



HAL
open science

Gas Clathrates: Environmentally Benign Materials for The Energy Transition.

Ahmed Omran, Nikolay Nesterenko, Valentin Valtchev

► **To cite this version:**

Ahmed Omran, Nikolay Nesterenko, Valentin Valtchev. Gas Clathrates: Environmentally Benign Materials for The Energy Transition.. The Catalyst Review, 2021, 34 (11), pp.6. hal-04258230

HAL Id: hal-04258230

<https://hal.science/hal-04258230>

Submitted on 25 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Gas Clathrates: Environmental Benign Materials for the Energy Transition

Ahmed Omran^a, Nikolai Nesterenko^{b*}, Valentin Valtchev^a,

^{a,*}Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14050, Caen, France

^bTotal Research and Technology Feluy, Zone Industrielle C, 7181 Feluy, Belgium

*To whom correspondence should be addressed:

(Nikolai Nesterenko) nikolai.nesterenko@totalenergies.com; Tel: +32 (0)4 86 20 73 22

1 Introduction

Clathrate hydrates are non-stoichiometric “ice-like” materials or inclusion compounds that are composed of water molecules connected by H-bonding in the form of three-dimensional cavities. They exist in nature or can be synthesized artificially. Hydrate cavities or ‘cages’ are usually stabilized by gases such as CH₄, H₂, CO₂, O₂, Ar, Kr or via some organic solvents. Thermodynamic analysis shows that the hydrate cages cannot be completely occupied which confirms the experimental observations of the non-stoichiometric nature of these compounds [1,2].

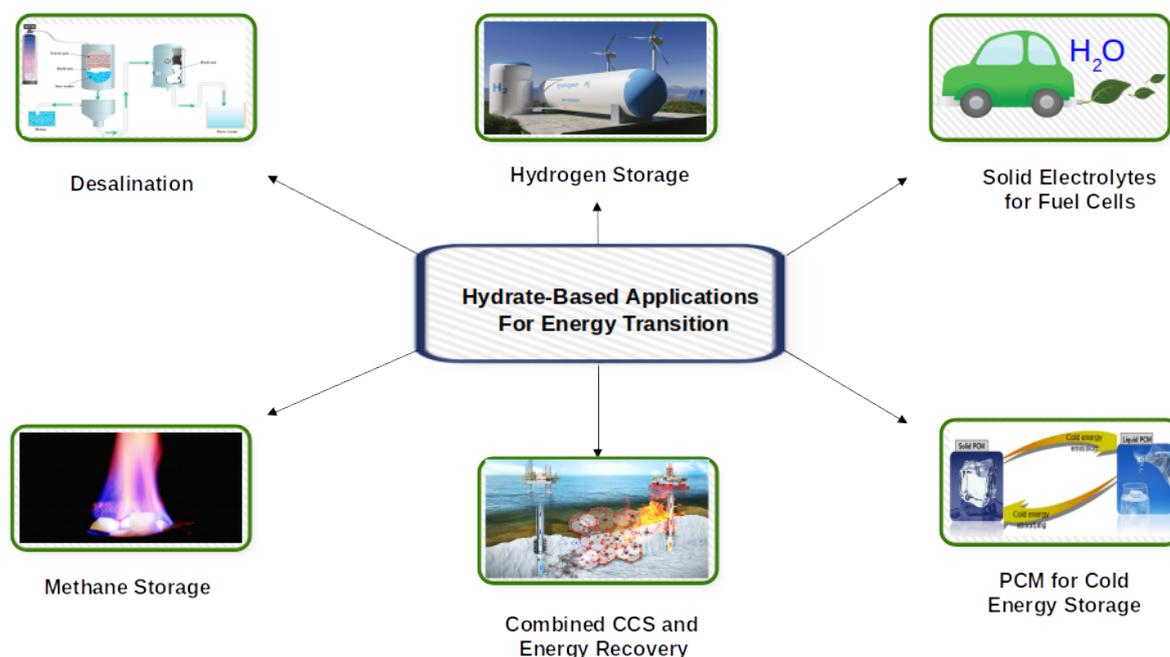


Figure 1: Gas hydrates potential technological applications for energy transition

The recent development of computational approaches and analytical tools has enabled us to accurately determine various gas hydrate structures. In situ XRD, NMR and Raman measurements provides a vital information about different molecules in the structure and cage occupancy in addition to thermodynamic and kinetic data. There are 3 kinds of interaction in clathrates: (1) host-host interactions between water molecules, (2) guest-guest interaction between encapsulated gas molecules and finally (3) guest-host interactions. They are all important to understand clathrate formation, stabilization, and dissociation. A nature of guest-host interaction is used to classify clathrates into two main categories (1) clathrate hydrate and (2) ionic clathrates or (semi clathrate).

Although there is a variety of clathrate hydrate structures, the most common ones are sI, sII, and sH. They attracted more attention due to their moderate formation conditions. The natural gas hydrates belong to this class of clathrate. Similar to other crystalline hydrates, the clathrate structure formation depends on factors such as pressure, temperature, and the nature of guest species. To illustrate, one can find that

methane forms sI clathrate below 120 MPa. If the pressure increased to 250 MPa, sII clathrate is obtained. Moreover, further increase to 600 MPa will transform that structure to sH.

