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Review

Benefits and drawbacks of clathrate hydrates: a review of their areas of interest

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Abstract

Clathrate hydrates are well known structures that were considered for many years as harmful by the oil and gas industry because of their annoying tendency to plug pipelines. However, hydrates are now attracting renewed interest in many fields. Indeed, gas hydrates naturally found in deep seas and permafrost may provide a large amount of methane. Other positive applications include carbon dioxide sequestration, separation and natural gas storage and transportation. Finally, the use of their dissociation energy can be applied in refrigeration processes and cool storage.

Keywords: Clathrate hydrates; Pipeline plugging; Natural gas storage; Carbon dioxide sequestration; Separation; Cool storage

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Contents

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1. Introduction

The term "clathrate", from the Greek word khlatron meaning barrier, indicates crystalline inclusion compounds in which small guest atoms or molecules are physically trapped in host cavities shaped by a three dimensional assembly of hydrogen bonded molecules. These compounds are called clathrate hydrates when they contain water and gas hydrates when the enclosed molecules are gases; the latter are much more commonly encountered. According to the size of the trapped molecule, three types of structures are observed: cubic I [1], cubic II [2] and hexagonal H [3]. These structures correspond to different arrangements of the water molecules.

Over a long period following their discovery by Sir Humphry Davy in 1810, interest in clathrate hydrates was purely academic. Intense research on natural gas hydrates was conducted by the oil and gas industry when it was pointed out that these compounds were responsible for plugging natural gas pipelines [4]. In fact, light gases such as methane or ethane present in petroleum products are easily trapped as guest molecules in hydrate structures.

The opposite is also true: other processes, such as separation technologies, employ these inclusion compounds favorably [5]. Thanks to their high gas concentration, hydrates can also be used propitiously for either carbon dioxide sequestration [6] or storage and transportation of natural gas [7]. Moreover, natural gas hydrates naturally occurring in deep seas and permafrost have high gas concentrations and, therefore, turn out to be a possible source of energy, provided that the environmental impact is taken into account. Finally, clathrate hydrates offer high latent heats of dissociation that can be utilized for refrigeration applications, such as cold storage or air conditioning [8,9]. The objective of the present review paper is to distinguish various areas of interest related to hydrates in accordance with their respective needs, either by combating these solid compounds or by taking advantage of their properties.

2. The drawbacks of clathrate hydrates: pipeline plugging

In 1934, Hammerschmidt indicated that the formation of gas hydrates was responsible for blocking pipelines [4]. Considering the significant economic risks in the gas and oil industry, a great deal of research has been conducted by the petroleum industry in order to inhibit this phenomenon. In fact, hydrate propagation tends to gradually form a plug that separates the pipe into two pressure sections: a high pressure section between the well and the plug and a second section at low pressure between the plug and the recovery division. In the upstream section, a pipe blast can occur due to the pressure rise. The plug can also behave as a projectile that destroys the pipe when the pressure difference between the upstream and downstream sections increases. Both events can imperil personnel safety and damage production equipment [10]. Preventing hydrate agglomeration in pipelines is a real challenge, since it happens in hostile environments, such as the Arctic where very low temperatures are encountered, and in subsea pipelines where pressure can reach high levels.

Four main processes were investigated in order to combat hydrate plugs and ensure regular flow: chemical, hydraulic, thermal and mechanical processes. The chemical method, which can be used either to prevent or to remove plugs, consists in injecting additives in the pipe that act differently on hydrate agglomeration according to whether the inhibitors are thermodynamic, kinetic or dispersant. The thermodynamic inhibitors, generally methanol [11–13] or glycols [14–16] and/or aqueous electrolyte solutions [13,17,18], are injected in order to shift the equilibrium temperature, thus enabling gas hydrate crystallization. This method is efficient but limited by the large quantity of additives implemented (60 wt%), which is, moreover, difficult to recover from water, and by the corrosive properties of salts (electrolytes) [19]. A new generation of additives has been developed: dispersants such as QAB (quaternary ammonium bromide) that prevent hydrate agglomeration [20]; kinetic inhibitors, generally polymers, that slow down hydrate crystal growth so much that it cannot disturb oil transport [20–24]. Only small amounts of dispersant and kinetic inhibitors are required to prevent pipeline plugging, making them economically attractive.

