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Natural Gas Hydrates

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1. Introduction

Sir Humphry Davy witnessed the first chlorine hydrate crystallizing in 1811. Couple of century later his discovery, natural gas hydrates has begun to play an important role in energy business. From being a mere chemical curiosity, they have proven to be a nuisance for the natural gas industry. The problem of hydrate induced blockage in “wet gas” flow systems has been widely reported and became a major flow assurance issue in the energy sector[1]. The importance of pipeline blockage increased in the 70’s when plugging of even the largest diameter pipelines from offshore, arctic fields or the wells from high-pressure underground storage facilities were reported. Studies over the past two decades showed that large gas hydrate plugs form most often after shut-in pipelines or wells begin to flow[2]. When a pipeline is shut-in, the fluid separates into the gas water and hydrocarbons as the temperature decreases[3].

Natural gas hydrates are non-stoichiometric, solid substances that consist of a low amount of gas molecules captured in a mesh cage system made up of water molecules. As seen in Figure (1), when the constituents of hydrates come into contact under high pressure and low temperature conditions a solid structure at different types of crystals with higher densities than typical fluid hydrocarbons[4] is formed. Hydrates are solid metastable compounds and their properties and stability depend upon temperature and pressure. Natural gas hydrates are dangerous compounds not only during construction stages but also during operation stages of process facilities such as platforms, pipelines and other engineering structures. Hydrates can easily form in pipelines and producing gas wells before the gas has been dehydrated. The prevention of hydrates requires substantial investments up to 10 to 15% of the production cost[5]. Flow assurance management has become one of the major critically important engineering practice in custody transfer of oil and natural gas and it is essential for successful and economic operation of oil and gas production systems[6]. Besides economical impact, an inherent problem associated with natural gas production and transportation with the presence of natural gas hydrates is the thread on operational safety. Natural gas hydrates may lead to safety hazards to production, transmission, and transportation systems. For both economical and operational safety perspective, understanding of formation kinetics, where and when natural gas hydrates form is necessary to better manage and mitigate this phenomena. Moreover, during the last decade several researchers pointed out that understanding the formation mechanism of natural gas hydrates may open new avenues in alternative ways of natural gas transportation. With the

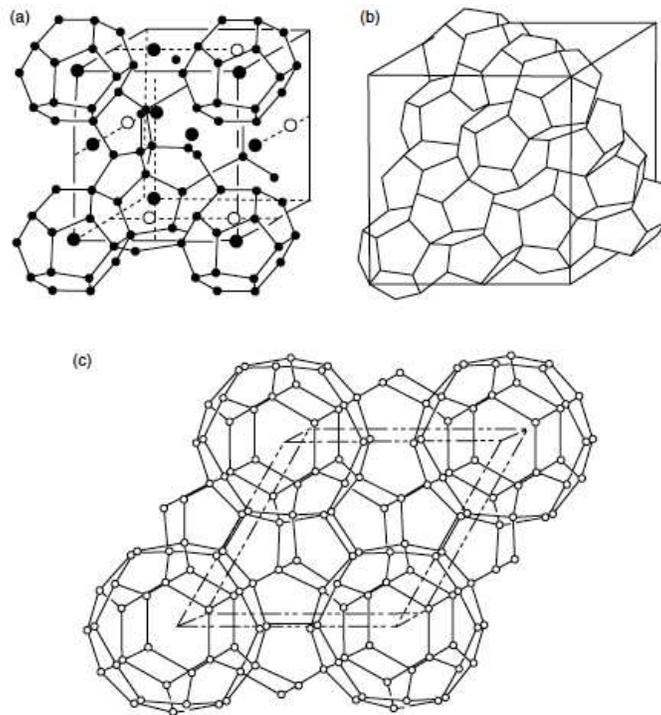


Fig. 1. Hydrate crystals (a) sI type, (b) sII type, (c) sH type[3].

increased demand for natural gas there is an additional incentive in exploring ways to monetize stranded gas that can not be economically developed due to low natural gas volumes to justify effective LNG facilities or lack of proper pipeline infrastructure[7, 8, 9].

Gas hydrates can form at the gas liquid interfaces along the entire length of the static pipeline. This can create small volumes of hydrate over time, but usually do not block the pipeline. However, when flow resumes, plugs can form at any point where the flow regime changes. Small-scale hydrate formation in the interface sometimes cannot be avoided in the pipeline. Moreover, under certain conditions, small-scale agglomerates are also observed in the bulk phase. Hydrate formation does not become a threat to pipe flow unless the agglomerates and hydrates formed at the interface start forming bridges. In such cases blockage occurs where the small accumulations of hydrates adhere to the walls and begin to bridge and reduce flow. This bridging can eventually shut down the entire pipeline or field until the hydrates have been removed[10]. Like hydrate formation, dehydration of hydrates in the pipelines is another major operational safety risk[6].

Hydrates form as a result of slow cooling of a fluid as in a pipeline or rapid cooling caused by depressurizing across valves or through turbo expanders. Studies have shown three conditions promote hydrate formation in gas pipelines and in petrochemical processes: *Coexistence of water, natural gas components and low temperatures and high pressures*. Other factors that favor hydrate formation can be listed as high fluid velocities, agitation, pressure, pulsations (or any source of fluid turbulence), the presence of CO_2 and H_2S [11].

Gas molecules ranging from C_1 to C_4 and including CO_2 , N_2 and H_2S are typical hydrate components. The water needed for hydrate formation can come from free water produced from the reservoir or from water vapor condensed by cooling the hydrocarbon fluid. At low temperature conditions, onshore pipelines suffer from hydrate formation during the winter

months. Offshore, below 900 m of water depth and at the ocean bottom, the temperature is remarkably uniform around 3.8 °C and the pipeline cools to this temperature within a few miles of the wellhead. This situation may lead hydrate formation[12].

