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# Natural Gas Hydrates: Possible Environmental Issues

# 16

Sotirios Nik. Longinos, Dionysia-Dimitra Longinou,  
and Spyridon Achinas

## Abstract

During the past 50 years, there has been a growing awareness of environmental issues related to energy technologies and natural resource utilization. A growing global population demands augmenting amounts of energy and goods without big discovery of conventional resources (apart from Zohr and Glafkos offshore fields in Mediterranean Sea, Egypt, and Republic of Cyprus, respectively); leading companies and countries turn their interest in unconventional resources such as shale oil, shale gas, and gas hydrates. Although gas hydrates are assumed part of the alternative energy sources of the future, they exhibit possible environmental risks for both the marine ecosystem and atmosphere environment. This chapter presents the fickleness of methane hydrate (MH) that either takes place naturally or is triggered by anthropogenic activities. Furthermore, it explains the climate change (methane discharged to the atmosphere has 21 times more global warming contingent than carbon dioxide) and the sea acidification (more than half of the dissolved methane retains inside seafloor by microbial anaerobic oxidation of methane) caused by methane hydrate release. Moreover, it presents the seafloor instability when methane hydrated block sediments due to augmentation of temperature or pressure difference. Finally yet importantly, environmental risks and hazards during the operation of production and drilling hydrate reservoirs occupy a significant position in the presentation of this research.

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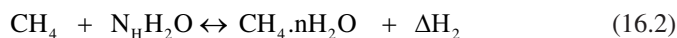
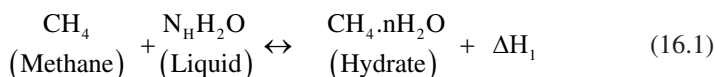
## Keywords

Climate · Energy · Environment · Natural gas hydrates

## 16.1 Introduction

Worldwide demand for energy is bound to rise substantially in the following periods as the human population expands. Referring to the case of US DOE 2016 International Energy Outlook, the global energy consumption will increase from 549 quadrillion BTU in 2012 to 815 quadrillion BTU in 2040, nominating 48% increase. The main contributors to this rise in demand are non-OECD developing economies, namely, China and India, where demand is predicted to augment by 112% between 2010 and 2040 (E.I.A Annual Energy Book 2013). While the expectation is that renewables and nuclear source can yield more energy as time advances, the amount produced is probably still far from meeting the huge augmentation in energy demand. By 2040, the projections indicate that more than 76% of energy will be of the carbon-based source (gas, oil, and coal), despite the expansion in other renewable sources (Exxon Mobil Outlook 2014). Of these three carbon-based energy sources, natural gas is projected to have the highest rate of increase (1.7% on yearly basis) in comparison with the other fossil energy sources (0.9% p.a. for liquid fuel and 1.3% p.a. for coal) (I.E.A World Energy 2013).

Approximately 80% of worldwide energy request is met by unconventional sources. Gas hydrates (GH) will play a leading role in the future (I.E.A World Energy 2011). Natural gas hydrates (NGH) are natural gas resources which have stayed stationary for millions of years until they have been found since the 1960s (Makogon 1965; Makogon et al. 2007). These icelike solid compounds, which contain hydrocarbons, are existent in permafrost and marine environments. Gas hydrate (GH) resources are distributed more diversely and are present in greater quantities than conventional and other unconventional resources combined, which led various research groups around the globe to take interest in the subject (Merey and Longinos 2018a, b). Natural gas hydrates (NGH), commonly called clathrates, are crystalline compounds that take place when water forms a cage-like structure around small-size gas molecules (Sloan 1991). Natural gas hydrates are nonstoichiometric solid compounds and they are formed when the components come into contact at high pressure and low temperature (Sloan 2003). Gas hydrates are composed of water and mainly the following gas components: methane, ethane, propane, isobutene, normal butane, nitrogen, carbon dioxide, and hydrogen sulfide (Sloan 1991). Makogon clarified the methane hydrate formation reaction as



where  $N_H$  is the hydration number approximately equal to 6 for methane hydrates (Sloan and Carolyn 2008). The hydrate formation reaction is an exothermic procedure, which produces heat, while the hydrate dissociation reaction is an endothermic process, which engrosses heat. The heat of configuration of methane hydrate from methane and liquid water is  $\Delta H_1 = 54.2$  kJ/mol, and the heat of configuration of methane hydrate from methane and ice is  $\Delta H_2 = 18.1$  kJ/mol (Grover 2008).

In 1778, Sir Joseph Priestley produced the first factitious hydrates. Sir Priestley noticed that there was an enhanced “ice” configuration during the time that cold water came into association with sulfur dioxide (Makogon 1997). After 20 years from Sir Joseph Priestley’s factitious hydrates, in 1810, Sir Humphry Davy reported on chlorine hydrates as a form of solid water. Davy’s evenly well-known assistant, Michael Faraday, also perused the hydrate of chlorine, and in 1823, Faraday mentioned the composition of the chlorine hydrate. Nevertheless, his outcome was not correct; it was the first time of determining the composition of a gas hydrate (Caroll 2009). GH became a significant subject of economic interest in the 1930s when their contingency to clog gas and oil in pipelines became conspicuous (HammerSchmidt 1934; Wilcox et al. 1941).

