor wall,^{85,92}

complicating actual production operations and sharply decreasing apparent gas storage.

- (iii) A large number of bubbles are generated during hydrate dissociation, which hinders industrial production. In a system containing amino acids, however, no bubbles are produced during hydrate dissociation,⁸⁹ although the apparent gas storage capacity is affected by the loose hydrate structure.⁹¹

4.3. Combination of thermodynamic and kinetic promoters

Baek *et al.*⁹³ used small CP hydrate seeds to accelerate the formation and growth of CH₄ hydrate in the presence of SDS. At 274.65 K (with an undercooling of 6.743 K), the volume storage efficiency reached 159 mL/mL H₂O within 50 min, with no induction period. In addition, Baek *et al.*⁹³ investigated the effect of the degree of subcooling on hydration formation kinetics, including formation time, conversion rate, and the volumetric storage capacity. The results showed a similar trend of reduced formation time in systems with higher subcooling, as illustrated in Figure 8.

Veluswamy *et al.*²⁸ achieved a water storage capacity of 3.5 kmol/m³ within 1 h in a system containing CH₄, 0.01 wt.% SDS, 5.6 mol% THF, and water at 293.2 K and 7.2 MPa. This demonstrates the synergistic effect of SDS and THF. Sun *et al.*⁹⁴ investigated the impact of L-arginine and isooctyl glucoside on CH₄ hydrate formation. Their results showed that L-arginine could replace traditional alcohols as hydrate inhibitors and that the isooctyl glucoside enzyme was an effective hydrate kinetic promoter for storing CH₄ in hydrate form. Shi *et al.*⁹⁵ investigated the impact of sucrose stearate on CH₄ hydrate gas storage. Their results showed that when the initial pressure exceeded 5.0 MPa, sucrose stearate

significantly increased both the formation rate of CH₄ hydrate and the gas storage. Therefore, the combination of kinetic accelerators and thermodynamic accelerators enables rapid hydrate formation under mild temperature and pressure conditions while achieving higher gas storage capacity.

5. Application of porous media

5.1. Application of dry water

TBAB, THF, CP, and SDS promote the rate of hydrate formation and gas storage by reducing the surface tension at the water/gas interface. However, using these substances can lead to issues such as foaming, precipitation, and hydrate formation on the reactor walls.

To identify new promoters, Li *et al.*⁹⁶ introduced nano-copper particles as a hydrate accelerator for 1,1,1,2-tetrafluoroethane in 2006. Due to its high thermal conductivity, copper can help to efficiently remove the heat released by hydrate formation. Dry water is a type of free-flowing powder consisting of a mixture of water, hydrophilic silica nanoparticles, and air, which is stirred at high speeds.⁹⁷ Wang *et al.*⁶⁴ used dry water to produce CH₄ hydrate, achieving a gas storage capacity of 175 v/v. This suggests that dry water is an excellent material for hydrate-based gas storage. Although the gas storage capacity and hydrate formation rate decreased after the material was used twice, subsequent stirring can improve the gas storage capacity. Hu *et al.*⁹⁸ investigated the formation and dissociation rates, storage capacity, and structural characteristics of dry water CH₄ hydrates. They found that the pressure–temperature conditions significantly influence the induction and reaction times of dry water CH₄ hydrates.