2. Natural gas hydrates structure and physical properties

Natural gas hydrates (NGH) form in raw multiphase flow as a result of crystallization occurring around the guest molecules at certain operating temperature and pressure conditions[13, 14, 15]. The most widely observed guest molecules in natural gas mixture are methane, ethane, propane, i-butane, n-butane, nitrogen, carbon dioxide and hydrogen sulfide. However, among those, methane based NGH occurs the most naturally[16, 17, 18, 19]. NGH are composed of approximately 85-mol% guest molecule; therefore they have physical properties very close to ice. They have crystal structure. The density of NGH varies somewhat according to former molecule(s) and the formation conditions[20]. NGH are part of a larger family of compounds called "Clathrates", which are inorganic container compounds[21]. Although there are many container-compounds and hydrate formers in crystal structure, the focus in this paper is NGH formers and NGH structures.

In general, hydrates are classified by the arrangement of the water molecules in the crystal structure. All common natural gas hydrates belong to the three crystal structures: cubic structure I (sI), cubic structure II (sII), hexagonal structure (sH) as shown in Figure (1). Structure I is formed with guest molecules having diameters between 4.2 and 6 Å, such as methane, ethane, carbon dioxide, and hydrogen sulfide. Nitrogen and small molecules including hydrogen ($d < 4.2 \text{ \AA}$) form structure II as single guests. Larger ($6 \text{ \AA} < d < 7 \text{ \AA}$) single guest molecules such as propane or iso-butane will form structure II. Still larger molecules (typically $7 \text{ \AA} < d < 9 \text{ \AA}$) such as iso-pentane or neohexane (2,2-dimethylbutane) can form structure H when accompanied by smaller molecules such as methane, hydrogen sulfide, or nitrogen[3].

The crystal structures of NGH consisting of water molecules are hydrogen-bonded in a solid lattice. The interaction or degree of bonding between individual water molecules and the guests is very weak, but the overall interaction of the guests with the host structure can be quite strong[22]. In the literatures, more than 130 compounds that are known to form clathrate hydrates with water molecules are mentioned and more emphasis observed to be given to sI and sII hydrates since these are by far the most common NGH structures[23, 24, 25, 26]. The sH structure NGH are well described by[27, 28, 29, 30, 31, 32, 33, 34]. Moreover very high-pressure hydrate phases are studied by[35, 36, 37, 38]. Crystal properties of NGH have been extensively studied by Sloan and Koh[3] and Jeffrey[24].

2.1 Crystal structure of sI, sII and sH type of NGH

In 1965, structure I type (sI) of hydrates was first observed by McMullan et al. and Jeffery [39] with definitive x-ray diffraction method on ethylene oxide hydrates. In Figure (1) sI structure, 46 water molecules present along with 8 polyhedra within the cubic structure. Moreover, Mak [40] observed structure II type (sII) hydrate crystal structure in the same year with definitive x-ray diffraction method. He showed that the sII type crystal consists of a face centered cubic lattice structure with a side dimension of 17.3 Å. Structure type (sII)

type hydrate's typical crystal structural view is given in Figure (1b). Later, Jeffrey[24] pointed out that the sII type structure voids are formed by connecting 16 polyhedra and might accommodate larger guest molecules than it is commonly observed in NGH structures. On the other hand, first structure H type (sH) of hydrates were discovered in year 1883 by de Forcrand during his studies with binary hydrates with iso-butyl chloride or bromide as the guest molecule (now, they are known as sH formers). However it was not recognized at that time. The first sH type structure was reported by Ripmeester et al. [41, 42] with his study conducted via NMR spectroscopy and X-ray powder diffraction methods on different clathrates. An important feature of sH type hydrate crystals is that two sizes of molecules are required to stabilize the hydrate structure. This typically happens with a smaller molecule such as CH₄ or H₂S and a bigger molecule such as dimethylbutane. sH type hydrate's typical crystal structural view is given in Figure (1c). This type crystal structures observed to have unit cell length of 12.3 Å. For sI, sII and sH type structures at usual pressures, only one guest molecule can be filled in the cavity. More information can be obtained about the crystal structure and cavity occupation by guest molecules in[43]. Scanning Electron Microscopy and other micro-imaging techniques are very powerful tools to study the porous structure of NGH's. Such techniques should accompany NGH crystal growth to understand better the relationship between thermodynamic conditions and structure. The conceptual crystal growth at the molecular level still remains a fuzzy area. Indeed the interaction between the contributory factors leading to crystallization of NGH is still not understood: kinetics, mass transfer and heat transfer. A great deal of fundamental work is still required to disentangle this interdependency.

