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Progress and prospect of hydrate-based desalination technology

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Abstract With the continuous growth of the population and the improvement of production, the shortage of freshwater has plagued many countries. The use of novel technologies such as desalination to produce fresh water on a large scale has become inevitable in the world. Hydrate-based desalination (HBD) technology has drawn an increasing amount of attention due to its mild operation condition and environmental friendliness. In this paper, literature on hydrate-based desalination is comprehensively analyzed and critically evaluated, focuses on experimental progress in different hydrate formers that have an impact on thermodynamics and dynamics in hydrate formation. Besides, various porous media promotion is investigated. Besides, the hydrate formation morphology and hydrate crystal structure with different hydrate formers are analyzed and compared. Moreover, molecular dynamic simulation is discussed to further understand microscopic information of hydrate formation. Furthermore, simulations of the HBD process by considering the energy consumption are also investigated. In conclusion, the hydrated based desalination is a potential technology to get fresh water in a sustainable way.

Keywords gas hydrates, desalination, crystal morphology, molecular dynamic, cold energy

1 Introduction

Freshwater is not only an essential natural resource but also a vital cornerstone of economic and social development [1]. Along with the global population growth, rapid economic technological development, and increasingly

serious water pollution, the shortage of freshwater has attracted global attention [2]. Desalination is a considerably important technology to require freshwater by removing salts from seawater. The traditional desalination technologies mainly include multi-stage flash distillation (MSF), membrane distillation (MD), forward osmosis (FO), reverse osmosis (RO), and electrodialysis (ED) [3]. Currently, RO is used worldwide, and MSF factories have been put into operation. However, these traditional desalination methods have to face the issues of high cost and high energy consumption [4].

After decades of development, the hydrate technology has been widely used in various fields such as gas separation, energy storage, and seawater desalination. Some technologies have entered the pilot stage or realized small-scale industrialization [5]. The hydrate-based desalination (HBD) technology is relatively mature and with the advantage of low energy-intensive because its operational temperature is above the normal freezing point of water [6]. Therefore, researchers pay close attention to the seawater desalination technology based on the hydrate method.

The HBD process uses a gas/liquid component that is captured in “cages” formed by hydrogen bonds in water molecules to form hydrate crystals from saline solution, thereby effectively separating themselves from the salt solution even at temperatures higher than the normal freezing temperature of water [7]. The salt ions hardly participate in the hydrate formation and are excluded from the hydrate cages [8]. Then, hydrate crystals can be dissociated into the freshwater and guest component with heating manners or depressurization, where the guest component can be reused for hydrate formation [9]. Thus, the HBD process has laid a foundation for the formation and decomposition of hydrates.

The proposal of HBD is not an entirely new concept. The HBD technology was proposed as early as the 1940s, but the slow development of the HBD technology could not be fully applied to industry and commercialization [10]. Currently, studies on HBD technology mainly focus

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on the increase of the amount of hydrate formation, the acceleration of the rate of hydrate growth, the shortening of the induction time, and the increase of the salt rejection rate and water recovery rate by adopting different hydrate formers and porous media. Besides, investigations on hydrate crystals of the mechanism, morphology, and microcosmic have been a spotlight in this research area [11,12].

However, there is still a long way to go to commercialize the HBD process. There are three major challenges that block the development of the HBD process: slow kinetics of hydrate formation, crystal separation from saline solution, and the energy consumption required for the HBD process. The state of knowledge on clathrate hydrates makes it possible to overcome crystals separating from the salt solution and slow kinetics of hydrate formation, which is considerably progressive for HBD. This review analyzes and discusses the latest improvement of the HBD technology based on the literature of the last decade.

2 “Special existence” of salt

The HBD process only involves physical changes, and hydrate crystals are non-stoichiometric clathrates [13]. Only water molecules and hydrate formers (gas or liquid) participate in the hydrate formation process that excludes salt ions from the hydrate crystals [14]. Moreover, the hydrate crystals can be removed from the concentrated brine by gravity separation or mechanical separation. After that, crystals can be resolved by depressurization or thermal stimulation. Once dissociated, hydrate crystals discharge pure water and hydrate formers. The concept of the HBD process is illustrated in Fig. 1.

It is crucial to investigate the characteristics of the concentration changes of salt ions during the formation of

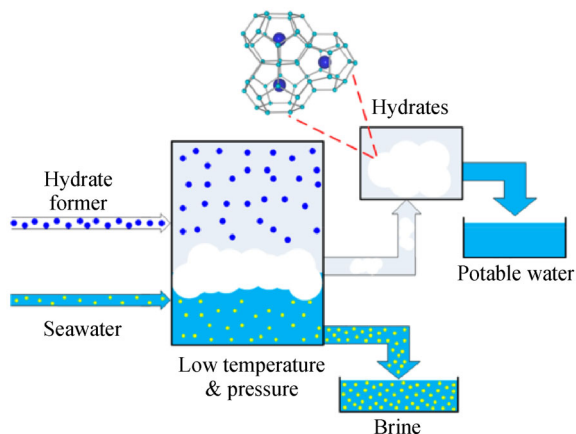


Fig. 1 Concept of HBD process (adapted with permission from Ref. [15]).

hydrates and the removal of salt ions from seawater. Park et al. [16] designed a novel prototype that continuously produced and granulated CO₂ hydrates through the squeezing operation of dual cylinder equipment. This apparatus was used to study the removal efficiency of each salt ion in seawater. It was found that ion removal in the process of hydrate formation greatly depended on the size and charge of the ions. Besides, they also found an interesting phenomenon that the removal rate of Ca²⁺ did not have a linear relationship with its radius and charge, which may be caused by the precipitation of CaCO₃. Cha and Seol [17] evaluated the removal efficiency of high simulated produced water (8.95 wt% salinity) using CO₂ and water-immiscible formers to form double hydrates, which indicated a salt removal rate of higher than 90%. Liang et al. [18] studied the removal rate of Na⁺, K⁺, Ca²⁺, and Mg²⁺, and the influence of ion radius and the number of charges on the salt rejection rate using methane and carbon dioxide as hydrate former. The results showed that the ion with a larger radius was easier to be excluded from the hydrate crystals. However, except for Ca²⁺, the salt rejection rate and the ion charge were nonlinearly correlated. As the charge increases, the electrostatic attraction between the ions and the hydrate particles increases, which resulted in much difficulty in discharging ions.