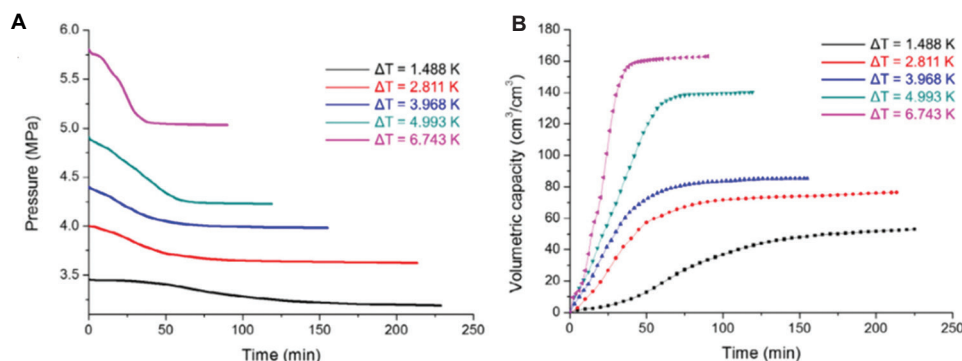


Figure 8. Changes in pressure and gas storage capacity during methane formation under various degrees of subcooling. (A) Pressure profiles and (B) volumetric efficiency profiles during methane hydrate formation with various degrees of subcooling. Reprinted with permission from Baek *et al.*⁹³ Copyright © 2017, Elsevier Ltd.

Park *et al.*⁹⁹ determined the hydrate equilibrium conditions and formation characteristics of dry water, which was produced by mixing water with hydrophobic silica nanoparticles at high speed. They suggested that the silica nanoparticles promote hydrate equilibrium at higher temperatures and lower pressures. This indicates that the rate of hydrate formation is greatly improved due to an increased gas-liquid contact area in the system. Nevertheless, following several cycles of hydrate formation and dissociation, the final hydrate fraction was approximately 20% of that formed during the initial cycle. In addition, Raman spectroscopy revealed that a layer of hydrate shell covered the surface of dry water particles. Following hydrate decomposition, the water produced cannot re-enter the dry water particles, resulting in a decrease in the cyclic gas storage performance. Therefore, it is necessary to address the harsh preparation conditions and limitations in the continuous storage of dry water before its application in hydrate-based gas storage.

5.2. Application of nanomaterials

In addition to silicon nanoparticles and metal oxides, some studies have examined other types of nanomaterials, such as single-walled and multi-walled carbon nanotubes. Zhou *et al.*¹⁰⁰ applied aqueous activated carbon to the hydrate formation system and found that gas storage increased due to the formation of CH₄ hydrates. Yan *et al.*¹⁰¹ investigated the gas storage capacity of CH₄ hydrate in activated carbon of various particle sizes and water-to-carbon mass ratios. In a 20–40 mesh activated carbon bed with a water-carbon ratio of 1.435, the obtained hydrate had a maximum gas storage capacity of 212 v/v at 280 K and 9.49 MPa. The apparent gas storage capacity increased gradually as the water-to-carbon ratio increased. But a rapid decrease in gas storage capacity occurs when the activated carbon particles are fully submerged in the aqueous phase.

Siangsai *et al.*¹⁰² investigated how the size of activated carbon particles affects the formation and decomposition of CH₄ hydrate. Their results showed that activated carbon of any particle size could promote the formation of CH₄ hydrate. Hydrate formation is faster in small-particle activated carbon beds than in large-particle beds. However, the larger connected cages between the large particles result in a higher final water conversion rate. In the experimental study, Siangsai *et al.*¹⁰² added activated carbon with particle sizes of 841–1,680 μm to the hydrate formation system, achieving a water-to-hydrate ratio of 96.5%. In addition, their decomposition

experiments revealed that the CH₄ recovery rate was higher for small particles than for large particles.

He *et al.*¹⁰³ investigated the formation of CH₄ hydrate in the mesoporous MOF MIL-101 using microsecond-scale molecular dynamics simulations. As illustrated in Figure 9, compared to dry MIL-101, the CH₄ storage capacity of water-saturated MIL-101 is significantly reduced compared to dry MIL-101 due to the cavities being occupied by H₂O. However, when the cavity is oversaturated with H₂O, additional H₂O molecules in its outer space can form considerable CH₄ hydrates, significantly increasing the CH₄ storage capacity.

Mu *et al.*¹⁰⁴ used hydrated ZIF-8 for CH₄ storage and obtained a maximum hydrate gas storage capacity of 190 v/v at 269.15 K and 3.0 MPa. However, the adsorption capacity of ZIF-8 accounted for over 55% of the total gas storage capacity, as its maximum water content was only 35.1 wt.%. Because the gas molecules are adsorbed in the ZIF-8 channel through van der Waals forces, once the adsorption equilibrium is broken, a large amount of gas will be rapidly desorbed. Increasing the moisture content of porous media can improve the gas storage density. However, exceeding a critical moisture content threshold results in a swift decline in gas storage capacity. This is because, when the moisture content is high, water blocks the gas channels in porous media, resulting in slow hydrate formation. Therefore, increasing the moisture content of the porous medium can improve the gas storage density to a certain extent, but the moisture content must be kept within reasonable limits.