2.2 Physical properties of NGH

NGH are solid materials which have higher densities than hydrocarbon components forming natural gas mixtures. In the open literature detailed investigation on NGH physical properties tend to focus mainly on mechanical, elastic and thermal properties. Compression deformation measurements on NGH sediments are conducted by Parameswaran et al.[44] and Cameron et al.[45] showed that strength of NGH is approximately similar to that of ice. Later Stern et al.[46] did compression deformation measurements at constant applied stress (creeping test) on NGH (methane hydrate) and his results showed the same trend as Parameswaran's and Cameron's. However, in 2003 Durham et al.[47] showed that the impurities in previous studies effected the previous studies in creeping tests and they determined that NGH was 20 times more creep resistant than ice[48]. Elastic properties of NGH can be estimated accurately since they are function of crystal structures and crystal structures are well defined. Whalley first proposed that the elastic properties of NGH are similar to that of ice in 1980[49]. Later this theory was confirmed with first experimental studies conducted by Whiffen et al. in 1982, Pearson et al. in 1984 based on experiments on simple hydrates via Brillouin spectroscopy method, which was later followed by Kiefte et al.[50, 51, 52]. More recently in 2002, Shimizu et al.[53] performed in situ measurements on NGH via improved Brillouin spectroscopy technique and looked at the effect of of pressure on shear stress as well as compression velocities. This study showed that the shear velocities of NGH (mainly methane hydrates) are similar to that of ice[53]. First experimental studies on thermal properties of NGH were conducted by Stoll and Bryan in 1979 and they showed that the thermal conductivity of NGH as 0.393 Wm⁻¹K⁻¹ at 215.15 K which is 5 times less than that of ice (2.33 Wm⁻¹K⁻¹)[54]. Low thermal conductivity of NGH is confirmed with several

studies later and a nice mapping of the thermal conductivity measurements from several experiments were recently published by Gupta[55, 56, 57].

3. The effect of NGH on the flow assurance

Flow assurance can be defined as an operation that provides a reliable and controlled flow of fluids from the reservoir to the sales point. Flow assurance operation deals with formation, depositions and blockages of gas hydrates, paraffin, asphaltenes, and scales that can reduce flow efficiency of oil and gas pipelines. Due to significant technical difficulties and challenges, providing safe and efficient flow assurance needs interdisciplinary focus on the issue and joined efforts of scientists, engineers and operation engineers[58]. It was mentioned by Guo et al.[59] that as a rule of thumb, methane caged NGH will form if the temperature is as high as 4.5 °C and pressures are as low as 11.7 bars. As seen in Figure (2), mild conditions are required for NGH formations. NGH predictions can be determined by using simulation software and computational methods. However, predicting hydrate formation requires more detailed experimental studies for each reservoir fluid since the operating conditions and compositions vary vastly. As a result of both theoretical and experimental investigations, five different NGH prevention methods have been implemented to provide flow assurance[6, 60]. These are:

- i. Dehydration of wet gas and water removal (onshore or offshore)
- ii. Avoid operation temperatures lower than the hydrate formation temperatures
- iii. Avoid operation pressures higher than the hydrate formation pressures
- iv. Injection of Thermodynamic Inhibitors (TI) such as methanol, glycol etc. to effectively decrease the hydrate formation temperature and inhibit or retard NGH crystal formation
- v. Injection of Kinetic Inhibitors (KI) to prevent the aggregation of hydrate crystals

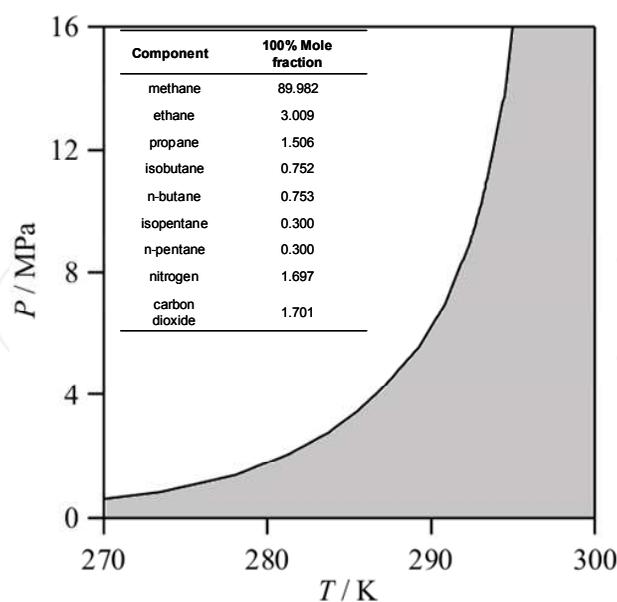


Fig. 2. Calculated pressure - temperature diagram for hydrate formation for the a typical lean multicomponent gas mixture which composition is indicated within the figure. Gray area shows the hydrate free region and white are the region where hydrate formation is possible. Calculation according to the Baillie and Wichert Method[136].

Above options are applied separately or in matching combinations. Selection of above options depends on fixed and operating cost restrictions, technology availability and know-how, system characteristics and operation/process flexibility.

NGH plugging up a pipeline may cost the gas industry in excess of approximately \$1 million each day that production is shut down[58] and once a hydrate plug has formed, it can take weeks or even months to dissociate it safely, or it will require complex operations such as pigging for plug removal[61]. The petroleum industry has tried to prevent hydrates from forming by drying and heating the oil as well as by adding TI such as glycol based antifreeze agents and methanol. Annual approximation of an operating expense is greater than \$500M, which is devoted to hydrate prevention via TI injections[62]. Hydrates are a problem not only for pipelines but also for wells drilling: the use of water based drilling fluids for offshore operations may lead to the formation of hydrates that strongly affect deep-sea drilling operations. Experimental studies on kinetic mechanism and when & how NGH forms are conducted in two major mechanisms: analytical equipment based and purpose made engineered apparatuses[63]. Such figures and the negative environmental impacts of the use of TI's and KI's have motivated the academia and research centers all around the world to conduct fundamental research on NGH and their mitigation. It has been observed that over the last couple of decades, fundamental NGH research tendency has shifted from time independent TI studies to time dependent KI studies[64]. The replacement of traditional TI and KI by biodegradable equivalent may be the subject of future work to reduce the environmental impact.