Salt is not only a thermodynamic inhibitor but also a kinetic inhibitor. Different types and concentrations of salt have distinct effects on hydrate formation. Chong et al. [19] studied the formation and decomposition of methane hydrate in MgCl₂ and KCl salt solutions in the presence of porous media. They proved that the presence of salt inhibited the kinetics of hydrate nucleation and growth. They also found that with the increase of the salt concentration the hydrate formation time increased, while the gas absorption rate and water conversion rate decreased. Compared to MgCl₂, KCl had a weaker inhibitory effect on the formation and decomposition of hydrates, as shown in Fig. 2. A better design of experimental apparatus is beneficial to achieve a high salt rejection rate and the water recovery rate in the HBD process. Babu et al. [20] employed an innovative prototype of a cylindrical annular bed reactor which included a scraper for scrapping the formed hydrate crystals on the mesh, as depicted in Fig. 3. They investigated the salt rejection rate and water recovery rate of a carbon dioxide/propane mixed gas as a hydrate former in porous media and found that the salt rejection rate and the water recovery rate could reach 87.5 (±1.84%) and 34.85 (±0.35%), respectively. However, the hydrate crystals separated from the salt solution still attached with salt particles, which was always a challenge to be addressed. It is necessary to consider more advanced separation methods to solve the existing problem, further improve the water recovery rate, and achieve salt rejection rate.

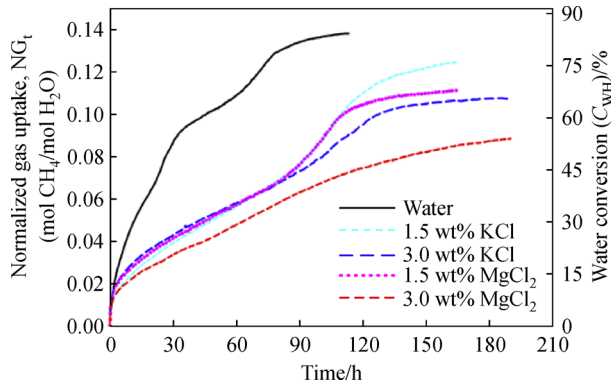


Fig. 2 Kinetics comparison of hydrate formation of water, KCl, and MgCl₂ (adapted with permission from Ref. [19]).

3 Hydrate formers

3.1 Gaseous formers

Due to a key component of hydration reaction, hydrate formers play a decisive role in the selection of pressure and temperature in the reaction process, so the choice of hydrate agents are of vital importance. Commonly used hydrate formers in seawater desalination are carbon

dioxide [21–24], propane [25–27], and methane [28–31], etc. Carbon dioxide is often used as a hydrate former due to its non-toxic and non-flammable properties. Kang et al. [32] believed that carbon dioxide was more suitable as a hydrate former because it had a lower pressure for hydrate formation and even higher salt rejection rate compared with methane. Yang et al. [33,34] discovered that the optimized pressure of carbon dioxide for HBD was 5 MPa by applying the MRI technology. Furthermore, Zheng et al. [35] summarized part of the experimental results of hydrate formation conditions with CO₂ former and mixed formers containing CO₂, as summarized in Table 1.

The formation conditions of a typical methane hydrate with molecular formula as CH₄(H₂O)_{5.75} in pure water are harsh. As the temperature is 5°C, the pressure needs to reach 4 MPa to promote hydrate nucleation. Hu et al. [41] and Lv et al. [42] conducted in-depth studies on the formation of temperature characteristics, phase equilibrium, and kinetics of methane-cyclopentane hydrate formation in saline systems. The results showed that hydrate formation conditions were far lower in the existence of cyclopentane (CP). Besides, the phase equilibrium pressure increased with the increase of temperature.

Propane as a hydrate former is under mild conditions,

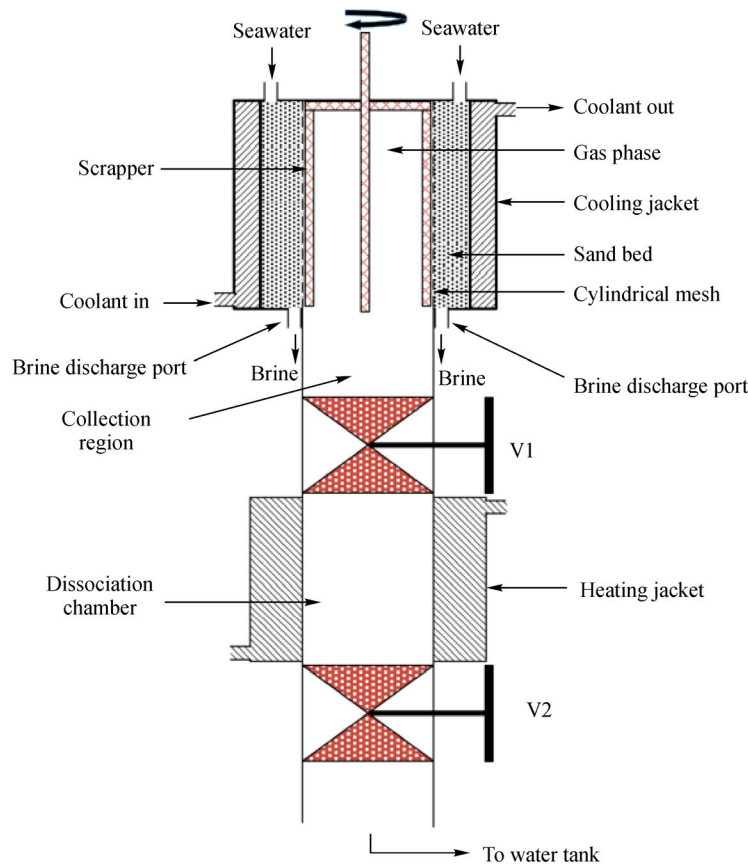


Fig. 3 Novel cylindrical annular bed reactor along with scrapper (adapted with permission from Ref. [20]).