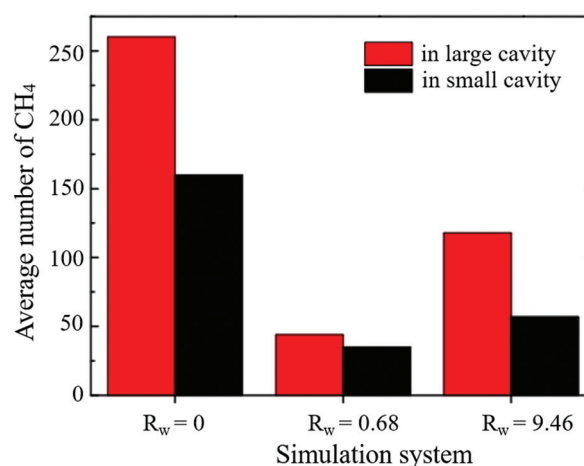


Figure 9. Average number of methane (CH₄) molecules in the large and small MIL-101 cavities with different H₂O contents: $R_w = 0$, $R_w = 0.68$, and $R_w = 9.46$. Reprinted with permission from He *et al.*¹⁰³ Copyright © 2019, American Chemical Society.

Park *et al.*¹⁰⁵ investigated the effect of a low mass fraction (0.001–0.006 wt.%) of multi-walled carbon nanotubes (MWCNTs) on CH₄ hydrate. Their results showed that, compared with the pure water system, the addition of MWCNTs had little effect on the phase equilibrium conditions; however, the induction time was significantly reduced. When the concentration of MWCNTs was 0.004 wt.%, the amount of CH₄ stored increased by almost 300%. Li *et al.*¹⁰⁶ measured the phase equilibrium of the CH₄ + TBAB + MWCNTs system at temperatures between 286.13 K and 293.04 K and pressures ranging from 0.55 MPa to 6.56 MPa. The addition of MWCNTs had a negligible effect on the phase equilibrium conditions; however, MWCNTs were found to significantly reduce the induction time of hydrate formation and increase its growth rate. When the concentration of MWCNTs was 1.0 wt.%, the time required for hydrate formation to begin was reduced by 79.5%. At a concentration of 0.1 wt.%, the addition of MWCNTs increased the hydrate growth rate by 61.5%.

Kim *et al.*¹⁰⁷ studied the formation of hydrates in a system containing CH₄, 5.56 wt.% THF, and 0.003 wt.% oxidized MWCNTs at 273.65 K and 3 MPa. They found that the oxidized MWCNTs had no effect on the phase equilibria in pure water or in a THF aqueous solution. However, the amount of CH₄ gas consumed increased by up to 5.2-fold, and the time taken for hydrate formation was significantly reduced.

Nashed *et al.*¹⁰⁸ studied the effects of carboxylated (COOH-MWCNTs), hydroxylated carbon nanotubes (OH-MWCNTs), and MWCNTs on the equilibrium phase boundary, kinetics, and “self-preservation” effect of CH₄ hydrate. The results showed that MWCNTs had no significant effect on the phase equilibrium conditions of hydrates, but the hydrate formation rate increased significantly when 0.01 wt.% COOH-MWCNTs and 0.03 wt.% SDS were added. The use of a mixed accelerator of SDS and carbon nanotubes was more effective than the use of SDS or carbon nanotubes alone, as shown in Figure 10. In addition, they reported that the “self-preservation” effect of CH₄ hydrate was more pronounced in the presence of carbon nanotubes.