3.1 NGH inhibition for subsea pipelines

In theory if all the water is removed from the natural gas stream, conditions for NGH formation will no longer be effective for the hydrate formation. Offshore dehydration may not be feasible for all the operations due to physical footprint constraints in the production facility at the offshore facilities. It may also not be necessary to have an offshore dehydration facility if the risers down in the sea bed do not have steep slopes, yet, temperature and pressure of the pipeline is as important as the riser slope. Having said that, dehydration facilities are not the most cost effective way of preventing NGH formation in subsea transport pipelines. Operationally, avoiding the pipeline conditions outside of the hydrate equilibrium loop (HEL) would also prevent NGH formation. To achieve these conditions, TI, KI and thermal methods can be applied to the pipeline. Manipulation the HEL can be achieved by injecting KI or TI to the pipeline. Some physical thermal methods are used in order to provide environmentally friendly HEL control without injecting chemicals to the pipeline. Heat conservation is the common practice for thermal methods and the application is made through insulation of the pipeline such as hot water jacket, concentric tube bundle or trace heating along the pipeline. Numerous alternative thermal method applications are available[65, 66, 67]. It is worth noting that under thermal methods, the so-called "memory effect" of NGH should be exploited to prevent hydrate formation again once the hydrate melted[3].

3.1.1 Thermodynamic inhibitors for subsea pipelines

Typical subsea pipelines do not have insulation and they require chemical inhibition not only for preventing NGH formation in the pipelines but also to prevent plugging during the start-up and shutdown conditions[68]. Both TIs and KIs are injected at the wellhead and

selection of both inhibitors is based on the recovery cost and easiness of the injected inhibitor. Historically, methanol and glycols were considered for NGH prevention as TI agents. Basically, these chemicals make hydrogen bond with water molecules and prevent them to form ordered cages to entrap gas molecules. Methanol can be separated from the flow easily since it has lower density, surface tension and viscosity under separation conditions (below -25°C). This brings lower cost in recovery of methanol in the system. Moreover, glycol based solutions are also used for plug prevention in the pipes. Typically ethylene glycol (or mono ethanol glycol known as MEG) is used due to lower cost, lower viscosity and lower solubility in liquid hydrocarbons. However, glycols must be added up to 100% of the weight of the water content present in the gas stream. This leads to economical issues since glycols are expensive inhibitors. Moreover, there is a need for a large footprint in onshore and offshore facilities. Difficult recovery and regeneration are other disadvantages of plug prevention via glycols[69, 70, 71, 72]. There are some other electrolytes used as TIs in NGH prevention[73]. All the TI molecule in combination with the water molecule in the flow changes the HEL by changing the chemical potential of the hydration[74] which results in a shift of the HEL towards the lower temperature and higher pressure side. Hammerschmidt[1] gives an empirical formula and rule of thumb calculation for lowering the temperature for the NGH formation.

On the other hand, once the reservoir conditions are considered, the stability of hydrates in a reservoir also depends on the interactions between minerals, surrounding reservoir fluids and hydrate. As the reservoir depth increases, the level of salinity increases. Moreover, the formation of hydrate then will lead to increased salinity of the fluids surrounding the formed hydrate. This may result in liquid pockets of residual aqueous solution with increased salinity and non-uniform hydrates[75].

3.1.2 Low dosage hydrate inhibitors for subsea pipelines

An observation of made on an ocean fish that bond itself with proteins in order to avoid freezing in severe sub-zero conditions led discovery of low dosage hydrate inhibitors (LDHI) and LDHI have caught the attention of researchers working on NGH in academia and industry shortly after its discovery. Kinetic Inhibitors (KI) have been the most widely investigated sub-class LDHI in the past decade. By contrast to TIs, KIs limit or delay the growth of hydrate formation[76] by reducing the nucleation rate of hydrate and preventing the formation of critical nucleus. In other words, hydrate crystal growth is controlled with KIs. However, it is not economically viable to ensure complete coverage of all the hydrate nucleation and growth sites with KIs; and thus, it might be required to have huge amount of KI dosages to ensure the complete crystal growth inhibition.

First KI studies were conducted under low/moderate pressure test chambers in early 90s. The first generation KIs were mostly water-soluble polymers. For instance, PVP was the first KI to be found as an effective plug former inhibitor[77]. KIs are typically polymer solutions such as Vinyl Caprolactam/VP/Dimethylaminoethyl Methacrylate Copolymer (known as VC-713), Polyvinylpyrrolidone (PVP), Poly(VP/VC), PVCap (polyvinylcaprolactam), Polyvinylmethylacetamide etc. KIs are preferred to TI's because they are more efficient in plug formation inhibition and injection is made in much lower quantities[74]. Many others followed PVP; Later studies in KI investigation has been shifted to higher pressure chamber applications and performance of KIs are modified for: *low temperature, high pressure, inhibitor*

concentration and *salinity*. KIs are time time-bound components and they can prevent the formation of NGHs for a limited period of time. There is rapid conversion of the remaining water into large accumulations of hydrates once this time period passes, which results in blockage. Use of KIs are not limited by the water cut, however, it is limited by the sub-cooling in the system that KIs will be used.

A KI is generally used in conjunction with surface-active agents. Surface-active agent along with KI polymer will cause emulsification to occur between the free water and gas/condensate phases in the pipe which then prevents the agglomeration of hydrate crystal well before the first crystal formation starts. In other words, KIs keep the particles small and well dispersed so that fluid viscosity remains low, allowing the hydrates to be transported along with the produced fluids[6].