Table 1 Several phase equilibrium experiments of hydrate systems containing CO₂

Author	Formers	Salt solution	Temperature/K	Pressure/MPa
Sun et al. [36]	CO ₂	NaCl	273–282	2.1–4.2
Yang et al. [37]	CO ₂	NaCl	269–284	1–5
Maekawa [38]	CO ₂	Acetone	269–281	1–4
Yang et al. [34]	CO ₂	NaCl	273–284	6–8
Yang et al. [25]	CO ₂ + C ₃ H ₈	NaCl	271–284	0.8–3.6
Zheng et al. [39]	CO ₂ + CP*	NaCl	280–286	0.5–3.6
Matsumoto et al. [40]	CO ₂ + CP*	–	287–293	0.9–3.5

Note: CP* represents cyclopentane.

which only requires about 0.6 MPa at 5°C to form propane hydrate. Besides, propane is also a hydrate promoter that can reduce the phase equilibrium pressure and increase the temperature required for hydrate formation. In recent years, an increasing amount of attention has been paid to investigating the mechanism of propane hydrate. Nambiar et al. [43] studied the influence of propane as a hydrate promoter on hydrate formation after mixing with nitrogen, argon, and carbon dioxide in porous media. They found an interesting phenomenon that in the process of propane hydrate formation, due to the migration of water molecules to the gas phase region, the water dispersed in silica sand can move to the hydrate formation areas to accelerate hydrate growth. Babu et al. [44] elucidated the same phenomenon that propane acted as a guest molecule to form hydrates in silica sand. Sahu et al. [45] selected five gases of carbon dioxide, methane, ethane, propane, and isobutane to simulate hydrate formation in different concentrations of brine, and predicted the phase equilibrium and gas solubility in the aqueous phase. They also discussed the influence of thermodynamic data on the HBD process and concluded that propane and ethane were the optimal choices for desalination.

3.2 Liquid formers

Some researchers have proposed a concept that uses the liquid as hydrate formers to form hydrates for seawater desalination. Currently, the commonly used liquid hydrate formers mainly include R141b [46], THF (tetrahydrofuran) [47], TBAB (tetra-*n*-butyl ammonium bromide) [48], R134a [49], cyclobutanone [50], and CP [51–53]. Some liquid can be used not only as hydrate formers but also as additives to promote hydrate formation, which can be divided into thermodynamic and kinetic promoters, as tabulated in Table 2. Liu et al. [54] employed THF to study

Table 2 Chemical additives for HBD

Thermodynamic additives	Kinetic additives
THF	SDS
TBAB	SDBS
CP	APG

the effect of subcooling on hydrate formation and the memory effect of the hydrate. The results showed that extreme subcooling and hydrate memory effect could accelerate hydrate formation and shorten the induction time. Due to the limitation in the enhancement of the single former, to obtain the desired results, it is extremely vital to combine the several different formers or use promoters and additives for hydrate formation [35].

The researchers found that CP is a promising liquid former for HBD since it can form hydrates at atmospheric pressure above freezing point and has a low solubility in water. The water conversion to hydrate and salt rejection rate when CP is employed as former under different reaction conditions are listed in Table 3. Lv et al. [55] illustrated the formation kinetics of CP hydrate in the CP dispersion system. The results showed that the temperature and the concentration of the solution were inversely proportional to the amount of hydrate formed. The amount of hydrate formed decreased, while the salt rejection rate increased with the climb of the temperature and solution concentration. Xu et al. [51] investigated the effect of CP hydrate on HBD at atmospheric pressure and a temperature below 7.7°C. The final results demonstrated that the hydrate formation time decreased and the conversion of hydrate increased with the increase of subcooling and agitation, as exhibited in Fig. 4. Besides, researchers found that mechanical methods including stirring [52], spraying [56], and bubbling [57,58] can enhance the amount and rate of hydrate formation. The reason for this is that mechanical methods can enlarge the contact surface of liquid former and water, which can improve the mass transfer rate.

CP can be used not only as a hydrate former but also as an additive to promote hydrate formation. Lv et al. [59] added a mixture of CP with methane to inspect hydrate formation and studied the effects of the CP/liquid phase volume ratio and the volume of the liquid phase on the rate of hydrate growth. The results showed that the higher volume ratio of the CP/liquid phase was beneficial to the rapid hydrate formation. Zheng et al. [39] discussed the thermodynamic properties of CO₂-CP hydrates, where CP was chosen as hydrate former. They found that the phase

Table 3 Water conversion to hydrate and salt rejection rate CP under different conditions

Author	Formers	Temperature/K	Pressure/MPa	Water conversion rate/%	Salt rejection rate/%
Lv et al. [55]	CP	274.1–277.1	–	–	69%–82%
Han et al. [60]	CP	274.1–277.1	Atmospheric	–	9%–98%
Xu et al. [51]	CP	271.15	Atmospheric	3.92%–35%	81%
Han et al. [53]	CP	274.1–277.1	–	41.2%–53.3%	53.7%–70.8%

equilibrium conditions of CO₂-CP hydrates moved to low pressure and high temperature along with the addition of CP.

4 Porous media for HBD

Due to the limited promotion of hydrate formers, it is better to combine the benefits of various types of porous media during the hydrate formation process to get the desired results. Currently, researchers considered porous media as a carrier that can enlarge the contact surface and is favorable to the hydrate nucleation resulting in improving

the formation kinetics [11,61–63]. The most commonly studied porous media include graphite, silica sand, and silica gel, activated carbon, and glass beads, as presented in Table 4. Li et al. [64] examined the kinetics of hydrate formation with methane as a co-guest in porous media and concluded that the initial gas and water saturation were important factors that determined the kinetics of hydrate formation. Moreover, the rate of hydrate nucleation was closely related to the initial phase saturation and the characteristics of porous media, which demonstrated that porous media had an extraordinary effect on the kinetics of methane hydrate formation. Linga et al. [26] compared two gas/liquid contact modes that were conducted in a silica sand bed with a stirred vessel for each gas/gas mixture to evaluate the rate of gas hydrate formation. The results implied that the hydrate formation rate in a silica sand bed was larger than that in a stirred vessel, which also led to a higher rate of water conversion. Li et al. [65] demonstrated that the desalination process supported CP hydrate via graphite at atmospheric pressure could promote the nucleation and growth of hydrate, which can solve the stochastic nucleation process and considerably reduce induction time. Furthermore, the added graphite can improve the salt rejection rate as well. After 5 h, the highest hydrate conversion rate was about 32.5%, which proved that graphite improved the conversion rate of a hydrate.