Concerning the GH fields, the Russian scientists measured a large amount of CH<sub>4</sub>-rich gas hydrate that supposedly existed in both permafrost regions (Makogon 1965) and marine sediments (Makogon et al. 1971). The first GH field was discovered in Siberian permafrost and then followed by discoveries in Caspian and the Black Sea in 1974 (Makogon 1997). Studying gas hydrates started to be significant due to the augmentation of energy prices in the 1970s. Table 16.1 presents the basic stages of gas hydrate discovery and posterior evolvement (Makogon 2010).

On the other side, there are some physical properties of GH that differ from those of ice. These properties are mechanical strength, heat capacity, thermal conductivity, etc. Table 16.2 compares the physical properties of the two most common hydrate structures with those of liquid water and ice (Koh et al. 2011).

**Table 16.1** Achievements on different aspects of hydrates

Period	Achievements
1778	Priestley acquired SO <sub>2</sub> hydrate in the laboratory
1811	Davy obtained Cl <sub>2</sub> hydrate in a laboratory and named it to hydrate
1934	Hammer Schmidt perused gas hydrates in industry
1965	Makogon showed that natural gas hydrates exist in nature and represent an energy resource
1969	Official registration of scientific discovery of NGH
1969 (24 December)	Start of gas production from the Messoyakha gas hydrate deposit in Siberia
1990s	Initial characterization and quantification of methane hydrate deposits in deep water
2000s	Attempts to quantify location and abundance of hydrates begin. Large-scale attempts to exploit hydrates as fuel begins

Adapted from Makogon (2010)

**Table 16.2** Physical characteristics of gas hydrates compared with those of ice (Koh et al. 2011)

Property	Water	Ice Ih	Structure I (sI)	Structure II (sII)
Thermal conductivity $\lambda$ ( $\text{Wm}^{-1} \text{K}^{-1}$ )	0.58 (283 K)	2.21 (283 K)	0.57 (263 K)	0.51 (261 K)
Thermal diffusivity $\kappa$ ( $\text{m}^2 \text{s}^{-1}$ )	$1.38 \times 10^{-7a}$	$11.7 \times 10^{-7a}$	$3.35 \times 10^{-7}$	$2.6010^{-7}$
Heat capacity $C_p$ ( $\text{Jkg}^{-1} \text{K}^{-1}$ )	4192 (283 K)	2051 (270 K)	20,319 (263 K)	2020 (261 K)
Linear thermal expansion at 200 K ( $\text{K}^{-1}$ )	–	$56 \times 10^{-6}$	$77 \times 10^{-6}$	$52 \times 10^{-6}$
Compressional wave velocity $V_p$ ( $\text{kms}^{-1}$ )	1.5	3.87 (5 Mpa, 273 K)	3.77 (5 Mpa, 273 K)	3.821 (30.4–91.6 Mpa, 258–288 K; C <sub>1</sub> -C <sub>2</sub> )
Shear wave velocity $V_s$ ( $\text{kms}^{-1}$ )	0	1.94 (5 Mpa, 273 K)	1.96 (5 Mpa, 273 K)	2.001 (26.6–62.1 Mpa, 258–288 K; C <sub>1</sub> -C <sub>2</sub> )
Bulk modulus $K$ (GPa)	0.015	9.09 (5 Mpa, 273 K)	8.41 (5 Mpa, 273 K)	8.482 (30.4–91.6 Mpa, 258–288 K; C <sub>1</sub> -C <sub>2</sub> )
Shear modulus $G$ (GPa)	0	3.46 (5 Mpa, 273 K)	3.54 (5 Mpa, 273 K)	3.666 (30.4–91.6 Mpa, 258–288 K; C <sub>1</sub> -C <sub>2</sub> )
Density $\rho$ ( $\text{kgm}^{-3}$ )	999.7 (283 K)	917 (273 K)	929 (273 K)	971 <sup>b</sup> (273 K); 940 (C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> )

<sup>a</sup>Calculated from  $k = 1/(r * C_p)$

<sup>b</sup>Calculated from Sloan (2003)

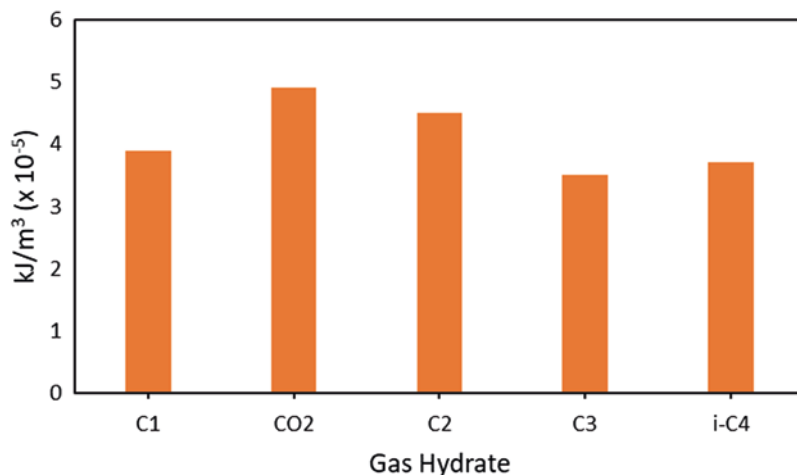
As methane hydrates are able to comprise between 150 and 180 v/v at standard temperature and pressure conditions, they provide distinct gas storage characteristics. The subsequent discovery of hydrate self-preservation, a property which permits hydrates to stay metastable under the conditions of some degrees lower than the ice point, while at atmospheric pressure (Sloan 2003; Makogon 1997), has influenced scientists to peruse the possibility of storing and transporting gas in the form of hydrates. Such research was conducted for the initial time by Gudmundsson et al. (1995) in the early 1990s; then, various scholars have published results in this area of research (Koh et al. 2011).