Deng *et al.*¹⁰⁹ studied the effect of the SDS + expanded graphite (EG) system on CH₄ hydrate at 273.2 K and 5.0–8.0 MPa. The results showed that EG promoted both hydrate nucleation and growth. The 0.08 wt.% EG + 0.03 wt.% SDS system was found to improve the hydrate formation kinetics to the greatest extent. At 273.2 K and 6 MPa, the maximum gas storage capacity reached 190.4 STP/g H₂O, and the maximum gas storage rate reached 20.84 cm³·g⁻¹/min. Furthermore,

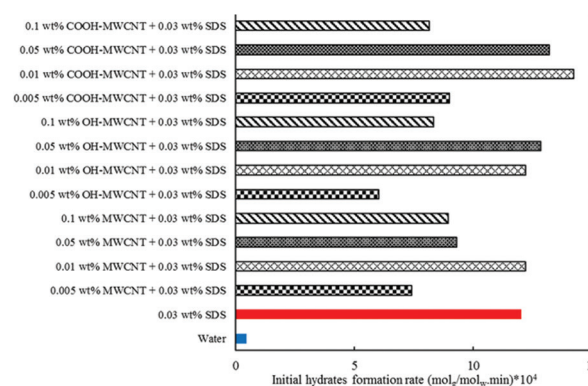


Figure 10. Initial methane hydrate formation rate for the blank sample, 0.03 wt.% SDS, and nanofluids (0.005–0.1 wt.% carbon nanotube + 0.03 wt.% SDS). Reprinted with permission from Nashed *et al.*¹⁰⁸ Copyright © 2019, American Chemical Society.

Abbreviations: COOH-MWCNT: Carboxylated carbon nanotube; OH-MWCNT: Hydroxylated carbon nanotube; SDS: Sodium dodecyl sulfate; MWCNT: Multi-walled carbon nanotube.

under the same temperature and pressure conditions, the gas storage capacity and average gas storage rate of the EG system increased by 1.12–1.37-fold and 1.67–30.17-fold, respectively, compared with other carbon materials such as graphite and carbon nanotubes.

In 2009, Zang *et al.*¹¹⁰ added 5A molecular sieve powder with a particle size of <245 μm to the THF + water system. The results showed that 5A molecular sieve powder increased the crystallization temperature and reduced the decomposition temperature of THF hydrate. The particle size and distribution of the powder also affected the formation and decomposition of the hydrate. In 2015, Kim *et al.*¹¹¹ investigated hydrate formation in a CH₄ + 0.01 wt.% 5A/13X molecular sieve + water system at 275 K and 3 MPa. The results showed that the gas storage capacity was higher in the reaction system containing 5A/×13 molecular sieve than in the oxidized carbon nanotube system. Furthermore, the gas storage capacity of the ×13 molecular sieve system was higher than that of the 5A molecular sieve system. In 2018, Zhao *et al.*¹¹² studied the interaction between the 5A molecular sieve and the accelerator in a CH₄ + 0.01 wt.% 5A molecular sieve + 6.15 wt.% THF/TBAB system at 285 K and 1.5/1.8 MPa. The results showed that a gas storage capacity of 80 mmol/mol of water could be achieved within 10 h.

He *et al.*¹⁰³ investigated the formation of CH₄ hydrate in the mesoporous MOF MIL-101 using microsecond-scale molecular dynamics simulations. They observed

that CH₄ hydrate formed preferentially in the outer region of the MIL-101 cavity rather than within it. The hydrate can only be formed stably in the MIL-101 cavity when outer-region formation is almost complete. This phenomenon occurs because the hydrate clusters formed in the nanopores of the cavity can easily dissociate. They also reported that the CH₄ storage capacity of water-saturated MIL-101 was significantly reduced compared with dry MIL-101. However, when water was supersaturated, water molecules in the outer space of the cavity could form more CH₄ hydrates, significantly increasing CH₄ storage capacity.

Cuadrado-Collados *et al.*¹¹³ studied the formation of CH₄ hydrate in the cavities of the hydrous Cr-soc-MOF-1 and Y-shp-MOF-5 materials. The results showed that the optimal cavity size should be slightly larger than that of a single CH₄ hydrate cell (1.2 nm). The channel of hydrous Cr-soc-MOF-1 contains an excess of CH₄ in the form of CH₄ hydrate, which is approximately 50% larger than the CH₄ adsorption capacity of dry Cr-soc-MOF-1 at 10 MPa. Compared with the pressure (10 MPa) required for CH₄ adsorption by dry Cr-soc-MOF-1, the pressure (2.5 MPa) required for CH₄ hydrate formation in aqueous Cr-soc-MOF-1 was significantly reduced.