Different types of porous media have different influences on the kinetics of hydrate formation and the location of hydrate nucleation. Babu et al. [69] investigated the formation and separation of methane hydrate in silica sand and activated carbon, respectively. It turned out that the hydrate crystals forming in the interstitial pores between silica sand particles were observed. However, hydrates nucleated on the surface of the activated carbon particles. Subsequently, Babu et al. [70,71] adopted an effective medium pressure hydrate-based gas separation (HBGS) process to evaluate the capability of silica sand and silica gel as a carrier. It was found that the rate of hydrate formation in silica sand increased as the water conversion rate improved. Compared with silica gel, silica sand is an effective porous medium for hydrate formation. Moreover, besides the influence of the type of porous media on the kinetics of hydrate formation, different pore diameters of the porous media and the filling height in the reactor also affect the kinetics and induction time of hydrate formation.

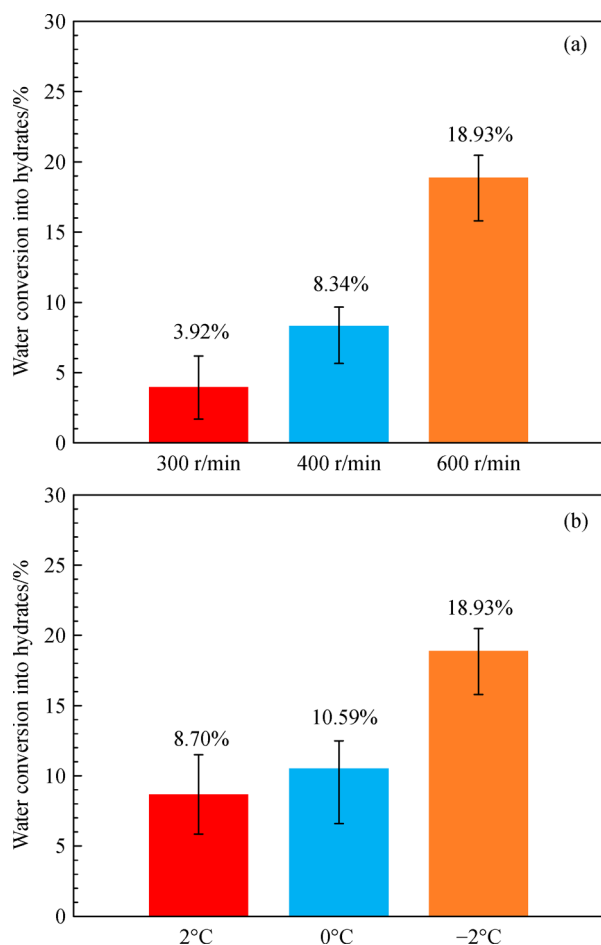


Fig. 4 Effect of (a) stirring speed and (b) operating temperature on hydrate formation (adapted with permission from Ref. [51]).

Table 4 Different types of porous media

Author	Type	Particle diameter/ μm	Temperature/K	Pressure/MPa	Water conversion to hydrate/(mol %)
Mekala et al. [66]	Silica sand	100–500	277.15	8.0–10.0	11.6
Kang et al. [67]	Silica gel	0.025–0.1	274.15	7.5–9.0	13
Siangsai et al. [68]	Activated carbon	250–1680	277.15	8	75.5–96.5
Li et al. [65]	Graphite	1.6–15	275.15	Atmospheric	86

Mekala et al. [66] conducted the methane hydrate formation in silica sand with different pore diameters and concluded that the small pore diameter could increase the rate of hydrate formation. Babu et al. [44] considered the formation of hydrate in different silica sand bed heights. The results indicated that the conversion of water, gas uptake, and the hydrate formation rate decreased with the increase of the bed height.

Porous media with a specific wettability may be a carrier that allows water molecular and hydrate formers to co-attach on the surface of the media, which can increase the connection surface between water and gas [72]. However, porous media which is used to accelerate hydrate formation has trouble in separating hydrate crystals from the porous media, and the formation of hydrate has mass transfer effects on porous media, which hinders the formation of hydrate to a certain extent [73]. Thus, researchers should focus on the development of novel devices that can easily separate hydrates from the mixture of porous media and salt solutions.

5 Morphology of hydrate

Clathrate hydrates are nonstoichiometric compounds that are formed when guest molecules are bound into hydrogen-bonded water cages by Van der Waals forces at moderate temperature and pressure [59,74,75]. It is reported that hydrates exist in three structures, namely sI, sII, and sH hydrates. They are dependent on shapes, cage sizes, lattice parameters, and the number of water molecules forming unit structure [76,77]. For example, sI hydrates include 46 molecules of water and comprise two small cages and six large cages. The sII unit cell composes 16 small cages and eight large cages formed by 136 water molecules while the unit cell of sH consists of three small cages, two medium cages, and one large cage contained by 36 molecules of water. Figure 5 displayed the concept diagram of the sII propane hydrate crystal formation.

With the development of the HBD technology, it is necessary to inspect the morphology of hydrate crystals. Morphology researches and visual observation are helpful in evaluating the hydrate nucleation and growth in macroscopic levels [78]. Morphological observation is a method to study the hydrate formation behavior on the microscale and comprehend the dynamic of hydrate growth based on the properties of hydrate crystals (sizes,

shapes, and the direction of hydrate growth) [79]. Furthermore, the purpose of HBD is to promote the kinetics of hydrate formation and decompose it to get freshwater. Thus, morphology studies will be favorable to design the appropriate reactor to realize fast gas uptake with rapid kinetics [80]. Hydrate morphology in the presence of salt provides better knowledge to understand the nucleation of hydrate at the interface and hydrate growth for the HBD technology. The nucleation of hydrates is stochastic, predominantly at the gas-liquid interface. Kishimoto et al. [81] studied the development of hydrate crystal with CP as co-guest and morphology at the interface with different mass fraction aqueous from 0.050 to 0.264. They found that the crystal morphology of CP hydrate crystal changed significantly with the subcooling degree ΔT_{sub} . Moreover, the shape of CP hydrate crystals covering the interface significantly varied with the degree of subcooling, as shown in Fig. 6. It can be seen the size of hydrate crystals decreased gradually with the increase of subcooling. Different hydrate crystal shapes were shown in Fig. 6, with irregular hexagon or pentagon becoming slender polygon. Besides, the growth rate of hydrate film decreased with the decrease of ΔT_{sub} and the increase of NaCl concentration.