Gas hydrates look like compact ice and can be burnt, and they usually smell like natural gas. One cubic foot of methane hydrate can compress around 164 ft<sup>3</sup> of methane at standard pressure  $P$  and temperature  $T$  (Makogon 1994). The density for GH varies, firstly according to the composition of the gas, secondly according to temperature  $T$ , and finally due to pressure  $P$ , which they are used to form hydrates. The values of density are measured from 0.8 to 1.2 gm/cm<sup>3</sup> (Makogon 2007) (Table 16.3).

Due to the fact that the density of GH is 0.920 gr/cm<sup>3</sup>, methane hydrate is less dense than the water. The cavities in the hydrate crystal for the degree of filling depended on the hydrate texture. The morphologies for GH can be varied due to gas composition and crystal growth conditions (Makogon 1981). The hydrate dissociation is an endothermic reaction. Figure 16.1 shows the heat of dissociation of different hydrates (Makogon 1997) (Table 16.4).

**Table 16.3** Properties of different hydrates (Makogon 1997)

Gas	Formula of hydrate	Hydrate density@273 K(gr/cm <sup>3</sup> )
CH <sub>4</sub>	CH <sub>4</sub> .6H <sub>2</sub> O	0.910
CO <sub>2</sub>	CO <sub>2</sub> .6H <sub>2</sub> O	1.117
C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub> .7H <sub>2</sub> O	0.959
C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>8</sub> .17H <sub>2</sub> O	0.866
C <sub>4</sub> H <sub>10</sub>	iC <sub>4</sub> H <sub>10</sub> .17H <sub>2</sub> O	0.901

**Fig. 16.1** Heat dissociation of different hydrates. (Adapted from Makogon 1997)

## 16.2 Hydrate Structures

Water molecules that synthesize the cavities, which are constituted of pentagonal and hexagonal faces, mold hydrates. The combination of alternative faces helps for the formation of different hydrate structures to the fact that geometric structures are significant to comprehend the nature of hydrates. Two structures (types) of hydrates are the most common in the chemical and petroleum industry, and these are the structure I (sI) and structure II (sII). Another structure (type) that is less common than the two previous structures is the structure H (Sloan and Carolyn 2008).

The structures (sI, sII, and sH) are described by the parameters of Table 16.5. The small cage (SC) of sI is connected in space by the vertices of the cages. In the small cage (SC) of structure sII, the faces are shared. The spaces for both of the structures between the SC are formed by a large cage (LC). As far as it concerns the structure sH, the face sharing occurs in two dimensions such that a layer of SC connects to a layer of medium and large cages (Sloan and Koh 2007; Ribeiro and Lage 2008). The three structures of gas hydrate embody alternative guest molecules into a single cell but, sH needs two different-sized molecules to form: One small molecule as a helping gas such as methane accomplishing the small cage and a large molecule (Sloan 1990).

**Table 16.4** Physical properties of gas hydrates compared with those of ice (Koh et al. 2011)

Property	Water	Ice Ih	Structure I (sI)	Structure II (sII)
Thermal conductivity $\lambda$ ( $\text{Wm}^{-1} \text{K}^{-1}$ )	0.58 (283 K)	2.21 (283 K)	0.57 (263 K)	0.51 (261 K)
Thermal diffusivity $\kappa$ ( $\text{m}^2 \text{s}^{-1}$ )	$1.38 \times 10^{-7a}$	$11.7 \times 10^{-7a}$	$3.35 \times 10^{-7}$	$2.60 \times 10^{-7}$
Heat capacity $C_p$ ( $\text{Jkg}^{-1} \text{K}^{-1}$ )	4192 (283 K)	2051 (270 K)	20,319 (263 K)	2020 (261 K)
Linear thermal expansion at 200 K ( $\text{K}^{-1}$ )	–	$56 \times 10^{-6}$	$77 \times 10^{-6}$	$52 \times 10^{-6}$
Compressional wave velocity $V_p$ ( $\text{kms}^{-1}$ )	1.5	3.87 (5 Mpa, 273 K)	3.77 (5 Mpa, 273 K)	3.821 (30.4–91.6 Mpa, 258–288 K; $C_1$ - $C_2$ )
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<sup>a</sup>Calculated from  $k = 1/(r * C_p)$

<sup>b</sup>Calculated from Sloan and Carolyn (2008)

Structure I gas hydrates comprise 46 water molecules per unit cell arranged in two dodecahedral voids and six tetrakaidecahedral voids which can accommodate at most eight guest molecules. The hydration number ranges from 5.75 to 7.67. Structure II gas hydrates comprise 136 water molecules per unit cell arranged in 16 dodecahedral voids and eight hexakaidecahedral voids, which can also accommodate up to 24 guest molecules with hydration number 5.67. The rarer structure of gas hydrates, which contain 34 water molecules per unit cell arranged in three pentagonal dodecahedral voids, two irregular dodecahedral voids, and one icosahedral void, can accommodate even larger guest molecules such as isopentane. The hydration number of sH is 5.67 like sII (Longinos 2015; Koh et al. 2011).