On the other hand, in deep and ultra deep water cases where very extreme conditions exist (i.e. Gulf of Mexico, North Sea and West Africa-Nigeria), Anti Agglomerant (AA) another sub-class LDHI, are observed to perform better rather than classical type KIs and they are often known as hydrate growth inhibitors[78, 79]. The concept of AA is basically preventing the formation and accumulation of large hydrate crystals into a composite hydrate blockage through having a hydrophilic head that is incorporated within the hydrate crystals and hydrophobic tail that disperses the hydrates into a liquid hydrocarbon phase[80]. Anti-agglomerant disperse the very small formed hydrate nuclei whereas kinetic inhibitors (although their mechanism of actuation is not fully clarified) bind to the forming crystals thus hindering, and delaying, their growing. Unlike KIs, AAs are not limited by the sub-cooling of the system and they can continue to be effective at sub-cooled conditions; however, they require the presence of a condensate hydrocarbon phase in order to suspend the hydrate crystals. Moreover, at high water cut conditions, dispersed hydrate crystals might cause an increase in the viscosity of the condensate phase, which might result in blockage of the flow due to increased viscosity. Often, it is required to have demulsifier for oil and water separation since AAs are based upon homogeneously dispersion polar hydrate crystals in the apolar oil and condensate phase. AAs have recently been more recognized in industrial use especially in the Gul of Mexico region[79].

In addition to classic KI's and TI's, biological hydrate inhibitors (BI) have also been investigated as well. Inhibitor proteins or in other words anti-freeze proteins (AFPs) and antifreeze glycoproteins (AFGPs) inhibit the hydrate formation by binding the surface of hydrate crystal nuclei[81]. Recent studies have also shown that AFPs also prevent the hydrate growth after the hydrate crystal is formed[82].

3.2 Experimental studies for NGH

Experimenting the nucleation stage for NGH is perhaps the most challenging step and it is essential in understanding the process of crystallization of gas hydrates. Sloan[19], Makogon[5, 83], and Koh[84] have provided an extensive reviews on the kinetics of gas hydrate crystallization in literatures. Theoretical description of the rate of hydrate nucleation has been attempted by Kvamme[85] from the perspective of the nucleation aspects of the crystallization process are concerned and models have been published on crystallization theory for the prediction of gas hydrate formation by Sloan[19].

Kashchiev and Firoozabadi[86] have measured the rate of gas hydrate formation after nucleation and they developed gas consumption rate models based on the early stage of the crystallization theory, which is, the hydrate growth stage.

NGH have been known since 1930s to have the potential to plug the oil and gas transportation pipelines, in particular when working under high pressure. This phenomena has started be even more problematic since the present trend of the natural gas industry to work at higher pressures will increase the hydrates problem for natural gas transportation. Since 1930s, thermodynamic conditions that lead to NGH formation have been the center of focus of researchers in academia and industry. Experimental studies started in late 1950s by Katz et al.[87] and followed by Makogan, Berecz and Balla-Achs[88, 89]. Main focus of the experimental research on NGH was to determine the thermodynamic conditions to operate the pipeline outside the hydrate formation region or HEL.

Okutani et al.[90] reported their high pressure hydrate dissociation curve determination apparatus with some experimental findings. Their method uses a high pressure, stainless steel isochoric cell without agitation to investigate methane hydrate equilibrium in water-hydrate-gas systems. They have investigated hydrate formation by monitoring pressure changes in the system under a constant cooling rate. Kim et al.[91] investigated the hydrate dissociation curve with a similar high-pressure cell by observing the dissociation temperature of the hydrates. Their design also included large observation windows. They formed hydrates by injecting methane and ethane samples through a water container with constant heating rate. They observed dissociation temperature with visual data. Seo et al [92] used a similar experiment and investigated three-phase hydrate equilibria in the methane+water+cyclic-ether and nitrogen+water+cyclic-ether systems using a temperature search method up to 120 bars. Sakaguchi et al.[93] described another interesting isochoric design. They investigated the formation and growth of hydrate crystals in a Pyrex cell visually using observations through CCD cameras connected to micrographic zoom lens at atmospheric conditions. Kang et al.[94] and Fleyfel et al [95] used a method known as "rocking cell". They used a visual rocking cell to observe hydrate formation in metastable methane, ethane, propane and water systems. They combined the constant pressure-rocking cell with NMR and observed the peak with NMR and visually confirm this.

Some researchers used x-ray diffraction, Raman spectroscopy and differential scanning calorimeter (DSC) methods to investigate hydrate formation and dissociation properties. Hester et al.[96] used Raman spectrometer to investigate hydrate compositions for the Hydrate Ridge in Oregon. Koh et al.[84, 97] studied hydrates using DSC. Using DSC, they quantified and compared the effect of various kinetic inhibitors. Le Parlouer et al.[98] investigated the thermodynamics properties and kinetics of hydrate formation within minerals. They modified a Setaram DSC 111 for pressures up to 400 bars with a temperature range of -45 °C to 120 °C. They have shown the dissociation temperature of hydrates with respect to methane pressure and heat flow versus temperature profiles at the dissociation peaks for different isobars. Dalmazzone et al.[99] used an approach similar to that of Le Parlouer for hydrate formation and kinetics investigation. They used a modified high pressure Setaram Micro-DSC for water-in-oil emulsions systems up to 40 MPa between 223 and 393 K.