6. Outlook

This review highlights a strategy often described as “killing two birds with one stone,” in which CH₄ gas storage and release, as well as saline wastewater treatment, are addressed simultaneously, providing a potential research direction for relevant researchers. However, current studies mainly focus on the use of multi-guest molecules to reduce the thermodynamic conditions required for hydrate formation, and only a limited range of guest molecules has been systematically investigated in the existing literature. The identification of more effective or environmentally benign guest molecules remains an open research question.

Although current studies provide valuable reference information, the application of hydrate technology continues to face challenges, particularly due to the strict formation conditions and relatively slow hydrate formation rates. As a result, many aspects of hydrate-based technology remain insufficiently explored, and further in-depth and detailed investigations are required. Based on the current state of research, the following prospects are proposed:

- (i) Existing evidence has confirmed that the hydrate method can extract pure water from salt-containing

wastewater; however, it remains unclear whether more effective guest molecules can be identified, partly due to limitations in current experimental detection methods. Future research may focus on systematically screening single or mixed guest molecules with milder hydrate formation conditions.

- (ii) Current studies summarized in the literature mainly focus on laboratory-scale experimental treatment of high-concentration saline wastewater; however, the factors affecting water treatment efficiency have not been fully studied. There is still room for optimization of the process flow, and the formation and separation of hydrates require further enhancement. Therefore, future work may involve pilot-scale hydrate-based water treatment studies to explore new solid-liquid separation methods, enhance separation efficiency, and shorten treatment time.

7. Conclusion

Regarding the treatment of saline wastewater using the hydrate method, research on this approach remains in its initial stages. Existing studies indicate that hydrates can form under high-salinity conditions, demonstrating significant potential and promising prospects for saline wastewater treatment using this method. Previous studies on the treatment of saline wastewater using the hydrate method have shown that the removal rate of metal ions can exceed 80%, and the water recovery rate can reach over 70%. This has both important practical value and significant research implications. Given the relative ease of meeting the thermodynamic conditions for hydrate formation, methane (CH₄) is considered a favorable component for hydrate formation.

Regarding CH₄ storage through hydrate technology, substantial progress has been made in hydrate-based gas storage research. Existing evidence has shown that, in the presence of accelerators, the volumetric capacity of CH₄ storage by the hydrate method can reach 100–160 v/v, which is still far from the ideal storage capacity of 216 v/v. On the other hand, the current hydrate method for storing CH₄ still operates at lower temperatures (around 273.15 K) or higher pressures (around 5 MPa). This indicates that the temperature and pressure conditions required for hydrate formation, as well as the formation and conversion rates, and the final gas storage capacity, still restrict the storage and transportation of natural gas using the hydrate method. According to the current research status, the following points are summarized:

- (i) When CH₄ is stored in pure CH₄ hydrate, the “self-preservation” effect of hydrate can be used to store CH₄ at relatively high temperatures and relatively low pressures. However, existing mechanical devices still need improvement, such as agitators and spray devices.
- (ii) The effect of a single accelerator is not ideal when CH₄ is stored by the hydrate method in the presence of accelerators such as TBAB, THF, CP, and SDS. The combined effect of multiple accelerators can be used to improve the temperature and pressure conditions, the rate at which hydrates form, and the gas storage capacity of the CH₄ storage method. Another aspect to note is that the toxicity and volatility of accelerators should be further studied and evaluated to address environmental issues.
- (iii) The formation rate of hydrates can be significantly improved with the help of porous materials such as activated carbon, carbon nanotubes, molecular sieves, and MOF compounds. However, the synergistic mechanism of these materials with accelerators such as TBAB, THF, CP, and SDS still requires further investigation.

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Conflict of interest

The authors declare that they have no competing interests.

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Availability of data

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