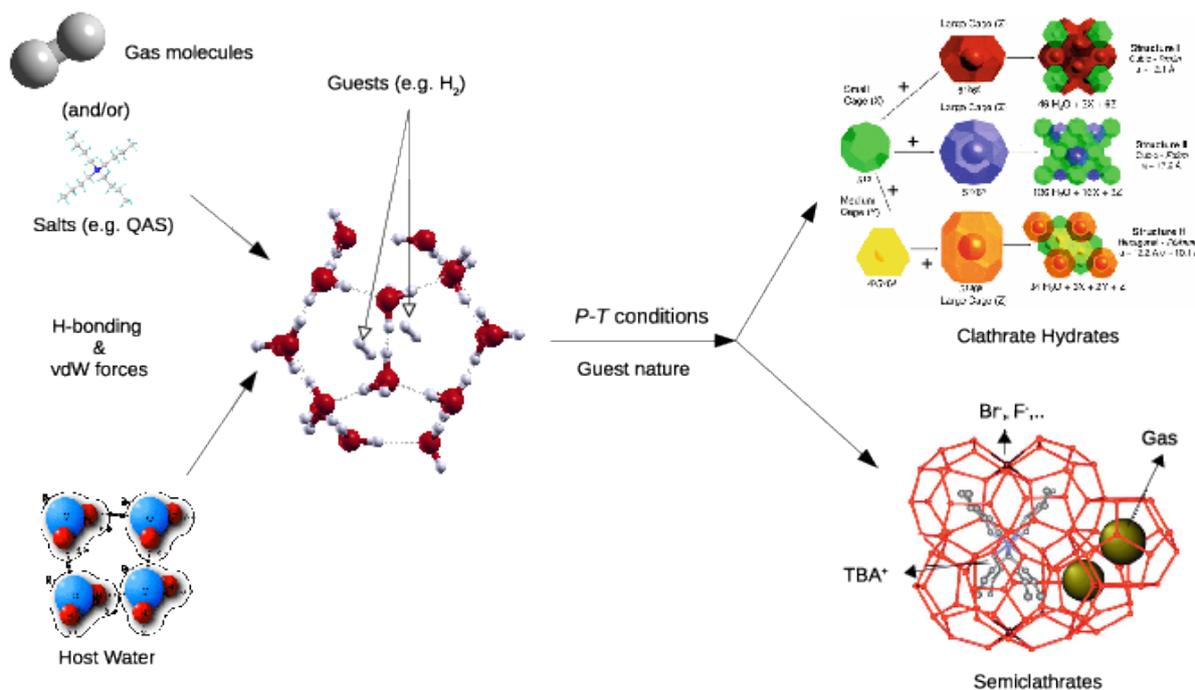


Figure 2: Common hydrate structures includes clathrate hydrates and semi clathrates

sI has unit cell consists of 46 water molecules and shows space group of $Pm3n$. The water molecules are arranged in two kinds of cages - 2 small cages of pentagonal dodecahedra (5^{12}), and 6 large cages of tetrakaidecahedra ($5^{12}6^2$). This structure is the most natural abundant clathrate on earth and can enclathrate small guest molecules (0.4-0.55 nm) such as pure CH_4 or CO_2 at relatively high pressures. sII consists of 136 water molecules organized in 16 (5^{12}) and 8 hexakaidecahedra ($5^{12}6^4$) with space group of $Fd3m$ and lattice parameter of 17.3 Å. This structure can accommodate larger guest molecules (0.6-0.7 nm) in its large cages. Finally, sH -reported to be isostuctural with hexagonal clathrasildodecaasil 1H- showed smaller unit cell of only 34 water molecule but with 3 different sizes of the cages: 3 small (5^{12}), 2 medium irregular dodecahedra ($4^35^66^3$) and a large icosahedra ($5^{12}6^8$) cages. Then, its cages can be occupied by both small and large guest molecules. One should note that it is not only the guest size that control the hydrate structure formation but also the nature of guest molecules and $P-T$ conditions. For example, hydrogen and nitrogen naturally form sII clathrate and they can transform from sII to sI under pressure. It should be noted that the cage occupancy -and thus storage capacity- depends for a great extent on whether each cage can afford multiple cage occupancies. In all structures, it is commonly reported that large cages can be fully occupied. However, small cages tend to have lower occupancies depending on the type of guest molecules and $P-T$ formation conditions. However, the cage occupancy is not a necessary requirement for clathrate stability although it can effectively contribute to that. To illustrate, a pure CH_4 sI hydrate can store about 172 v/v, the maximum storage capacity of binary CH_4 -THF sII can reach approximately 112 v/v only but at relatively lower pressure.

Semi-clathrate hydrate is an important class of clathrate, which has received less attention until they showed increased number of examples in gas separation [3] and energy storage [4]. They can be distinguished from clathrate hydrates by showing partial hydrogen bonding between the guest species and the water host cages in addition to van der Waals interactions. This type of clathrate is considered ionic due to the encapsulation of hydrophobic cations or anions into hydrate cages and the incorporation of counter ions into the water framework. In other words, the walls of cages are partially removed or replaced by anions or apart from guest molecules in addition to the hydrophobic inclusion that exist in clathrate hydrates. Consequently, this class of hydrates showed relatively high thermal stability in atmospheric conditions, ionic and hydrogen conductivity. Those feature makes them suitable for applications such as solid electrolytes. The thermal stability at ambient conditions along with non-volatile

nature of the component of ionic clathrates is a crucial features when it come for hydrogen and carbon dioxide storage and gas separation [5].

2 Hydrate-based Applications for Energy Transition

In the last decade, gas hydrates showed great potential for many practical applications that includes but not limited to CO₂ capture and sequestration (CCS), gas separation, energy storage, gas transportation, fuel cells, and desalination. The focus of current studies on gas hydrates is shared equally between three main areas: (1) their natural occurrence and flow assurance, (2) environmental impact and (3) their technological applications. The recently discovered enormous hydrates reserves, usually filled with methane, can represent affordable sources of natural gas. The traditional importance of hydrate for oil and gas industry persists due to the potential risk due to hydrate interruption of hydrocarbon supply chain and affecting drilling process reliability. The environmental issues are related to a possible methane release from clathrate-bearing sediments which can accelerate global warming, a phenomenon called the “clathrate gun hypothesis” [6]. The third area that attracts growing attention is the green technological applications of hydrate for energy transition and sustainable economic development.