In contrast to static high-pressure cell approaches, researchers also have investigated hydrate formation mechanism and kinetics using dynamic models and techniques. Gaillard et al.[100] investigated methane hydrate formation in a recirculating flow loop and perform kinetics modeling of hydrate formation. They essentially studied the kinetics of methane hydrate formation and inhibitor performance in a laboratory scale mini flow loop under pressures up to 75 bars. Lee et al. [101] used a laboratory scale mini flow loop to study the mechanism of hydrate plugging and examine inhibitors that prevented hydrate plugging in natural gas pipelines up to 8 MPa. Some sections of the loop also had visual access. Urdahl et al.[102] and Lund et al.[102, 103] used loop design in a relative motion flow loop and studied gas hydrate formation and inhibition in hydrocarbon gas-water-oil systems. Their 150 bar loop had a temperature range of -10 to 150 °C and was fully automated. It enabled visual detection of hydrate formation. They studied methane rich methane+ethane+propane+water systems in the presence of several different KI's. Mork[104] described one of the most detailed flow assurance and loop experiment for gas hydrates in the literature. He studied the rate of methane hydrate and natural gas hydrate formation in a 100 bar flow loop between 7 and 15 °C to understand the performance and scale-up of a reactor for continuous production of natural gas hydrates. He has shown that the rate of hydrate formation is strongly influenced by gas injection rate and that the pressure the effect of stirring rate is less significant.

Additionally, many patented experimental setups and procedures have been proposed and published for gas hydrate investigation. The most widely accepted designs are flow loops such as those of Guo et al.[59], Hatton[105], Larue et al.[106], Behar et al.[107], Mitchell and Talley et al.[108, 109].

Much of the available funding of NGH research was granted for industrial field experiments and academic testing of field characterization. This was aimed at establishing secure transportation conditions by avoiding plugging in pipelines. Results of the industrial and academic experiments may not be available in the open literature completely due to the confidential nature of the data to the companies and governments[4] funding such work.

It is highly desirable to initiate research work on NGH that is aimed at not only mitigating the effects of NGH, but also the risk and safety aspects. The impact of a NGH plug dislodged by pressure differential can be very dangerous and may cause the pipeline to rupture leading to casualty in operating personnel as reported by Sloan[3].

3.3 Instrumental analysis for NGH

NGH formation is an exothermic crystallization process. Characterization of NGH can be made by investigating the nucleation single crystals, crystal growth and agglomeration[110, 111]. The kinetics of hydrate growth is concerned with the rate at which the hydrate phase grows after the induction time that marks the onset of hydrate crystallization[112]. Mostly gas uptake rates at which hydrate interface advances are investigated operationally by measuring pressure, temperature and composition of the different fluid phases in the investigated system. On the other hand, molecular studies and analytical techniques are used for hydrate crystal structure, composition, and cage occupancy determination. For these purposes Powder X-ray diffraction (PXRD), Raman and Nuclear Magnetic Resonance (NMR) techniques have been used for solid phase structural analysis at molecular level for NGH[113, 114, 115, 116, 117, 118]. Characterization of NGH sH structure crystals (methane type) and several large organic molecules are recently done by Susilo et al. via NMR and

Raman techniques[119]. They showed that when a molecule is trapped and encaged in hydrate structure, Raman and NMR spectra gas/liquid signals are shifted and showed distinctive behavior during hydrate formation. The distinct methane behavior in sI, sII and sH type hydrate structures is observed as lower frequency when compared with free gaseous state components in Raman spectroscopy measurements[120]. Raman spectroscopy is used mostly on determining the cage occupancies and the hydrate compositions quantitatively after careful calibration of the observed peaks for the specific system under study[120, 121, 122]. On the other hand, the distinct methane behavior in all three-hydrate structures in NMR is characterized by lower field outputs in comparison to free gaseous state components[122, 123]. If accurate data acquisition is provided with both NMR and Raman spectroscopy, cage occupancies of NGHs are determined accurately and the results are comparable between both methods[124, 125].

4. NGH as a potential energy source: Storage and transport issues

It was previously indicated that hydrates are one of the major problems that oil and gas industries suffer from in operations. Since the discovery of the hydrates, majority of the research efforts has been spent on the determination of the hydrate crystal structure, kinetics of hydrate formation, thermodynamic behavior and mechanisms to avoid plug formations in the pipelines. However, NGH are also called as “white coal” and they have great potential due to its capacity to store huge amounts of methane in its cage structure. On average, NGH volume gains are estimated almost as 155 times smaller than the equivalent amount of natural gas at standard conditions[126]. Volumetric gain changes depend on the crystal structure of the NGH[83]. Estimation of the volumetric gain has been done by Berner[127] and for typical sII type crystal structure NGH with no impurities nor inclusions have an approximate 191 m³ of gas per 1 m³ of NGH. With 5 vol% impurities and 96% occupancy of cavities in the crystal structure this value is estimated as 174 m³, and with 8 vol% impurities and 96% occupancy it is 160 m³. Storing and transporting natural gas in NGH form will require natural gas stream with some water content treated at 5 to 15 °C under 10 to 25 bars to process 155 m³ of natural gas in order to produce 1 m³ of NGH. On the other hand, similar or slightly better volumetric gain is achieved by well established liquefied natural gas (LNG) and compressed natural gas (CNG) processes. However, for LNG processes -163 °C and for CNG processes pressure operations up to 200 bars is required[128]. Successful implementation of natural gas transport in the form of NGH may reduce the operational cost dramatically by avoiding very low temperature operation cost in LNG production and compressing requirement in CNG production. Conversely, stability of the end product is a major concern. It has been proved that the stability of the end NGH product stayed stable up to 2 years in solid hydrate form in cold climates such as Russia and Norway[129]. With all the potential in NGHs, it may become an attractive means of transportation of natural gas located in the small and unutilized gas fields. Transportation of gas as NGH requires export terminals with natural gas with water to produce NGH and receiving ports equipped with re-gasification facility to extract gas from the hydrate cage. Mitsui Engineering and Shipbuilding Corporation in Japan are working on engineering and feasibility investigation of such application with a capacity of 600 kg/day[7]. In today's world it has been estimated that about 70% of the total gas reserve is either too far from an existing pipeline or too small to justify a liquefaction facility