### 16.3 Location of Gas Hydrates

After 1920 when the pipelines started to transport methane from gas reservoirs, there was more knowledge about hydrate applications. In low temperature, there was a plug in pipelines which sometimes put obstacles for the gas to flow through them. In the beginning, these blocks were construed as frozen water. The correct description about these blocks was given in the 1930s, and it was hydrate. About

**Table 16.5** Structures of gas hydrate cells

Structure	I	II	H
Crystal system	Cubic	Cubic	Hexagonal
Space group	Pm3n (no. 223)	Fd3m (no. 227)	P6/mmm (no. 191)
Ideal unit cell	$2(5^{12})6(5^{12}6^3) \times 46\text{H}_2\text{O}$	$16(5^{12})8(5^{12}6^4) \times 136\text{H}_2\text{O}$	$3(5^{12})2(4^3 5^{16}6^3) \times 34\text{H}_2\text{O}$
Ideal hydration number	5.750	5.667	5.667
Cages	Cages	Cages	Cages
Average cavity radius (Å)	Small 3.95	Small 3.91	Small 3.94
Variation in radius (%)	Large 3.4	Large 5.5	Medium 4.0
Water molecules per cavity	20	20	20
		Large 28	Large 20
		Large 4.33	Medium 4.04
		Large 14.4	Large 5.79
		Large 24	Large 15.1
		Large 4.73	Large 36
		Large 1.71	

Space group reference numbers from the International Tables for Crystallography (Sloan and Koh 2007)



98% of the GH resources are concentrated in marine sediments, with the other 2% beneath the permafrost. The majority of occurrences of GH have been found by scientific drilling operations, and the inferred GH accumulations have been clarified by seismic imaging (Boswell et al. 2010).

In 1946, Russian researchers nominated that the conditions and resources for hydrate formation and stability exist in nature, in regions covered by permafrost (Makogon 1997). After this proposal from the Russians scientists, there was a discovery of the naturally occurring hydrates. This fact took place in 1968 at Byrd Station in western Antarctica where ice cores including hydrates were educed during scientific drilling program (Miler 1969). In the 1970s, researchers after drilling programs explored hydrates taking place amply in deep water sediments on outer continental margins. Lately, hydrates have been noticed on the seafloor, and in one occasion, hydrates were located in the surface of a fishing net (Riedel et al. 2014). The last appearance of hydrate on the surface in sediments happened due to gas seeps which are also called cold vents such as those in the Gulf of Mexico (GoM) and off the Pacific Coast of Canada. Scientists noticed that hydrates can take place in many places of the world and the depth range varies from 100 to 500 m beneath the seafloor. Important hoardings of hydrates have been defined on North Slope of Alaska, in northern regions of Canada, in the Gulf of Mexico (GoM), in Japan, in China, in India, and in South Korea (offshore reservoirs) (Brook et al. 1986; Merey and Longinos 2018a, b, c).

The four important plays that hydrates could be discovered were sand-dominated plays, fractured clay-dominated plays, huge quantities of gas hydrate formations exposed at seafloor, and low-concentration hydrates disseminated in a clay matrix. It is also found that hydrates exist in fracture fillings in clay-dominated systems in shallow sediments (Merey and Longinos 2018a, b, c). The NGH in marine sediments are regulated by the hoardings of particulate organic carbon (POC) which is microbial transformed into methane, the thickness of the GH stability zone (GHSZ) that methane ( $\text{CH}_4$ ) can be ensnared, the sedimentation rate (SR) that checks the time that POC and the produced methane( $\text{CH}_4$ ) stays within the GHSZ, and the distribution of  $\text{CH}_4$  from deep-seated sediments by ascending pore fluids and gas into the GHSZ (Pinero 2012).

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## 16.4 Gas Seepages

The seeps of natural gas are caused by upward migration of light hydrocarbons which formed in source rocks before being confined in reservoirs. Seeps include mud volcanoes, dry seeps, and springs rich in  $\text{CH}_4$ . They offer invaluable knowledge for hydrocarbon exploration and geology, structural and tectonic research, and environmental concerns, for example, geohazards and greenhouse gas budget. The impetus for seeps is pressure gradients in hydrocarbon subsurface accumulations. These are known historically to being crucial driving forces behind hydrocarbon exploration worldwide (Rhakmanov 1987). Additionally, they aid hydrocarbon utilization in the

area of geochemical and pressure alteration assessment in fluid extraction. They are also vital for defining the petroleum seepage system (Abrams 2005).

Both tectonic discontinuities and rock formations with enhanced secondary permeability can be identified effectively by the existence of seeps. They provide knowledge of the location and depth of gas-bearing faults. Due to its sensitivity to seismic activity, mud volcanism, particularly, has been examined comprehensively (Mellors et al. 2007). Studies conducted on ecological problems, such as aquifer contamination and underground gas storage feasibility, could benefit from seeps. However, they have been identified as a hazard for humans and constructions also (Etiopie et al. 2006). When CH<sub>4</sub> concentrations touch the explosive levels (5–10% in the presence of air), sudden flames and explosions are likely to happen in gas-rich environments, such as soil and boreholes. The combination of CH<sub>4</sub> and hydrogen sulfide (H<sub>2</sub>S) (e.g., in salt diapirism zones) gives seeps the ability to be toxic and, sometimes, fatal under certain conditions. Another cause of hazards is highly fluid mud, particularly in mud volcanoes. It can promote the development of “quicksand” which is known to present risks for fauna and human beings.