One of the promising technological applications of clathrates is their usage as energy storage material to store and transport gases such as methane, ethane in moderate pressure and temperature conditions [7]. Methane clathrate can be obtained from both natural and synthetic origins. The amount of methane in natural gas hydrate reserves gas is higher than all carbonaceous fuel reserves of the planet. However, for natural gas storage and transportation, synthetic gas hydrates or solidified natural gas (SNG) are more appropriate and is currently an emerging technology alternative to storing natural gas in underground inventories, CNG (compressed natural gas), LNG (liquified natural gas), ANG (adsorbed natural gas). While storing natural gas in its gaseous form through tanks and pipeline network (PLG) is the most used technology, it requires expensive infrastructure that is not always available for discrete, small, inaccessible, or remote gas resources. Many studies showed that SNG plant (CAPEX) has almost half cost of LNG one of the same capacities. Moreover, the costs of transportation will be 18-25% lower for SNG case.

Although it is expected not to achieve the on-board DOE targets for methane storage, clathrate hydrates are a promising mean for discrete and large-scale methane storage for the following reasons:

1. Safety: it has non-explosive nature and can be well-controlled for safe storage and recovery,
2. Environmental benign: it is composed mostly from water and very low concentration of ecofriendly promoters
3. Fully reversible: there is almost complete recovery by simple stimulation as methane is stored in its molecular form.
4. Economical storage conditions in terms of low pressure and close to room temperature. This could be further improved by using suitable promoters.
5. Lower specific energy consumption and compact mode of storage.

Despite the above advantages, the applications of hydrate-based technology in industrial scale are limited due to the slow kinetics, poor heat transfer, gas diffusion limitation, lower storage capacity in presence of promoter, and scale-up challenges.

Promoters are additives that are introduced to either catalyze the kinetics of hydrate formation (kinetic hydrate promoter or KHI) or reduce the *P-T* requirements (thermodynamic hydrate promoter or THP). Understanding the kinetics of hydrate formation is essential for developing potential industrial applications of hydrates. However, it is a challenging task to model the kinetics as it combines a chemical reaction with phase transition. It is also crucial to increase the rate of gas hydrate formation for feasible gas storage and separation process. The crystallization process can be divided into two main steps: nucleation and growth. In the first step, a crystalline phase appears gradually either directly from liquid state (homogeneous nucleation) or at nucleation sites of foreign particle or surface (heterogeneous nucleation). This step is usually slow and is distinguished by its stochastic nature. After adsorption of guest molecules in the liquid phase, it is enclathrated within the hydrate precursors and nucleation then can be detected from the simultaneous rapid pressure decrease and temperature increase due to the exothermic reaction. The time elapsed until the appearance of a detectable volume of hydrate phase or,

equivalently, until the consumption of a detectable number of moles of hydrate former gas is known as induction time (or lag time). In the second step, the crystal growth is distinguished by rapid increase in the particle size up to the full crystalline form. This step is rapid, and the gas is more concentrated in the hydrate cages than those in the vapor. Well-control of such step will enhance the gas diffusion that may be hindered by the formation of 'hydrate film' at the liquid-gas interface. A worth noting a so-called "memory effect" phenomenon that is closely related to the understanding of nucleation process. The phenomenon consists in the reduction of the induction time by using dissociated hydrate or ice melted water. It is suggested that the residual precursors structures may act as nucleation sites that accelerate the nucleation period. So, the methane hydrate formation can be started from ice with a high yield that can reach 100%. However, this approach may not be feasible due to the high energy requirement, additional cost of ice formation for each cycle, and the long reaction time.

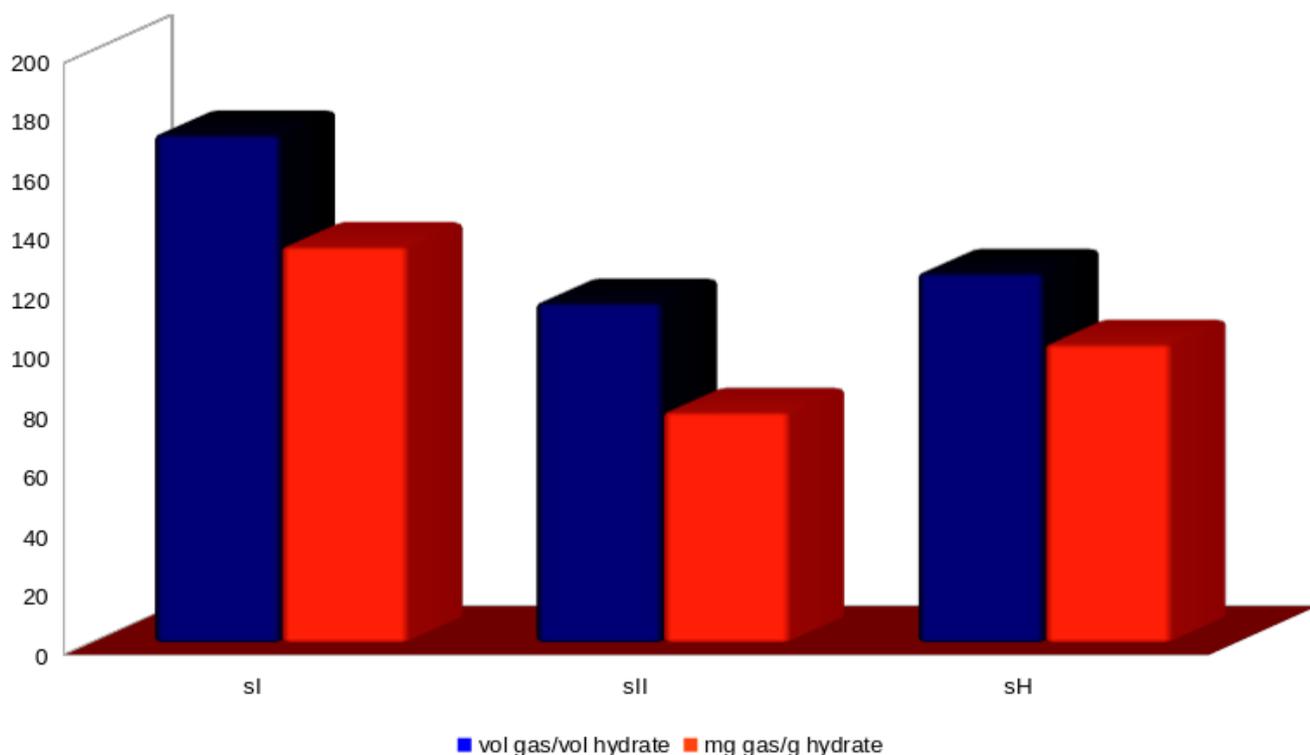


Figure 3: Estimated volumetric and gravimetric analysis of common clathrate hydrate structures.