The hydraulic removal method is based on the dissociation of the hydrate plug by depressurization. This method seems promising, given the porous structure of the gas pipeline plugs [10,25]. However, it is not suitable for liquid hydrocarbons, since depressurization induces its vaporization.

The thermal method consists in delivering locally a heat flow towards the plug through the pipe wall in order to raise the system temperature above the hydrate formation point. This method is possible for external pipelines but unsuitable for subsea equipment [19].

Finally, a mechanical method, such as pipeline pigging, can be used to prevent hydrate plugs. Pipeline pigs are inserted into the pipe and travel throughout the pipeline, driven by product flow. These projectiles then remove the obstacles or deposits they encounter [10].

Despite all these methods, pipeline blockage by gas hydrates remains a concern in the oil and gas industry, and ongoing research is being conducted in this field. In particular, transmission lines are increasingly being placed in deepwater pipelines. The selection of an optimal method involves taking into account the type of products (gas, liquid hydrocarbon or crude oil) transported and the type of pipeline (external, subsea) used. Sometimes, several processes can be combined to destroy plugs more efficiently, for instance, chemical inhibitors can be used in conjunction with a mechanical removal method [19].

3. Methane hydrates as a possible energy source: an environmental dilemma

The important amounts of gas hydrates in the Earth's crust might be considered as a new source of sustainable energy [26]. Kvenvolden [27] and Makogon [28] pointed out that the amount of gas in known hydrate reserves up until 1988 was at least twice as much as the energy contained in the total fossil fuel reserves. Indeed, one volume of methane hydrate can yield 164 times more methane than one volume of gaseous methane under the same pressure conditions and at standard temperature [29]. This study was completed by Collett and Kuuskraa [30], who estimated that these gas reserves range from 1.4×10^1 to 3.4×10^4 trillion cubic meters (tcm) for permafrost areas and from 3.1×10^3 to 7.6×10^6 tcm for oceanic sediments. Gas hydrate deposits, principally considered as the result of a permanent migration of natural gases throughout Earth fractures, are mainly distributed offshore due to the high pressure and low temperature conditions at the seabed and more parsimoniously encountered in permafrost [19,31]. Nevertheless, fossil fuel resources are currently sufficient to face worldwide energy needs, and thus, gas-hydrate exploitation is dedicated to being a distant prospect, especially for offshore hydrates [32].

In order to anticipate future needs, however, some prospective plans are being studied to develop viable extraction schemes from hydrate sediments; one such project is the Mallik 2002 Gas Hydrate Research Well Program concerning permafrost deposits exploitation in the Canadian Arctic region [33]. Gas recovery is generally based on in situ hydrate dissociation by either heating or depressurization [34]. The thermal approach generates huge heat losses and, therefore, seems less exploitable than [35] depressurization that requires high porosity hydrate deposits [36]. Moreover, the transport stage can be problematical, since extracted gas and water may re-crystallize into gas hydrates inside the transmission lines and then provoke pipe plugging.

Even though they are considered as the main hydrocarbon source for the future, gas hydrate deposits might represent a real threat to the environment. Indeed, when considering offshore hydrates as a global methane reservoir, exploitation of these sediments in unfavorable circumstances could drastically modify the marine ecosystem and even generate underwater gas blowouts [37]. Moreover, destabilizing hydrate sediments plays an undeniable role in climate change. According to Brewer [38], a slight global warming would raise the hydrate temperature above the equilibrium point, involving dissociation and the release of a great quantity of methane. Given that a mole of methane is about 24 times more effective at absorbing infrared radiation and affecting the climate than a mole of carbon dioxide [39], such discharge would cause a chain reaction mechanism. However, methane hydrate sediments may be reinforced by injecting chemical promoters and, thus, limiting the predictable safety risks.