Peng et al. [82] and Cai et al. [83] also demonstrated that the morphology of hydrate crystals was dependent on the subcooling degree of the system. The size of hydrate crystals decreased with the increase of subcooling, while

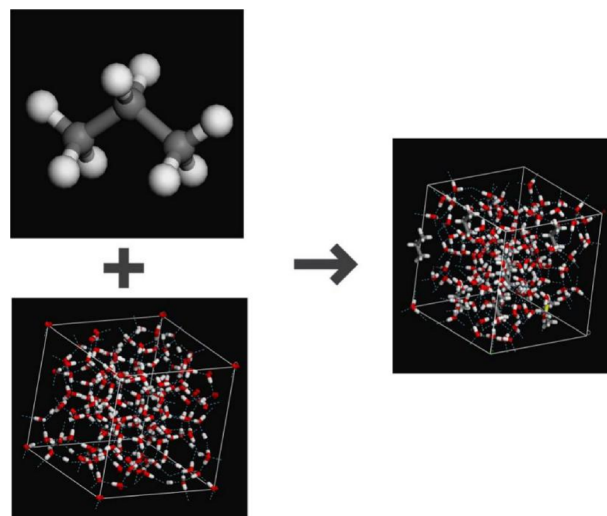


Fig. 5 Concept diagram of the sII propane hydrate crystal formation.

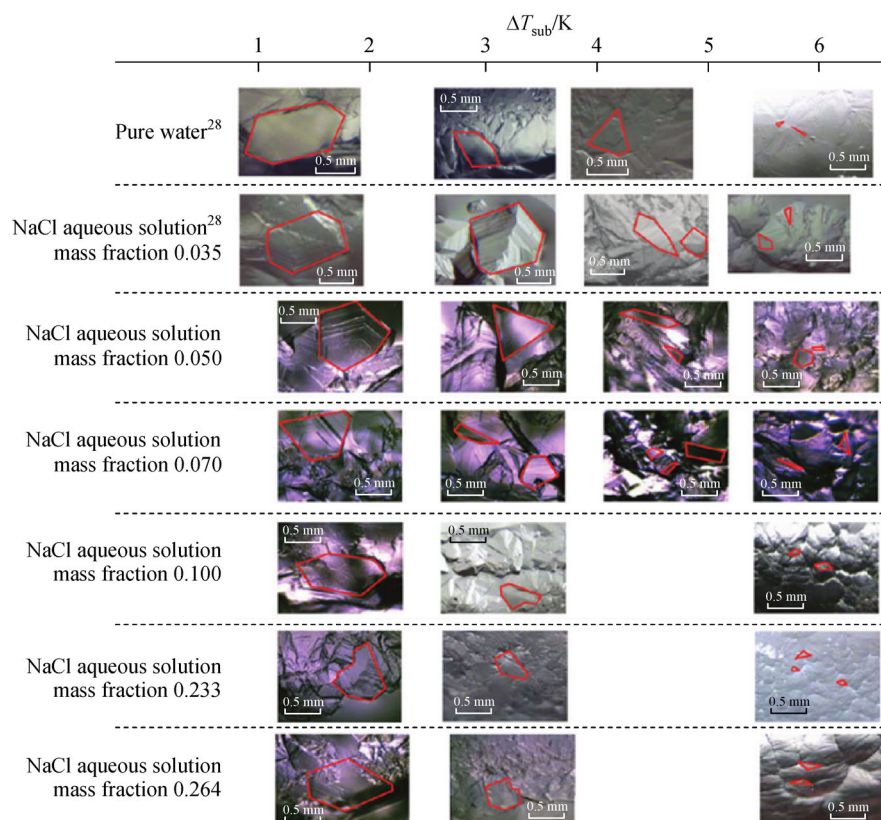


Fig. 6 Categorization of hydrate crystal observations along shaft of subcooling and aqueous solution (adapted with permission from Ref. [81]).

the type of guest molecules had small impacts on the size of hydrate crystals. Some morphology studies investigated hydrate crystals using porous media including silica sand, activated carbon, graphite, and hollow silica [71,84–86]. Babu et al. [71] compared the formation and separation of methane hydrate in the two porous media of activated carbon and silica sand and found an interesting phenomenon in the experiment. The hydrate formation in activated carbon occurred together with hydrate decomposition, as shown in Fig. 7. When the time was 400 s, the shape of hydrate can be seen. However, when the time reached 800 s, the hydrate crystals were decomposed. In spite of many morphological observations that have been investigated for hydrate promoters, there are lack of studies on the mechanism of hydrate formation with hydrate formers in porous media.

6 Molecular dynamic simulation study of hydrate formation

Currently, researchers have concentrated on experimental research to observe hydrate nucleation and formation by macroscopic measurements. However, experimental methods to realize microscopic observation on hydrate growth

process is still greatly limited [87,88]. The molecular dynamic (MD) simulation technology has proved to be an all-powerful tool to investigate the behavior of complex systems, which can give information on structural and dynamical properties at the molecular level. Therefore, molecular dynamic simulation is an effective method to deeply understand the nucleation and growth mechanisms of clathrate hydrate [89–91].