To solve the problem of slow kinetics, kinetic promoters (KHP) is added to enhance the rate of hydrate formation without influencing the thermodynamics or the P - T condition of hydrate formation. This type of promoters are predominated by surfactants with all its classes (anionic, cationic and non-ionic) [8]. The most common example of those surfactants is the anionic surfactant sodium dodecyl sulfate (SDS). In concentration close to or above its critical micelle concentration (CMC), it is observed that SDS increased the hydrate formation rate significantly compared to other surfactants. This may be explained by micelles formation which increases methane solubility and initiates the nucleation. However, many of hydrate-based processes suffer from foam formation especially during gas recovery (hydrate dissociation). This challenge along with the environmental concerns are directly linked with recyclability of surfactants and makes difficult the application of the surfactants on large industrial scale. To overcome those drawbacks, other KHPs are suggested such as the biodegradable amino acids and silica or carbon-based porous materials. It has been found that amino acids -the biodegradable building blocks of proteins- can increase the rate of hydrate formation and is an important area of current research. Porous materials such as carbons (such as activated carbon and carbon nanotubes), silica in different shapes (silica gel, silica sand, hollow silica and nano-silica), zeolites and even MOFs were used to promote hydrate formation. In general, these materials can be utilized in two different ways: (1) in low concentrations as a nucleation sites for heterogeneous nucleation and (2) as host for hydrate using the confinement effect to enable mild hydrate formation conditions. In contrast with KHP, THPs shift the hydrate formation equilibrium condition to milder P - T which will lower the energy requirements. Depending the promoter nature, the structure of hydrate formed in presence of promoters is commonly sII or sH. The most common sII hydrate former is tetrahydrofuran THF, which is a hydrate former by itself. It is also reported to improve

the kinetics either as stand alone or with SDS. Other examples of sII formers are cyclopentane, dioxane, acetone. sH promoters are usually larger in size compared to sII and it can theoretically store methane in both small and medium cages rather than the small cages only in case of sII. Despite that advantage, the application of those promoters in industrial scale is hindered by factors such as potential environmental hazards and high cost. The solvent losses result in higher operating costs. The ongoing research direction is to find the optimal promoter concentration and maximize the storage capacity in near-ambient or ambient conditions [9].

2.3 Replacement of CH₄ in clathrates with CO₂ for natural gas extraction and carbon sequestration

Replacing CH₄ in discovered hydrate reservoirs by the more stable CO₂ clathrates is another important application that became the focus of recent research studies [11]. The interest of that technology comes from the fact that it could achieve the double benefit of simultaneous energy recovery and carbon sequestration in the deep ocean. Last but not least, clathrate applications cannot be only regarded as "stand-alone" but also they can be integrated within exciting technologies such as LNG or biogas production.

The tremendous reserves of natural gas hydrates (NGH) require an appropriate approach for gas extraction which are often chemical inhibitor injection, depressurization, and thermal stimulation. However, each of these methods are far to be ideal. For instance, the methane encapsulated in a crystal that decomposes under depressurization or thermal stimulation may result in gas release in an uncontrolled or even explosive manner. The latter could affect global warming and similar to what is called "clathrate gun hypothesis".