Buildings and infrastructures can be impaired by seeps and mud volcano plumbing in two mechanisms: gas pressure buildup under the soil and overall degrading of geotechnical characteristics of soil foundations. To conclude, both onshore and offshore seepage, including microseepage, are among the main greenhouse gas sources, due to the estimations yielding that seepage is the second most significant natural source of CH<sub>4</sub> in the atmosphere, after wetlands (Etiopie and Milkov 2004). Identification of methane source (i.e., biogenic from carbonate reduction, biogenic from acetate fermentation, thermogenic, inorganic) offers information regarding the environment and process behind its formation. With this knowledge, seepage gases can be utilized for tracing hydrocarbon reservoirs, as well as indicating geodynamic processes, hazards, and their role in worldwide changes (Etiopie and Klusman 2002).

Visible manifestations (macroseeps) could be formed by gas seepage. These, in general, disturb soil settings and surface morphology. More often, we have microseepage, which is invisible yet prevalent, diffuse emission of light hydrocarbons from the soil. It can be distinguished using standard analytical procedures. Microseepage is capable of reducing the methanotrophic consumption taking place in dry and/or cold soils. Hence, it leads to positive fluxes of methane to the air through large areas (Etiopie and Klusman 2008). Both macro- and microseepage normally result from gas advection. The latter is driven by pressure gradients and permeability (Darcy’s law) through faults, fractures, and bedding planes (Brown 2000). Advection comprises single-phase gas movement and two-phase flows, as density-driven or pressure-driven continuous gas-phase dislocating water in saturated fractures, the floating motion of gas bubbles in aquifers and water-saturated fractures, in the form of slugs or microbubbles (Etiopie and Martinelli 2002). The slow gas motion driven by concentration gradients, known as diffusion (Fick’s law), is dominant only in long-term and small-scale gas flow through more homogeneous porous media, for example, primary hydrocarbon migration from source rocks to reservoirs or into nearby pools.

Per se, we cannot invoke it for source seeps. Macroseeps have three main subcategories: mud volcanoes, water seeps, and dry seeps. Mud volcanoes emit a three-phase (gas, water, and sediment) mix (Dimitrov 2002). Water seeps discharge a profuse gaseous phase, alongside water release (bubbling springs, groundwater, or hydrocarbon wells), in which the water can have a deep origin and there is probability of it being interacted with gas through its rise to the surface. Dry seeps have only gaseous-phase emissions, such as gas vents from outcropping rocks or via the soil horizon or by river/lake beds (Etiopie et al. 2009).

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## 16.5 Environmental Impacts of Gas Hydrates

In the last decades, the attention of both scientific and political community on climate alteration has augmented (Sanjairaj et al. 2012; Pryor and Barthelmie 2010). Marine ecosystems have accepted environmental impacts due to decrease of oxygen concentration dissolved and the augmentation of sea temperature (Deutsch et al. 2015). Both governments and industrial sector must face the treatment of climate change dominantly, and more financial backing and coating in green technologies must be supported (Watts et al. 2015). Furthermore, EU countries agreed to have a 20% decrease in their greenhouse gas emissions by 2020 compared to 1990 (Roos et al. 2012).

Nevertheless, there are limited studies targeting the policies concerning GH-urged climate alteration and recommended solutions. It is obvious that until GH become an attainable energy source, it will be needed to overcome different present difficulties (Sanjairaj et al. 2012). Any try of a production test of GH could be a contingent danger for both marine and atmospheric environment (Hautala 2014). The process of releasing methane gas from hydrate in either marine environment or the atmosphere by anthropogenic actions or natural causes may create environmental impacts on component poise, sea environment, and even global climate alteration. In addition to the devolution into a gas from solid-phase GH and the continued reduced aid to the sand grains that take place in the surroundings, it creates seafloor instability and sometimes submarine landslides (Zhao et al. 2017).

Anthropogenic activities may cause the instability of methane hydrates, or methane hydrates may dissociate naturally. For example, a little temperature rise in the deep sea can cause methane hydrates to start dissociating. Temperature rise that occurs in deep parts of the ocean might trigger surface climate alteration and the outcome being the release of crucial amounts of methane from GH. Therefore, these result in the increase of carbon in the atmosphere (Schiermeier 2008). Besides temperature alterations in the high depth of the sea, the ocean motion encourages the release of gas-hydrate-derived methane (Thomsen et al. 2012). The period and strength of wobbling currents strongly influence methane seepage. Actually, motions produced by winds, daily rock waves, or internal semi-quotidian tides create the eruptions of intense bottom current. Typical spatial scales over 100 km and time periods up to several weeks characterize the inertial motions (Jordi and Wang 2008).

According to Thomsen et al., methane dissolution rates are changing linearly with friction velocity (Lifshits et al. 2018). Long periods (100–1000 years) of

ventilation take place in the high depth of the sea. Hence, it takes a new equilibrium methane hydrate inventory 1000–10,000 years. Likewise, the fraction of methane from the bottom of the sea that attains the atmosphere is precarious and depends on the function of transportation like bubbles (Boldyreff 2016).