An original perspective proposed by other authors [40,41] would consist in swapping methane, encased in hydrate, with carbon dioxide and, thus, limiting disturbances in underwater layers and preventing sub-oceanic landslides.

4. The benefits of clathrate hydrates

4.1. Marine carbon dioxide sequestration

About 64% of the enhanced greenhouse gas effect is due to carbon dioxide emissions [42], of which more than 6 Gt/yr are attributed to anthropogenic activities [43]. Given that the greenhouse effect is undeniably responsible for climate warming [44], reducing the quantities of CO_2 released into the atmosphere is a major environmental challenge. Carbon dioxide can be partially taken up by various methods such as chemical absorption in amines [43,45,46] or sequestration in geological media and oceans [47,48]. Such can be performed by releasing the CO_2 in water using a process adapted to the injection depth [49,50]. Down to 400 m (shallow sea), gaseous CO_2 is injected and then trapped by dissolution in the water [51]. Between 1000 and 2000 m (deep water), CO_2 in the liquid state diffuses and also dissolves in the ocean [52]. In addition, CO_2 hydrates can appear from 500 to 900 m in CO_2-rich seawater [50] and then sink, owing to their density [53], towards the deep sea bottom where they stabilize in the long term [6,54]. Marine carbon dioxide sequestration is presently at an experimental stage, implying further research on CO_2 solubility [50,55–57], CO_2-hydrate formation kinetics [6,53,58,59] and CO_2 hydrate stability [54,59,60].

4.2. Separation processes

Desalination or gas–liquid fractionation also use hydrates in a beneficial manner. During the 1960s and early 1970s, the feasibility of seawater desalination via hydrates was demonstrated, but the process was not developed industrially since it was not economically viable [5]. This process is based on gas hydrate formation by refrigerant injection in seawater. After separating the hydrate crystals from the residual concentrated brine solution, pure water is recovered by heating the hydrates. Other authors [61] pointed out that the hydrate desalination process may be difficult to implement because of the slurry texture of the hydrates.

Other research work exploring the potential of hydrates to act as a gas separation mechanism is being conducted in order to extract CO_2 from flue gas exhausted by large power plants [62]. The US Department of Energy (DOE) is developing a high pressure process for carbon dioxide separation [63]. It focuses on the low temperature SIMTECHE process, where a shifted synthesis gas stream (CO_2, H_2 and other gases) is combined with pre-cooled nucleated water in a CO_2 hydrate slurry reactor. The outlet mixture (CO_2 hydrate slurry, H_2 and other gases) flows into a hydrate slurry gas separator which divides the flow into two streams: CO_2 hydrate slurry and H_2 rich product gas. Another process named hydrate base gas separation (HBGS) has been investigated with tetrahydrofuran (THF) chosen as a hydrate promoter [60]. THF is used for lowering the equilibrium hydrate formation pressure and, thus, for expanding the gas hydrate stability region. According to the authors, the HBGS process makes it possible to recover more than 99 mol% of CO_2 from the flue gas. This process has several advantages, such as moderate operational temperatures in the range of 273–283 K and continuous operations, making it possible to treat a large amount of gaseous stream.

4.3. Natural gas storage and transportation

For a few years [64], gas capture via methane hydrates has been implemented for storage and transportation of natural gases, partially thanks to the ability of hydrates to provide a high gas concentration [29]. This new process involves hydrate production, transportation to the place of use, and gas recovery by dissociation of the hydrate structure [65]. The first step is generally achieved by mixing gas and water under hydrate formation conditions (275–283 K; 8–10 MPa) [65]. In order to increase the hydrate formation rate, surfactants can be added to the solution [66–68]. A novel exploratory production method consists in heating a mixture of melting ice particles and natural gas, thus initiating hydrate crystallization [69]. During the transportation stage, the hydrates are cooled to approximately 258 K at atmospheric pressure to ensure their stabilization during storage in insulated bulk carriers [70]. In the last step, the hydrates are slowly melted, releasing gas from the resulting water. This storage and transportation process is possible thanks to the metastability of methane hydrates [69]. Indeed, the latter tend to exhibit metastable behavior between 193 and 348 K at atmospheric pressure [71]. Provided that it is performed at higher temperature and lower pressure levels than those required for liquefaction and compression, respectively, gas transportation using hydrates seems to be as viable as these classical processes. In addition, the use of structure H hydrate [72] or surfactant promoters is currently being considered to increase storage capacity [67,68,73].