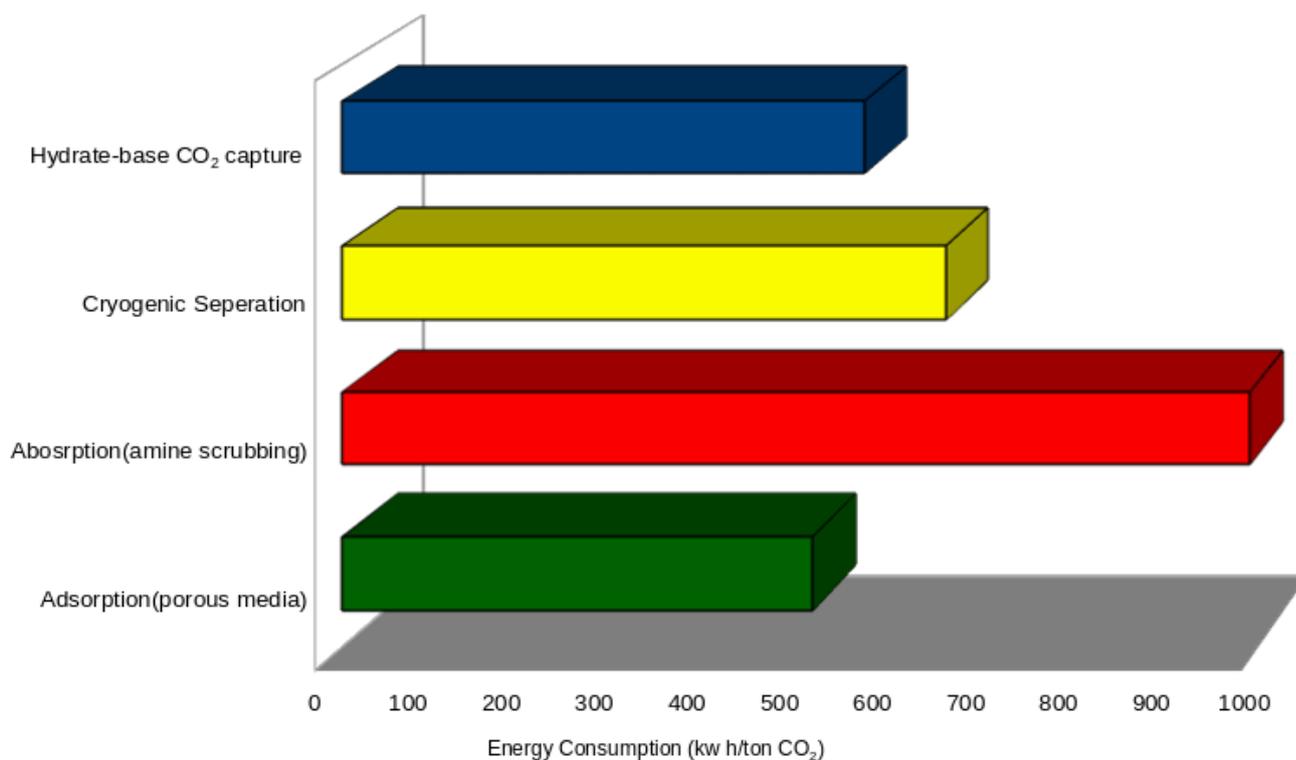


Figure 4: Energy consumption benchmark in different carbon capture methods [10].

To solve the problem of the uncontrolled methane release, replacement of CH₄ with the more stable CO₂ clathrates structures could be used that involves both energy recovery and sequestration of combustion products [11]. Moreover, this exchange between injected CO₂ and methane hydrate is more energetically advantageous than gas recovery via decomposition. The technique has also other advantages: (1) there are only minor -if any- change in the existing geological microstructures, (2) gas recovery based on the guest exchange is safer than mining processes and (3) the overwhelming amount of water usually associated

with gas hydrate dissociation can be avoided. Therefore, this method is both economically attractive and eco-friendly for NGH exploitation. However, the application of the technique is hindered by a limited understanding of the exchange process and inability to predict the amount and rate methane reserves that can be recovered. Those latter two elements are important to evaluate the economic feasibility of the process.

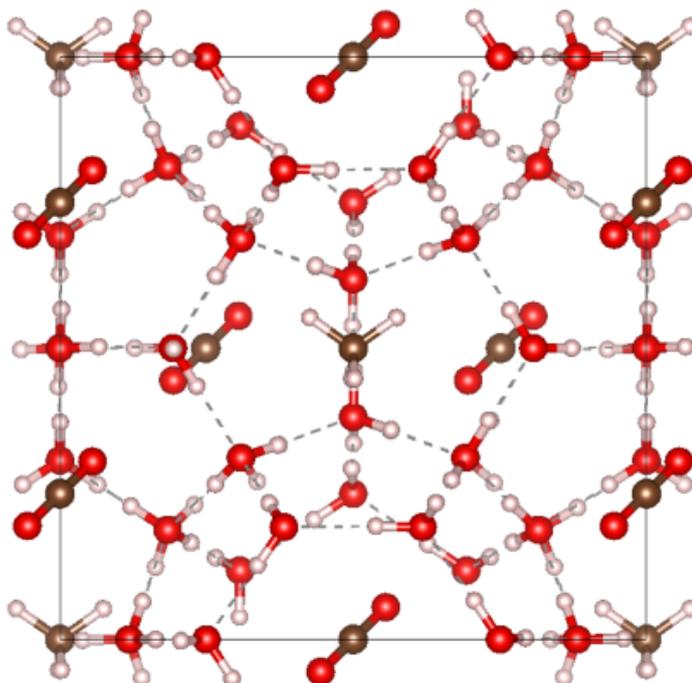


Figure 5: Structure I methane clathrate after replacement with CO₂

2.3 Hydrogen Storage

The safe, economically affordable, and practical hydrogen storage represents the major challenge and bottleneck to both onboard and large-scale applications and limit a pace of implementation for a hydrogen economy. Conventional storage systems include pressurized hydrogen gas at very high pressure above 200 bar or a liquid hydrogen kept at temperature near 20 K.

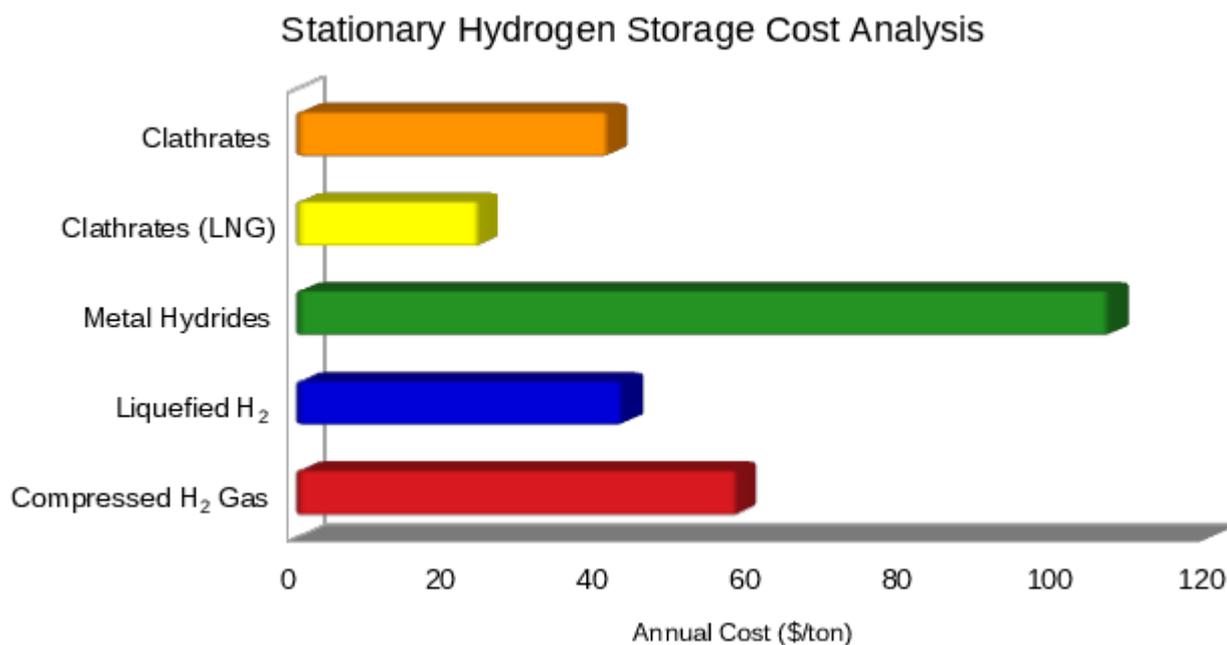
Gas clathrates offer potentially an elegant solution for effective hydrogen storage at milder conditions with energy efficient and well controlled extraction of the stored gas. The maximum theoretical storage capacity of the sII hydrogen hydrates is estimated to be approximately 5.3 wt% of H₂. However, storing H₂ in pure sII hydrogen clathrate is still challenging, because of their slow formation kinetics and dependence on severe thermodynamic equilibrium conditions (i.e., ~2000 bar at 250 K). Once the sII hydrogen clathrate has formed, it is then stable up to 145 K at ambient pressure.