Another interesting aspect of NGH which attracted the scientific community to conduct research on is the large sediments and deposits of NGHs located on the ocean floor. Yet, there are estimations and speculations on the NGH depositions on the ocean floor, which is greater than the combined total energy resources that we have currently in all means (see Figure (3)). Englezos estimated that total amount of NGH in ocean floor is about 10^{16} m³[130]. There are 50 proven locations of NGH sediments on earth where large quantities of NGHs present[128]. However, quantification of how much methane, ethane, propane, i-butane and n-butane is trapped in these sources is difficult to ascertain and has not been done for the majority of the sources. The difficulty of handling these deposits are: *to reach the source and bring them above the ocean floor and they dissociate very quickly with the pressure applied on those (even a mechanical arm used to carry them above sea level)*. In order to prevent quick dissociation of these deposits following solutions are proposed: *reduce the temperature of deposit in a separate chamber and increase the deposit density* [126]. On the other hand, another alternative method has been proposed by Fanklin, which is based on removing these deposits under controlled dissociation. This idea is proposed by applying: *increase temperature of the deposit with sensitive control, decrease the deposit weight, decrease the penetration rate and apply controlled pressure on the deposits*[131]. Such techniques remained as theories and have not gained importance so far[132].

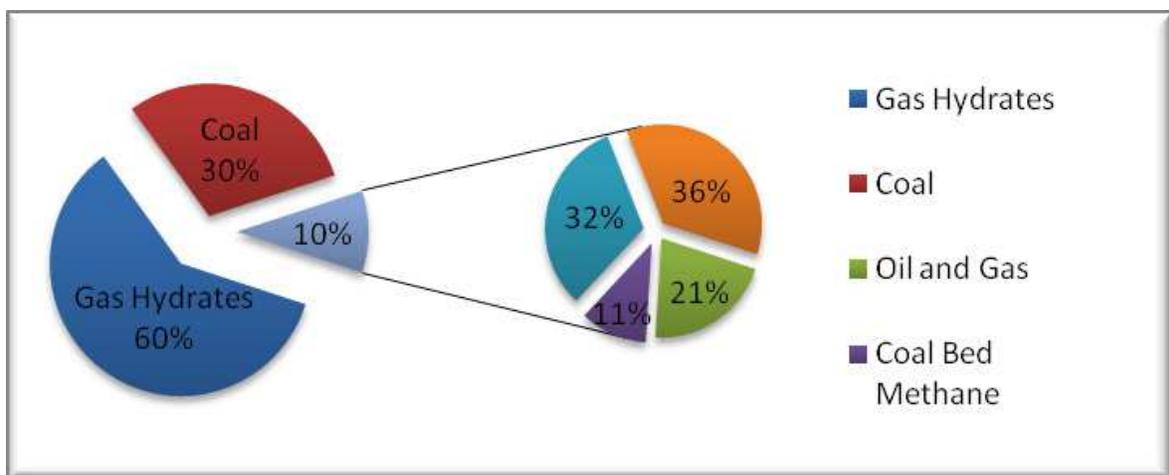


Fig. 3. Fossil energy resources. (Tboe: trillion barrels of oil equivalent).

Another biggest problem standing against the production of energy via NGH from the ocean bed deposits is the possibility that removal of the methane hydrates may trigger the uncontrolled release of methane gas to the ocean, which may increase the salinity of the oceans dramatically. This uncontrolled incident may result in global climate change since methane in the atmosphere is known to be the biggest contributor to the global warming[133, 134]. Utilizing NGH deposits in the ocean floor may power the planet in the future and the challenges stated above will become more important for the academia for further and detailed investigation in near future.

5. NGH safety and hazards

Gas processing plants and sites that experiences NGH problem considers the safety aspect of NGH has two different ways; in storing and pipeline transportation. Since the crystals

matrix in hydrate systems has a high latent energy must melt before gases are released; explosive release of gas during accident is inherently inhibited in a hydrates system when compared with LNG and CNG. As transportation point of view, when ignited, NGH will burn slowly and will not explode. For this reason, once the wall of hydrates carrier is breached, the natural gas hydrates will not readily flow out of the carrier vessel, as is the case for LNG. On the other hand, from the view of hydrate plug formation in the transportation pipelines, there are bigger safety concerns exist especially during the removal of the hydrate plug. During the dissociation of hydrate plug in the pipeline, great pressure drop is occurred when the plug detaches from the pipe wall. This pressure difference might cause solid hydrate plug mass to reach to an approximate speed of 300 km/h within the pipeline. This phenomena will help to compress the downstream gas further which will result in blowouts, ruptures and damages in the pipeline[12].