Molecular dynamic simulation studies primarily focus on methane and CO₂ hydrate nucleation and growth in pure water [92–96]. Tung et al. [95] discussed the growth rate of methane hydrate and growth mechanisms of methane hydrate by MD simulation, as shown in Fig. 8. It turned out that three key factors dominate the rate of methane hydrate formation: the methane solubility in the liquid phase, the adsorption of methane by incomplete water cages methane filled with methane at the solid-liquid interface, and the diffusion rate of methane in water. Bai et al. [91] investigated the mechanism of CH₄ hydrate replaced by CO₂ molecules through microsecond MD simulations. First, they melted CH₄ and then replaced CH₄ hydrate by CO₂ molecules. They found that a large number of hydrate residuals of CH₄ hydrate facilitated the CO₂ hydrate nucleation and enhanced the dynamic of the hydrate formation process, confirming the existence of the

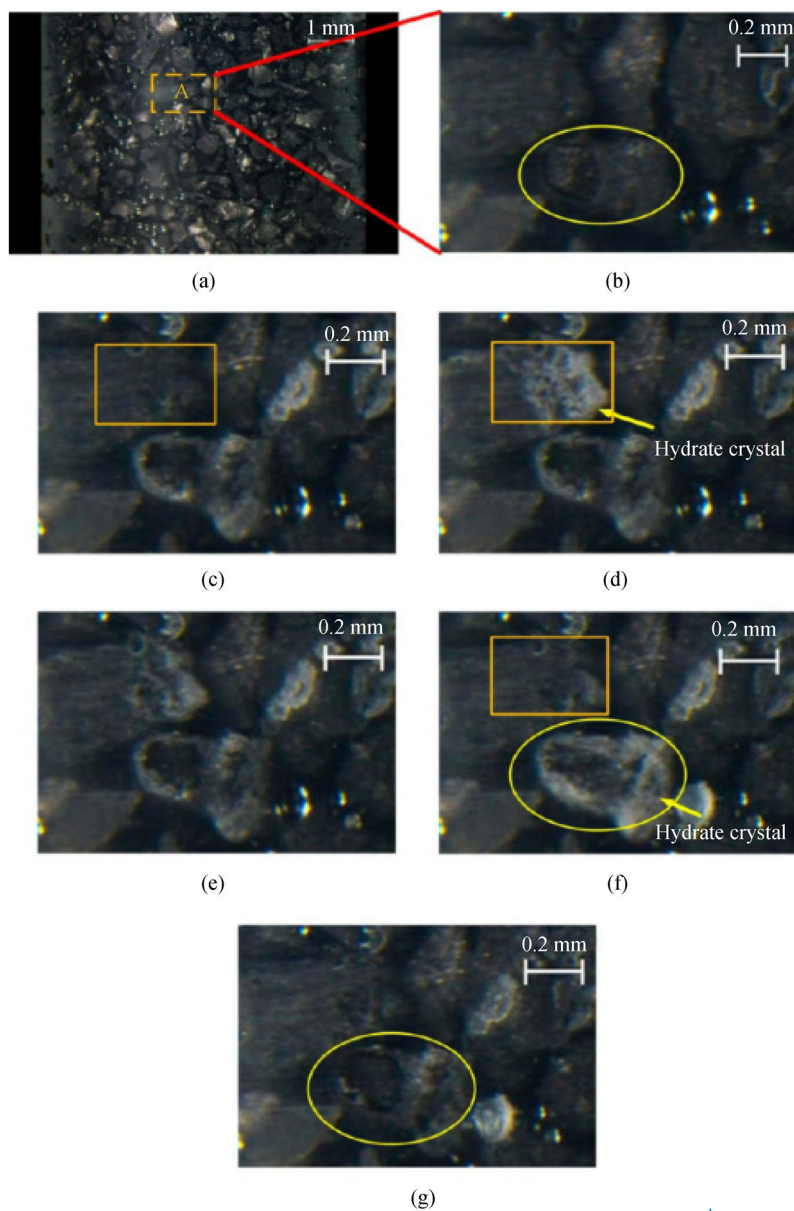


Fig. 7 Sequence images of methane hydrate formation in activated carbon (adapted with permission from Ref. [71]).
 (a) $t = 0$ s; (b) close up of (A), $t = 25$ s; (c) $t = 250$ s; (d) $t = 275$ s; (e) $t = 300$ s; (f) $t = 400$ s; (g) $t = 800$ s.

so-called “memory effect.” Liu et al. [97] discussed the mechanism of CO_2 hydrate formation in order to understand the displacement process and the variations of relevant parameters.

Few studies were conducted on MD simulation of hydrate in the presence of sodium chloride. In recent years, due to the popularity of the HBD technology for salt removal, some researchers introduced MD simulation of hydrate with the presence of NaCl, one of the major components in seawater [98–100]. Tung et al. [101] investigated the methane hydrates such as structure, thermodynamic, and dynamic characteristics in salt solution and confirmed that NaCl was a thermodynamic

inhibitor. Based on MD simulation, it could be clearly observed that salt particles replaced water molecules to participate in the construction of the cage. Bai et al. [99] constructed a simulation box with 7000 water molecules and 500 methane molecules to simulate methane hydrate nucleation and growth in salt solutions, as shown in Fig. 9. The results proved that electric charge and concentration of ions inhibited the formation of hydrate, and ions had dual influences on CH_4 mass transfer. Regarding molecular dynamics simulation, which mainly studied the nucleation and growth of methane and CO_2 (sI hydrate) hydrates, there is a lack of literature on MD simulation of sII hydrates formation. Thus, researchers should pay more

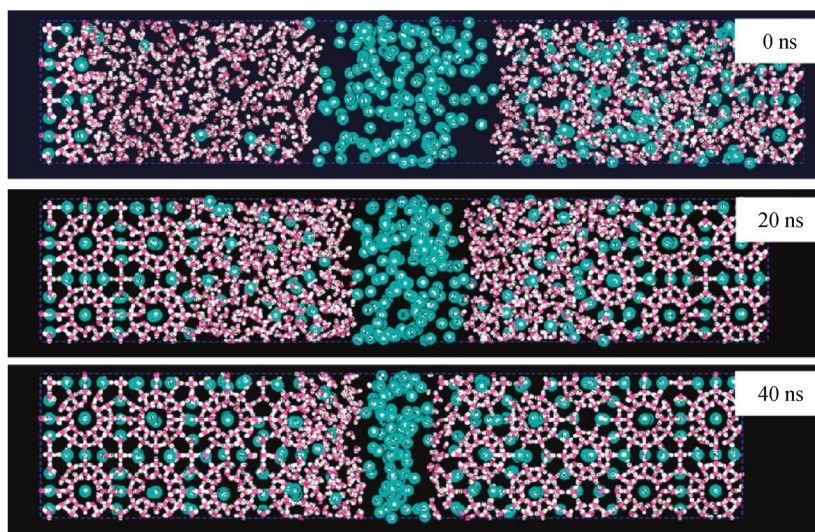


Fig. 8 Snapshots taken from methane hydrate growth simulation at 60 MPa and 260 K (adapted with permission from Ref. [95]).