In order to bring the formation conditions to reasonable ranges H₂-THF binary clathrates have been widely studied. However, storage capacity has been significantly reduced to about 1 wt% since H₂ enclathration is limited to 5¹² small cages, while the 5¹²6⁴ large cages are occupied by THF. Thus, boosting the hydrogen capacity using this approach upon reasonable pressure-temperature conditions remained a challenge far from being met.

To overcome those problems, a second generation of gaseous THP promoters are suggested for hydrogen hydrates. The main purpose of using those gases promoters is to allow hydrogen occupancy in large cages as well as the small cages for optimum storage capacity. Thus, Ar can simultaneously occupy the large cages with hydrogen. N₂ promotes hydrogen multiple occupancy in sII clathrate in presence of THF and pyrrolidine (PRD). Greenhouse gases such as SF₆ and CO₂ allow the occupation of large cages in double benefit process. These types of combinations allowed reduce the thermodynamic requirement. ~~the hydrogen storage to 2-3 wt%.~~

Semi-clathrates were also used to store hydrogen due to their inherited thermal stability. However, they showed low storage capacity (0.7 wt%) and can preferably use for purification purposes. So, utilization of liquid promoters can reduce the hydrate formation *P-T* requirements and increase the hydrate stability but on expense of storage capacity. An interesting finding with semi-clathrates lays in a combination of physical and chemical form of hydrogen storage. The latter allowed increasing the overall storage to

~1.5wt%. The concept is utilization of regenerable guest compound such as tetra-n-butyl ammonium borohydride ((nBu)₄NBH₄). With hydrolysable BH₄⁻, thus, the (nBu)₄NBH₄ clathrate hydrate has two independent hydrogen sources. The first is physically trapped hydrogen in the 5¹² cage and the second is chemically bound hydrogen in the host lattice [5].



Figure

6: Estimated cost of different hydrogen storage technologies. Clathrate storage cost is assumed with and without LNG cold energy utilization and volumetric capacity of 3.03 wt% [13]

Recently, storing hydrogen along with light alkanes (methane) has attracted significant attention as they are anticipated to meet the US Department of Energy (DOE) targets of energy density while showing affordable formation and storage conditions [14]. The system H₂-CH₄-H₂O at a pressure of 20 MPa and 40 mol% of hydrogen content in the initial gas mixture resulted in sI formation with cell parameter of 11.86 Å at 133 K [15]. H₂-CH₄ hydrates prepared at various conditions may result in sI or sII depending on pressure, temperature, composition, and formation time. More importantly, in some cases sI can be formed first even before the thermodynamically stable sII and these hydrates can be formed at more moderate conditions than H₂-THF binary hydrates. The hydrogen storage in binary hydrogen-methane clathrate hydrates showed that methane concentration of 6 wt% stabilizes the cubic sI [16]. The pre-synthesized CH₄ and CO₂ sI clathrate as a “templates” for hydrogen clathrates show less than sII storage capacities but prove the concept that H₂ can occupy both small and large cages and multiple cage occupancy is feasible in case of sI. It should be noted that CH₄ and CO₂ sI clathrate were synthesized at 11 and 1.7 MPa, respectively. Consequently, there is a big chance that cages, especially large ones, accommodate hydrogen together with CH₄ or CO₂. Our investigation showed that mixed occupation is probable, and it greatly impact the estimated storage capacity of those clathrates, which reach 3-5 wt% of H₂. Current research activities involve also introducing H₂ into natural gas blends to increase the hydrate storage capacity and make use of existing infra-structures. Utilization of ethane and propane as a co-guest with hydrogen can also reduce the thermodynamic requirements and is extensively reported [12].

2.4 Other Applications

There are many attractive hydrate-based applications for the energy transition and low carbon development. *Energy storage applications* Hydrates can be used for cold energy storage because of their temperature zone, suitable latent heat of fusion and better heat transfer efficiency. They could be also a suitable phase change material (PCM) to utilize energy from renewable sources, used in flow battery applications to store the cheap off-peak electricity, oil, and gas industry waste heat as well as the energy losses in LNG regasification in terminals. The latter is increasing rapidly with estimated 6.6 x 10¹⁴ kJ (20928 MW) released annually [17]. Semi-clathrate hydrates are well-suitable for that and can be tailored with different species and concentrations in wide range (melting point varies from -66 to 31 °C) to fit the

requirements of many cooling applications.

Desalination Hydrate-based desalination is crystallization technique that represent a potential to compete with traditional desalination processes when it is coupled with LNG as reliever for the external refrigeration cycle. In properly selected P - T range, the brackish or sea water can form hydrate in which the water molecules engage the hydrate former leaving the salts and other impurities excluded. Although known for long time, its commercialization faces some challenges related to separating the hydrate phase from brine and lack of commercial feasibility studies. Ongoing research in that field include using CO_2 hydrate collected from flue gas stream to develop double benefit technology for carbon capture and water desalination.

Electrolysis and electrocatalysis Finally, acidic clathrates (such as $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$) and semi clathrate clathrate (such as $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$) can work as solid electrolytes and showed high ionic conductivity that can compete with well-known commercial solid electrolytes such as Nafion in addition to excellent proton conductivity [5].