There is an abundant amount of methane hydrate beneath permafrost and seabed. Yet, this potential energy source can be a major trigger of global warming. Methane has a global warming potential (GWP) of 21, which means that a tonne of methane, when dissociated into the atmosphere, has the warming potential 21 as compared to a tonne of carbon dioxide released over 100 years which has a warming contingency of 1 (Hope 2006). Because of the higher quantity of carbon dioxide compared to methane in the atmosphere, methane has less saturated infrared radiation bands (Change IPOC 2007). Thus, a high quantity of methane which is released naturally to the atmosphere might be an intrinsic parameter of global warming. Organic materials which are agglomerated from the photosynthesis both in terrestrial and in marine environments are degraded and lead to the formation of methane. Due to the unsteadiness of methane hydrates beneath the earth, methane hydrate (MH) is essentially vulnerable to be released. The vast quantity of methane which can be released unexpectedly might attenuate the present climatic conditions.

Due to climate alterations, there is a global elevation of temperature which might lead to the deduction of permafrost in the Arctic and the release of stored methane gas. Hence, the deterioration of the climate change is attributed to the greenhouse gases (i.e., methane). Actions could be taken, firstly, to audit the escape of methane from hydrates and, secondly, to capture gas released, for the removal of the phenomenon of global warming. A 3 °C positive temperature change could release 35–94 GtC of methane gas, which may increase 12-fold the methane percentage in the atmosphere. As an outcome of this, there would be an extra 0.5 °C of global warming (Saxton et al. 2016).

Methane dissociation from hydrates in the sea areas might lead to sea acidification and oxygen reduction. Microbial anaerobic oxidation of methane (AOM) could retain more than 50% of the dissolved methane within the seafloor (Knittel and Boetius 2009). AOM transforms oxygen and methane into carbon dioxide, which is the main substance of affecting the oceanic pH (Biaostoch et al. 2011). Both induced methane and anthropogenic carbon dioxide are the main factors for the deterioration of the oceanic acidification (Solomon 2007). Adverse effects on the sea environment may be imposed by oceanic acidification. When the pH in the marine system is lowered, fertilization and reproduction of sea species may be influenced. This will lead to a decrease in species population, as well as a calcification at larval and settlement stages. Shellfish such as oyster, clams, and corals can be influenced by the higher partial pressure of carbon dioxide (Kurihara 2008).

Through the formation of methane hydrate within the sediment pore spaces, there is immobilization of solid-form methane and water. The imposing stresses of the sediment emerge because water cannot be expelled into it. Due to the augmentation of the temperature or the pressure lessening, methane hydrate solidifies the sediment and becomes erratic. The hydrate-bearing sediments will be consolidated by gas mixture, and liquid water will be dissociated by the hydrate. Then, the

resulting methane release will lead to the formation of a zone with a low shear strength (Dou et al. 2011). Subsequently, deformation of the seafloor exists, which results in a submarine landslide, an earthquake beneath the seabed, and even a tsunami. Furthermore, it is supported that every mass failure produced by the catastrophe of continental slope is correlated with one or another way with the diminishment of sea level due to climate change.

The quick diminishment of sea level creates instability to gas hydrate deposits, and this leads to triggering the slope malfunction and the glacial mass transport of deposits (Thomsen et al. 2012). The slope failure and the glacial mass transport of deposits could be triggered by the quick change of sea level destabilizing gas hydrate reservoirs in the mainland (Maslin 1998). Moreover, in hydrate reservoirs in oceans underlain by sediment comprising gas hydrate, the diminishment of sea plump could commence the dissociation along the base of gas hydrate, which successively would congest the escape of large volumes of gas into the sediment augmenting the pore-fluid pressure and diminishing the slope firmness (Zhang et al. 2016).

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## 16.6 Gas Hydrate Environmental Issues in Drilling Operations

Nowadays worldwide, there is quite enough knowledge about drilling conventional gas and oil wells both in the shoreward and in seaward environment. Nevertheless, trying to drill a gas hydrate well needs knowledge, which is not quite existent yet. Researchers and engineers should estimate how to drill a gas hydrate well without enough features. Hence, it is obvious that the function of drilling gas hydrate reservoirs may be hazardous. Several essential dangers are observed: (1) When hydrate is formed, it blocks the borehole; (2) when gas hydrates are dissociated abruptly, it creates blowout; (3) when gas hydrates are separated abruptly, there is danger of slope failure; and (4) when gas hydrates are separated, there is difficulty in both instability of the wellbore and danger in wellbore subsidence because of the loose sediments (Tan et al. 2005).

When the procedure of drilling starts, the management of temperature and pressure in the wellbore must be audited to limit reservoir's hydrate dissociation together with annulus mud. Another challenge during drilling operations in hydrate reservoirs is the correct casing design to resist high values of pressure. Furthermore, when fracture gradient and pore pressure are very close (there are limited window margins), there is a high possibility for kick or formation fracture risks, which lead to the collapse of the well. Finally yet importantly, in drilling operations in gas hydrate reservoirs, there must be frequent good control for gas kick circulation or abrupt gas flow for unconsolidated formation (Motghare and Musale 2017). All these challenges may create huge environmental problems especially in offshore locations (95% of hydrate reservoirs) with countless consequences on the sea chain.

More specifically, hydrate drilling risks can be separated into drilling and testing processes. In a casing program, the well part must be drilled with a drilling fluid that provides high relative density, which will give the maximum wellbore pressure and the

highest possibility for hydrate risk. The intensity of heat present and pressure field in the wellbore at alternative pumping proportions of drilling fluid can be prognosticated by the assistance of heat and mass transfer model in which parts such as heat devolution between the fluid in the drill string, the wall of the drill string, the fluid in the annulus, and the ambient environment are examined. Due to geothermal gradient at the starting state, the temperature in the wellbore during drilling process was acquired through time-repetitive estimation along the converse flow movement of drilling fluid up to the heat in the wellbore of the field arrived approximately in a stable situation, although the pressure inside the reservoir was estimated due to fluid friction loss in drill string and annulus and the pressure difference (decrease) at the drill bit.