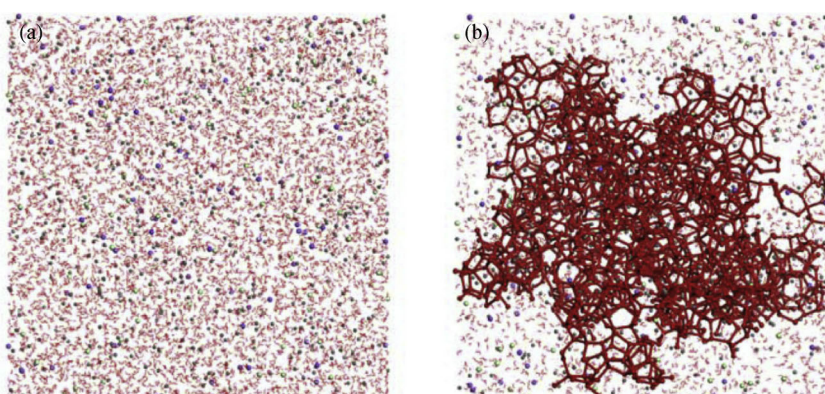


Fig. 9 Simulation box (adapted with permission from Ref. [99]).
(a) Typical initial constructions of the simulation system; (b) hydrate growth stage.

attention to investigating nucleation and growth of sII hydrates such as propane and CP, preferably in saline solution, which could provide further guidance and reference for the HBD technology.

7 HBD system

One of the reasons why HBD technology could not be commercialized is high energy consumption to achieve the required low temperature and high-pressure [100]. Although many studies focused on studying suitable promoters, surfactants, porous media, and innovative equipment for the HBD technology, few research were conducted on the HBD technology from the perspective of process system engineering to reduce energy consumption. The hydrate formation process is energy-consuming because the formation of hydrate crystals from salt solution

requires low-temperature and high-pressure conditions and additional energy [103]. It is imperative to improve its energy-intensive defects and increase its technical and economic performance. Javanmardi and Moshfeghian [104] discussed the energy consumption and economic efficiency of the proposed HBD technology. Compared with other desalinations, they found that the HBD technology was more competitive. Long et al. [105] introduced a novel HBD process based on the improvement of the compression refrigeration cycle and analyzed the energy-intensive and economic performance of the process. The results indicated the yield of freshwater had a significant impact on energy consumption and production costs. As the yield ratio increased, the corresponding total energy consumption and total production costs decreased. However, increasing the yield of freshwater required improving the kinetics and thermodynamic of hydrate formation and choosing appropriate promoters. Deng et al.

[106] used a self-developed double reactor with a storage tank container to conduct different levels of desalination and analyzed the economic and energy consumption of seawater desalination in different processes. Yang et al. [107] proposed an HBD plant using CO_2 with a compression refrigeration cycle. They analyzed the exergy and energy consumption of the CO_2 HBD unit with the compression refrigeration cycle and found that the exergy loss of the throttling device and the remaining components was 15 kJ/kg and 3–8 kJ/kg, respectively.

Recently, the combination of the HBD technology with the LNG cold energy utilization technology has attracted extensive attention. The employment of LNG cold energy can significantly improve the energy utilization and operation efficiency of the system. He et al. [108] simulated the traditional hydrated-based desalination process with a model in Aspen HYSYS. The methodology adopted LNG cold energy to replace the external refrigeration cycle during the traditional HBD process to cool down the hydrate former, seawater, as plotted in Fig. 10. The results showed that the utilization of LNG waste cold energy for the hydrated-based desalination process could reduce the lowest specific energy consumption to 0.60 kWh/m³, which indicated that this process was

charming to the industry. Chong et al. [109] evaluated the economic feasibility of the HBD process based on LNG cold energy utilization in Singapore. According to a comprehensive assessment of equipment investment and operating costs, the levelized cost of water (LCOW) could be reduced from \$9.31/m³ to \$1.11/m³ by integrating LNG cold energy, as shown in Fig. 11.

He et al. [102] further studied the HBD technology with CP as hydrate former using LNG cold energy. They compared the unit energy consumption of propane and CP as hydrate and discussed the influence on the rate of water recovery, the temperature of hydrate formation and pressure of heating seawater, exergy efficiency, and fixed capital investment (FCI). Future research should focus on reducing the specific energy consumption and improving the technical and economic performance of the HBD process with different hydrate formers or additional external conditions to strengthen the energy-water nexus.

8 Conclusions and prospect

Based on the analysis of the literature in recent years, this paper discussed the latest research progress and applica-