3 Engineering and Economic Challenges

Hydrates is an attractive gas storage option due to moderate production and storage conditions and easy and safe gas recovery techniques in comparison to the traditional technological means. The later makes gas hydrates very appropriate for on-board applications. Methane in form of hydrate could be stored at 240-271 K and slightly positive pressure (e.g. 2 bar) for several weeks relying on hydrate self-preservation phenomena. This phenomenon describes the ability to store sI clathrate despite it should dissociate at 193 K at atmospheric pressure from thermodynamic point of view. Natural gas hydrates (NGH) -as an example- can store high volumetric capacity of methane in ecofriendly safe and non-explosive manner compared to LNG or CNG.

NGH technology process chain can be described in five steps: NGH formation, dewatering step to remove unreacted water, cooling and depressurizing, and pelletizing step to for hydrate pellets ready for storage step. While steps like dewatering, pelletizing and storage are well established engineering practices, the NGH formation is still challenging from both engineering and economical perspectives. Overcoming the slow kinetic problem of hydrates formation can be by working on two aspects (1) reactor design and (2) selecting proper promoters. The effective reactor design can significantly enhance the hydrate kinetics by improving the gas-liquid contact, heat transfer, mass transfer and reduce energy intensity. For KHP, the research directions are concentrating on the use of (1) environment friendly (2) cheap and (3) non-foaming kinetic promoter that enhance the kinetic conditions without significantly compromising the methane uptake. Intensive research in this direction includes the use of biodegradable compounds and nanoparticles of porous materials in low concentrations as KHP promoters. The utilization of confined spaces of porous material can also significantly improve the thermodynamic requirements due to their confinement effect. So, the porous materials can be also used as THP promoters. Using THP can effectively reduce the hydrate formation P - T requirement and result in extended storage for years in mild conditions. The use of gaseous THP such as higher hydrocarbons (ethane and propane), or small gases CO_2 or even H_2S that normally exists the in the natural gas mixture, can improve the thermodynamic requirement of methane storage significantly. This also highlight the advantage of NGH as they are relatively insensitive to the presence of such impurities in the stored gas stream. Safety-wise, hydrate-based technologies are among the safest options to store gases in non-explosive and compact form. Hazard identification studies (HAZID) showed that hydrate dissociation will result in water that overcome the explosive nature of natural gas stored by conventional technologies such as CNG or LNG. Several economic studies show that for the transportation for 1000-6000 km distance of 1-1.5 million ton per year, NGH could be more cost efficient compared to LNG and CNG [18]. Other studies compared the total life cycle cost (including OPEX, CAPEX, GHG, and shipping) and showed that NGH hydrate can reduce the cost in the range of 16-48% compared to LNG [19]. The bottom-line of these studies that NGH is optimum for short- medium range distance while LNG prevail for long distances. However, the situation is completely different when it comes for long-term stationary storage. LNG requires continuous refrigeration of methane up to -161°C and recompression of boil-off gases. On the other hand, sI methane clathrate can be stored for -at least- weeks at only -20°C which can be extended for years when THP is utilized. NGH represent a promising opportunity to reduce the cost compared to conventional storage as it possesses a big advantage for both small and large volume methane storage from discrete or remote

locations and can easily fit with small reservoirs where LNG or pipeline are not feasible. Example of such cases can be flue gases from offshore terminals and biogas facilities or remote shale gas reservoirs. It should be noted that due to their simple construction and operation, NGH can not only work as standalone technology but also combined with other existing technologies utilizing the already existing infrastructure and enhance the economic feasibility. Future directions of NGH research could include improved reactor design, optimization of THP concentration, selection optimized (P-T) conditions, and pushing them toward the ambient ones, understanding the self-preservation and memory phenomena, structural transformation (e.g. sI to sII), using seawater instead of desalinated or pure water, and performing detailed economic studies.

Hydrate-based CO₂ storage is a promising technique as it's insensitive to impurities and moisture process, with an easy recovery by depressurization or thermal exchange with ambient atmosphere, energy efficient and cost effective with estimated energy consumption of 0.57 kWh per ton CO₂. However, it suffers from the same problems of NGH of slow kinetics. One of the drawbacks of this approach is that the *P-T* conditions become more demanding when the feed mixture has low CO₂ concentration. So, it is hardly suitable for CO₂ capture at low concentration. Such problems can be resolved by the combination of hydrate with other CO₂ concentration techniques. For example, the hydrate-membrane hybrid CO₂ capture is relatively more economic than standalone hydrate-base process and can obtain high purity. Similar conclusion is still valid for the cryogenic-hydrate combination as the cold energy of liquid CO₂ from the cryogenic separation will compromise the energy requirement of hydrate formation.

When it come for hydrogen storage, there some main factors that should be taken into consideration such as (1) safety, (2) environment, (3) moderate *P-T* for storage, (4) storage capacity, and (5) the overall costs. First and foremost, hydrogen hydrates are much safer compared to storing hydrogen at very high pressure at gaseous form, chemical or liquid forms. Moreover, it requires less energy (lower carbon footprint) in comparison to other physical and chemical storage techniques for extraction. Both the cost analysis and specific energy consumption show the promising potential of hydrogen clathrates. However, the main obstacles that hinder hydrogen clathrate application is large scale are the cooling requirements, extreme formation condition, slow kinetics, and relative low storage capacity. The cooling requirement can be reduced by synergistic coupling with cold energy source such as LNG facilities which will make it more cost effective than compressed hydrogen gas, LOHC, and metal hydrides. Hydrogen storage with natural gas (C₁-C₃) OR "Hythane" can be a good compromise between storage capacity and the thermodynamic requirements and will be developed in near future [7]. In fact, the presence of higher hydrocarbons can have a dual benefit of being both KHP and THP while increasing energy storage in hydrates. Development of an appropriate value chain for hydrogen hydrates may in near future represent an attractive option competing with the traditional solutions for storage and production hydrogen on board.