At the wellbore temperature of the reservoir at alternative drilling fluid pumping values, the intersected part between the wellbore temperature curve and the hydrate temperature curve is the good section with hydrate risk. It is also known that at alternative drilling fluid pumping rate, the wellbore section is different. Hence, the good section at water depth between specific meters is under hydrate risk, and the highest value of undercooling temperature is at high temperature and takes place at seabed mud line (Bangtang et al. 2014; Bo 2007; Yonghai et al. 2008).

As far as it concerns the testing process when the well arrives at the design depth, the casing will be put for the cementing process, and the drill string will be utilized for gas production testing. At the time that there is perforation at the correct layer, the testing fluid of the drill string will be dislocated by the natural gas and blown to the surface connected with a short amount of formation water under throttle control. At another time, the pressure field and wellbore temperature during testing of alternative gas values and water contents were prognosticated by the use of heat and mass transfer model of deepwater production well. The wellbore pressure is estimated by the use of Orkiszewski method, while the estimation of wellbore temperature regards the heat transfer between the fluid in test string and annulus, the cement sheath and the rock below seabed, and seawater above seabed, while the whole temperature value can be estimated by using the discrete coupling formula of pressure and temperature reservoirs from the bottom to the wellhead (Zhang et al. 2014).

It can also be noticed that if it's shut down long enough during testing, the wellbore temperature will be equal as the ambient temperature. At the initial moment of the testing, the pressure in the test string augmented slowly but surely, when the natural gas changes the testing fluid from downhole to the surface, but the highest undercooling temperature in the test string will not go up to the case when the test is paused with the test string filled with natural gas. Through throttling open flow, the test string will be loaded with natural gas and a small amount of formation water. Augmentation in both gas values and water concentration is positive for decreasing pressure and increasing temperature in the wellbore, which will lead to shorten the well part with hydrate risk (Yang et al. 2013).

Two field examples of hydrate problems in the face of drilling activities took place in US west coast in the depth of 350 m and in the Gulf of Mexico in 950 m, respectively. In the initial occasion of 350 m drilling operation, gas inserted in the well and the kill process endured 1 week, and then, hydrates were generated in riser, choke, and kill lines and blowout preventer (BOP). The second occasion of 950 m

took place in the Gulf of Mexico where an elongated well control process ensued from malfunction of the BOP to work suitably due to hydrates. As an outcome, unpropitious implications of hydrate formation in the phase of well control process took place such as the plugging of kill and choke lines which obstruct well circulation. The audit of well pressure below the blowout preventers (BOPs) is obstructed due to the plugging formation at or below BOPs. The drill string rotation is hindered due to hydrate formation plugging the riser, BOPs, or casing. The total aperture of BOP is blocked from hydrate formation plugging the cavity of a closed BOP (Baker and Gomez 1989).

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## 16.7 Conclusion

Worldwide demand for energy is bound to rise substantially in the next decades as human society expands. Referring to the case of US DOE 2016 International Energy Outlook, the global energy consumption will increase from 549 quadrillion BTU in 2012 to 815 quadrillion BTU in 2040, indicating a 48% increase. Natural gas hydrates may be considered as both a promising future energy source and a possible contributor to the global climate change. The relationship between gas hydrates and climate is not clear; however in geological history, there were clear facts showing that high amount of release of methane gas from hydrates had a probable potent effect on global climate. This fact can be easily understood. Although the residence time of gas hydrate release is limited in the atmosphere over the lifetime, methane as gas compared to carbon dioxide is around 20 times more effective in terms of its total greenhouse contamination. Moreover, the ongoing methane release in sea environments may be spliced to alter the climate with the objection that the historical data of these inferences is little and needs verifications.

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## References

- Abrams MA (2005) Significance of hydrocarbon seepage relative to petroleum generation and entrapment. *Mar Pet Geol* 22:457–477
- Bangtang Y, Xiangfang L, Baojiang S et al (2014) Hydraulic model of steady state multiphase flow in wellbore annuli. *Pet Explor Dev* 41(3):359–366
- Barker JW, Gomez RK (1989) Formation of hydrates during deepwater drilling operations. *JPT* 41(3):297
- Biaostoch A, Treude T, Rüpke LH, Riebesell U, Roth C, Burwicz EB et al (2011) Rising Arctic ocean temperatures cause gas hydrate destabilization and ocean acidification. *Geophys Res Lett* 38:L08602
- Bo W (2007) Research on the method of wellbore temperature and pressure calculation during deep-water drilling. China University of Petroleum, Dongying
- Boldyreff VM (2016) Water vapor and “greenhouse effect”. *Inf Agency Regnum*. <https://doi.org/10.3334/CDIAC/atg.032>
- Boswell R, Collett T, Cook A (2010) Developments in gas hydrates. *Oil Field Rev* 1:18–33
- Brooks JM, Cox HB, Bryant WR, Kennicut MC (1986) Association of gas hydrates and oil seepage in the Gulf of Mexico. *Org Geochem* 10(1–3):221–234