4.4. Cool storage application

Research and development on refrigerating systems with a reduced impact on the environment have become urgent since the ratification of the Montreal Protocol (1987) and the signing of the Kyoto Protocol (1997). Secondary refrigeration can be a promising alternative to face this problem by the containment of a reduced load of primary refrigerant (HFCs) in an engine room. The refrigerating capacity delivered to the secondary refrigerant is then transported towards the places of use [74–77]. The system's exergy can be partially improved by implementing a phase change material (PCM) in the secondary refrigerant [8,9,78]. Indeed, the PCM largely contributes to the heat transfer thanks to its latent heat of melting. The two phase secondary refrigerants thus formed may be ‘‘ice slurries'' [78–81] or ‘‘hydrate slurries'' [8,74,82], in which the carrying fluid is an aqueous solution and the PCM ice or hydrate crystals, respectively.

In fact, the first implication of clathrate hydrates in refrigeration processes was related to refrigerant (CFC) hydrate crystallization, which unfortunately occurred in expansion valves [83]. However, clathrate hydrates were favorably reconsidered at a later date, specifically for cold storage, since their large heat of melting was confirmed by various authors [8,61,79,84–86]. Moreover, since their phase change temperature is above the freezing point of water [8,61,85,87,88], the use of hydrate energy is clearly relevant for the field of air conditioning. Moreover, hydrate slurries are fluid enough, up to operating solid concentrations, to flow easily through the secondary refrigerant loop [8,61,74,82,89]. At this time, advanced research on hydrate slurries is being conducted with guest molecules, such as TBAB hydrate, that are more environmentally friendly than CFC refrigerant [8]. Other work is devoted to implementation of the CO_2 hydrate under moderate pressure [9]. From an energy point of view, the nature of the guest molecule is not obvious, since, according to Sloan [19], the heat of dissociation of the hydrate could be related to only its host structure, made up of water molecules held together by hydrogen bonds. A notable outcome on hydrate heat of dissociation using the Clausius–Clapeyron equation shows that structure I is less energetic than structure II (excluding the less common occurrence of structure H) [90]. As pointed out by Kang and Lee [60], it is possible to shift ($CO_2 + N_2$) hydrate from structure I to structure II by adding THF in the aqueous solution. A Cemagref group is currently investigating this property for a more favorable use of CO_2 hydrate slurry energy [91].

5. Conclusion

The main purpose of this paper was to determine the role of hydrates in various areas of interest. Historically, hydrates were only studied in the gas and oil industry because of their harmful tendency to plug pipelines. More recently, they were encountered in refrigeration where their crystallization occurred in expansion valves. However, combating these drawbacks has made it possible to acquire substantial knowledge of hydrates, including their existing conditions, their crystalline structure, their ability to store gas and their heat of dissociation. Some of these characteristics have been emphasized by various authors for positive applications. Indeed, the huge amounts of natural gas stored in the methane hydrates of the Earth's crust can be considered as a future sustainable energy source, provided that environmental risks are taken into account. Hydrates can be a useful means of partially mitigating climate change thanks to carbon dioxide sequestration in submarine areas. This capacity to capture carbon dioxide may also be used in the separation process used for flue gases. This storage capacity is even more relevant for methane and facilitates natural gas storage and transportation. Finally, cold storage using hydrates as phase change materials is a promising application in secondary refrigeration thanks to the large amount of energy of hydrate dissociation (higher than the melting heat of ice). In a nutshell, even if many studies focus on the disturbing aspect of hydrates, the positive prospects are numerous and encouraging.

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