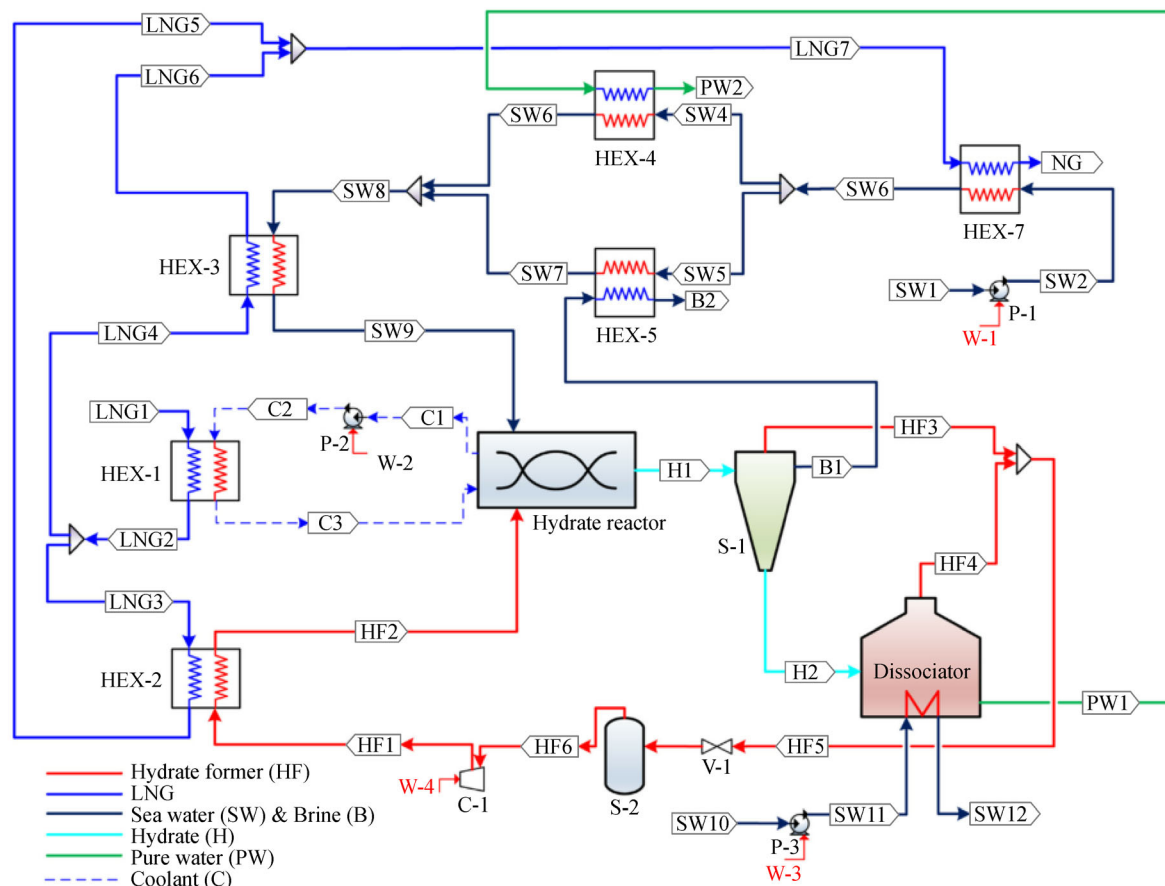


Fig. 10 Flowchart of Cold En-HyDesal process with hydrate former recycling (adapted with permission from Ref. [108]).

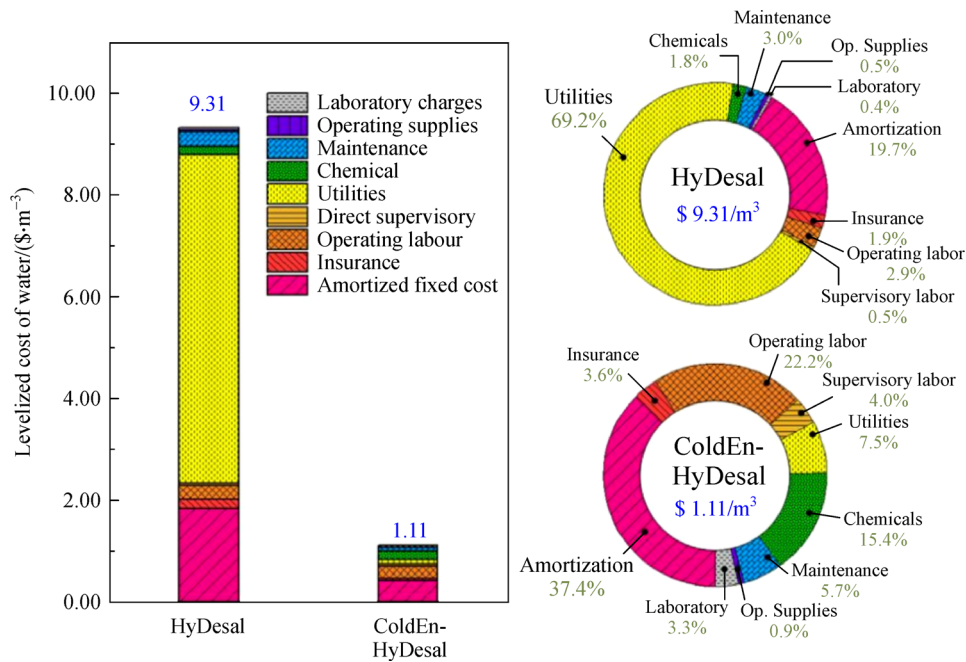


Fig. 11 Break down of LCOW for HyDesal and ColdEn-HyDesal (adapted with permission from Ref. [109]).

tions of the HBD technology. First, the selection of hydrate formers and the effect of different types of porous media on the rate of hydrate formation and salt rejection were analyzed and summarized. Then, different forms of hydrate crystals and molecular dynamics simulation were evaluated to study the mechanism of hydrate formation and decomposition. Finally, through the combined process of LNG cold energy with the HBD process, the unit energy consumption of freshwater can be greatly reduced, indicating that the utilization of LNG cold energy is a hopeful solution to realize the commercialization of the HBD technology.

However, the challenges of slow hydrate formation kinetics, the potential environmental pollution, the crystal separation from brine, and the high energy consumption for the HBD technology have not yet been completely resolved. Therefore, future research should focus on developing sustainable technologies combining the utilization of LNG cold energy, choosing suitable gas/liquid as a guest, and reforming reactor designs, and focusing on the combinations of diverse hydrate formers to shorten the induction time. Besides, energy analysis and cost estimation are also critical factors affecting the industrialization of hydrate desalination. It is necessary to further develop innovative energy-efficient technologies.

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Notations

APG	Alkyl polyglycoside
CP	Cyclopentane
ColdEn-HyDesal	HBD using LNG cold energy
FCI	Fixed capital investment
HBD	Hydrated-based desalination
HBGS	Hydrate-based gas separation
HyDesal	Hydrate-based desalination
LNG	Liquefied natural gas
LCOW	Levelized cost of water
MD	Molecular dynamic
SDS	Sodium dodecyl sulfate
SDBS	Sodium dodecyl benzene sulfonate
THF	Tetrahydrofuran
TBAB	Tetra- <i>n</i> -butyl ammonium bromide

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