4 Conclusion

There is a strong increase of research interest for hydrate-based technologies in various fields related to the energy transition and decarbonization thanks to their uniqueness for safety improvements and potential for industrial applications. We also demonstrated the advantages of NGH for methane storage in comparison with existing technological options such as CNG and LNG. NGH are insensitive to impurities and very suitable for large scale stationary methane storage that can collect methane from discrete and small sources such as biogas plants and shale gas reservoirs. We concluded that NGH is flexible to work either standalone or in combination with other existing technologies for more economic methane storage. Hydrogen storage with natural gas (C₁-C₃) or "Hythane" in clathrates can be a good compromise between storage capacity and the operating conditions. Hydrates can also be interesting opportunity for CCS that can be combined with energy recovery as CH₄-CO₂ replacement. A major advantage of technology is in its ability to combine both the carbon capture with sequestration in a single step. Then, we discussed hydrogen clathrate as a safe and environmentally friendly option for both large scale and on-board hydrogen storage. We have also explained some other hydrate potential uses for desalination, energy storage, and proton conductivity. We finally discussed in detail the engineering and economic aspects to enable the scale of hydrate-based technologies. Focusing the research in area such as innovative reactor design to improve heat and mass transfer, promoter concentration optimization, use gaseous KHPs/THPs, combining hydrate with existing technologies and detailed life-cycle economic studies will help to solve the main problems facing hydrate-based technologies. There is a strong hope that the development in gas

hydrate will offer many useful technological solutions to reach net zero objectives by 2050.

References

- [1] Makagon Yuri F., *Hydrates of Hydrocarbons*. Pennwell, 1997.
- [2] I. N. Tsimpanogiannis and I. G. Economou, "Monte Carlo simulation studies of clathrate hydrates: A review," *J. Supercrit. Fluids*, vol. 134, no. September 2017, pp. 51–60, 2018.
- [3] Y. Kamata, Y. Yamakoshi, T. Ebinuma, H. Oyama, W. Shimada, and H. Narita, "Hydrogen sulfide separation using tetra-n-butyl ammonium bromide semi-clathrate (TBAB) hydrate," *Energy and Fuels*, vol. 19, no. 4, pp. 1717–1722, 2005.
- [4] A. Davoodabadi, A. Mahmoudi, and H. Ghasemi, "The potential of hydrogen hydrate as a future hydrogen storage medium," *iScience*, vol. 24, no. 1, 2021.
- [5] K. Shin, J. H. Cha, Y. Seo, and H. Lee, "Physicochemical properties of ionic clathrate hydrates," *Chem. - An Asian J.*, vol. 5, no. 1, pp. 22–34, 2010.
- [6] M. Maslin, M. Owen, S. Day, and D. Long, "Linking continental-slope failures and climate change: Testing the clathrate gun hypothesis," *Geology*, vol. 32, no. 1, pp. 53–56, 2004.
- [7] Y. H. Ahn *et al.*, "One-step formation of hydrogen clusters in clathrate hydrates stabilized via natural gas blending," *Energy Storage Mater.*, vol. 24, no. March 2019, pp. 655–661, 2020.
- [8] Q. Nasir, H. Suleman, and Y. A. Elsheikh, "A review on the role and impact of various additives as promoters/ inhibitors for gas hydrate formation," *Journal of Natural Gas Science and Engineering*, vol. 76, no. February. Elsevier B.V., p. 103211, 2020.
- [9] M. E. Casco *et al.*, "Methane hydrate formation in confined nanospace can surpass nature," *Nat. Commun.*, vol. 6, 2015.
- [10] Y.-S. Yu, X. Zhang, J.-W. Liu, Y. Lee, and X.-S. Li, "Natural gas hydrate resources and hydrate technologies: a review and analysis of the associated energy and global warming challenges," *Energy Environ. Sci.*, 2021.
- [11] S. F. Cannone, A. Lanzini, and M. Santarelli, "A Review on CO₂ Capture Technologies with Focus on CO₂-Enhanced Methane Recovery from Hydrates," *Energies*, vol. 14, no. 2. p. 387, 2021.
- [12] M. R. Ghaani, S. Takeya, and N. J. English, "Hydrogen storage in propane-hydrate: Theoretical and experimental study," *Appl. Sci.*, vol. 10, no. 24, pp. 1–10, 2020.
- [13] A. Gupta *et al.*, "Hydrogen Clathrates: Next Generation Hydrogen Storage Materials," *Energy Storage Mater.*, vol. 41, no. June, pp. 69–107, 2021.
- [14] W. L. Mao *et al.*, "Hydrogen clusters in clathrate hydrate," *Science (80-.)*, vol. 297, no. 5590, pp. 2247–2249, 2002.
- [15] S. S. Skiba, E. G. Larionov, A. Y. Manakov, B. A. Kolesov, and V. I. Kosyakov, "Investigation of hydrate formation in the system H₂-CH₄-H₂O at a pressure up to 250 MPa," *J. Phys. Chem. B*, vol. 111, no. 38, pp. 11214–11220, 2007.
- [16] V. Belosludov *et al.*, "Theoretical modelling of phase diagrams of clathrate hydrates for hydrogen storage applications. Molecular Simulation Theoretical modelling of the phase diagrams of clathrate hydrates for hydrogen storage applications Theoretical modelling of the phase di," 2012.

- [17] Z. Yin, J. Zheng, H. Kim, Y. Seo, and P. Linga, “Hydrates for cold energy storage and transport: A review,” *Adv. Appl. Energy*, vol. 2, no. March, p. 100022, 2021.
- [18] T. Nogami, N. Oya, H. Ishida, and H. Matsumoto, “Development of natural gas ocean transportation chain by means of natural gas hydrate (NGH),” *6th Gas Hydrates Int. Conf. [ICGH] (Vancouver, Br. Columbia, 7/6-10/2008) Proc.*, no. Icgh, 2008.
- [19] S. Nakai, “Development of natural gas hydrate (NGH) supply chain,” *Int. Gas Union World Gas Conf. Pap.*, vol. 4, pp. 3040–3049, 2012.