Hydrates contain as much as 180 volumes of gas at standard temperature and pressure per volume of hydrate. Hydrates dissociation by heating causes rapid gas pressure increase in the system. Field engineers often call this phenomenon "hail-on-a-tin-roof". Small hydrate particles can contain considerable volume of gas. Attempts to blow the plug may rupture the pipe. In order to determine the best approach to remediation of hydrate blockage, the knowledge of the location and length of a hydrate blockage is very critical. During plug dissociation, there might be multiple plugs exist in the pipeline which threatens the pipeline both from safety and technical perspectives. As investigated by The Canadian Association of Petroleum Producers there are two key points to consider in that regard[135, 136]:

- i. Always assume multiple hydrate plugs in the flow loop. There may be high pressure points between two plugs.
- ii. Attempting to move hydrate plugs can rupture pipes and vessels in the flow loop.
- iii. While heating a plug, the heating procedure should commence from the end of a plug rather than the middle section of the pipe.
- iv. Single sided depressurization can potentially launch a plug like a high-speed bullet and result in ruptured pipes, damaged equipments and uncontrolled release of hydrocarbons to environment.
- v. Actively heating a hydrate plug needs to be done in such a way that any released gas will not be trapped

6. Molecular simulations of natural gas hydrates

Compared to thermodynamic hydrate inhibitors like methanol and glycol, Low dosage kinetic inhibitors have several advantages in terms of cost and environmental impact. They are active in low concentration, less than 1% of water phase, and generally they are not toxic. However, despite the studies have been done over the last years, the formation mechanism of hydrates, the kinetics of the process and the action mechanism of how LDKI's work are not fully understood. This lack of knowledge and the limitations of surface sensitive techniques prevents the development of more efficient LDKI's. Over the last two decades, Molecular simulations have been proven to become a powerful technique to study the molecular level details of solid/liquid interfaces and it provides valuable information about gas hydrates nucleation, growth mechanism together with a basic understanding of the action mechanism of LDKI's.

Liang et al. reviewed recently the studies that uses molecular simulations to analyze the properties of hydrates growing and inhibition[137]. Rodger et al.[138] analyzed the effect of an inhibitor based on quaternary ammonium zwitterions by molecular simulations methods and showed that its activity is comparable with the common kinetic inhibitor : PVP. Basically, molecular simulations allow to test new families of potential inhibitors before synthesizing the molecules or before doing expensive and time-consuming laboratory or field tests. There have been several computational studies that support these conclusions[139,140,141,142]. Kvamme et al. showed how computational experiments provide valuable information to select kinetic inhibitors and to understand the action mechanism of inhibiting hydrate formation[143].

Molecular simulations have also been used successfully to analyze other aspects related with hydrates area in several recent works. Myshakin *et al.*[144] used molecular dynamics simulations to analyze the methane hydrate decomposition process, showing an Arrhenius type behavior and analyzing the regrowing process. Tanaka *et al.*[145] investigated the thermodynamic stability of the structure I and II hydrates using molecular simulations. Erfan-Nia *et al.*[146] have used molecular simulations to analyze the structure of hydrates formed from the methane+ethane mixture, showing that type I hydrates are formed in the whole composition range. Also, they used molecular simulations to show the methane storage capacity of structure II hydrates with the help of large guest molecules such as propane, i-butane, tetrahydrofuran etc[147].

7. Conclusion

This chapter reported the progress made to better understand natural gas hydrates and their mitigation in pipeline transportation. Whilst one acknowledges the benefits of techniques such as injection of inhibitors such as TI and KI to maintain gas production, the associated cost and negative environmental impact clearly signal to additional fundamental research in the area. Such work may include the use of more effective and environmentally friendly additives, a better understanding of the interaction between mass transfer, heat transfer and kinetics of NGH crystal growth and a better utilization of imaging techniques to support experimental work on NGH crystal growth. These studies must imperatively be conducted using properly designed reactors to produce hydrates under carefully controlled conditions. The field of "in-situ" hydrate formation detection is still far from being a reality and constitutes a desirable objective since this would make the continuous use of additives redundant and facilitate the use of selective local heating of pipeline where possible, or in the worst case, inject selectively the correct doses of KI's. This has been termed as "time dependent" growth model studies in the literature without providing any clues on how this might be achieved in practice.

The potential of NGH's as alternative state of natural gas during transportation still remains untapped even though it has been acknowledged given the abundance of natural gas in the form of hydrate in deep seas. This area of work would necessarily involve NGH stability studies.

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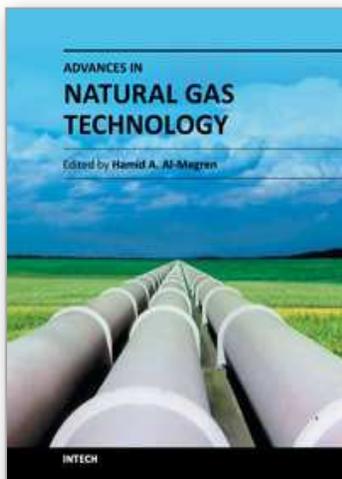
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Advances in Natural Gas Technology

Edited by Dr. Hamid Al-Megren

ISBN 978-953-51-0507-7

Hard cover, 542 pages

Publisher InTech

Published online 11, April, 2012

Published in print edition April, 2012

Natural gas is a vital component of the world's supply of energy and an important source of many bulk chemicals and speciality chemicals. It is one of the cleanest, safest, and most useful of all energy sources, and helps to meet the world's rising demand for cleaner energy into the future. However, exploring, producing and bringing gas to the user or converting gas into desired chemicals is a systematical engineering project, and every step requires thorough understanding of gas and the surrounding environment. Any advances in the process link could make a step change in gas industry. There have been increasing efforts in gas industry in recent years. With state-of-the-art contributions by leading experts in the field, this book addressed the technology advances in natural gas industry.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Mert Atilhan, Santiago Aparicio, Farid Benyahia and Erhan Deniz (2012). Natural Gas Hydrates, *Advances in Natural Gas Technology*, Dr. Hamid Al-Megren (Ed.), ISBN: 978-953-51-0507-7, InTech, Available from: http://www.intechopen.com/books/advances-in-natural-gas-technology/natural_gas_hydrates

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