- Brown A (2000) Evaluation of possible gas micro seepage mechanisms. *Am Assoc Pet Geol Bull* 84:1775–1789
- Carroll JJ (2009) *Natural gas hydrates – a guide for engineers*, 3rd edn. Elsevier, Amsterdam
- Change IPOC (2007) *Climate change 2007: the physical science basis, Agenda*, vol 6. Cambridge University Press, Cambridge, p 333
- Deutsch C, Ferrel A, Seibel B, Pörtner H-O, Huey RB (2015) Climate change tightens a metabolic constraint on marine habitats. *Science* 348:1132–1135
- Dimitrov L (2002) Mudvolcanoes the most important pathway for degassing deeply buried sediments. *Earth Sci Rev* 59:49–76
- Dou B, Jiang G, Qin M, Gao H (2011) Analytical natural gas hydrates dissociation effects on globe climate change and hazards. ICGH, Edinburgh
- E.I.A. US (2013) *Annual energy outlook 2016*. U.S. Department of Energy, Washington, DC
- Etiopie G, Klusman RW (2002) Geologic emissions of methane to the atmosphere. *Chemosphere* 49:777–789
- Etiopie G, Klusman RW (2008) Micro seepage in drylands: flux and implications in the global atmospheric source/sink budget of methane. *Glob Planet Chang* (in press)
- Etiopie G, Martinelli G (2002) Migration of carrier and trace gases in the geosphere: an overview. *Phys Earth Planet Inter* 129(3–4):185–204
- Etiopie G, Milkov AV (2004) A new estimate of global methane flux from onshore and shallow submarine mud volcanoes to the atmosphere. *Environ Geol* 46:997–1002
- Etiopie G, Papatheodorou G, Christodoulou D, Ferentinos G, Sokos E, Favali P (2006) Methane and hydrogen sulfide seepage in the NW Peloponnesus petroliferous basin (Greece): origin and geohazard. *Am Assoc Pet Geol Bull* 90(5):701–713
- Etiopie G, Feyzullayev A, Baciu C (2009) Terrestrial methane seeps and mud volcanoes: a global perspective of gas origin. *Mar Pet Geol* 26:333–344
- Exxon Mobil (2016) *The outlook for energy: A view to 2040*, Technical Report
- Grover T (2008) *Natural gas hydrates-issues for gas production and geomechanical stability*. PhD thesis, Texas A & M University, Texas, pp 6
- Gudmundsson JS, Hveding F, Bomhaug A (1995) Transport of natural gas as frozen hydrate. In: *Proceedings of the fifth international offshore and polar engineering conference*, The Hague, The Netherlands, June 11–16
- Hammerschmidt EG (1934) Formation of gas hydrates in natural gas transmission lines. *Ind Eng Chem* 26(8):851–855
- Hautala SL, Solomon EA, Johnson HP, Harris RN, Miller UK (2014) Dissociation of Cascadia margin gas hydrates in response to contemporary ocean warming. *Geophys Res Lett* 41:8486–8494
- Hope CW (2006) The marginal impacts of CO<sub>2</sub>, CH<sub>4</sub> and SF<sub>6</sub> emissions. *Clim Pol* 6:537–544
- I.E.A (2011) *World energy outlook special report: are we entering the golden age of gas?* International Energy Agency, Paris
- I.E.A (2013) *World energy outlook*. International Energy Agency, Paris
- Jordi A, Wang D-P (2008) Near inertial motions in and around the Palamós submarine canyon (NW Mediterranean) generated by a severe storm. *Cont Shelf Res* 28:2523–2534
- Knittel K, Boetius A (2009) Anaerobic oxidation of methane: progress with an unknown process. *Annu Rev Microbiol* 63:311–334
- Koh CA, Sloan ED, Sum AK, Wu DT (2011) *Fundamentals and applications of gas hydrates*. *Annu Rev Chem Biomol Eng* 2:237–257
- Kurihara H (2008) Effects of CO<sub>2</sub>-driven ocean acidification on the early developmental stages of invertebrates. *Mar Ecol Prog Ser* 373:275–284
- Lifshits SK, Spektor VB, Kershengolts BM, Spektor VV (2018) The role of methane and methane hydrates in the evolution of global climate. *Am J Clim Chang* 7:236–252
- Longinos S (2015) *Analysis of gas hydrates by using geochemical instruments*. Thesis, Ankara
- Makogon YF (1965) A gas hydrate formation in the gas saturated layers under low temperature. *Gazov Promst* 5:14–15
- Makogon, Y.F., F.A. Trebin, Trofimuk A.A., (1971) Finding of a pool of gas in the hydrate state: *DAN SSSR*, v. 196, p. 197–206



- Makogon YF (1994) Russia's contribution to the study of gas hydrates. *Ann N Y Acad Sci* 715:119–145
- Makogon YF (1997) *Hydrates of hydrocarbons*. Pennwell Books, Tulsa, p 482
- Makogon Y (2010) Natural gas hydrates – a promising source of energy. *Nat Gas Sci Eng* 2:49–59
- Makogon YF, Holditch SA, Makogon TY (2007) Natural gas-hydrates – a potential energy source for the 21st century. *J Pet Sci Eng* 56:14–31
- Maslin M, Mikkelsen N, Vilela C, Haq B (1998) Sea-level–and gas-hydrate–controlled catastrophic sediment failures of the Amazon Fan. *Geology* 26:1107–1110
- Mellors R, Kilb D, Aliyev A, Gasanov A, Yetirmishli G (2007) Correlations between earthquakes and large mud volcano eruptions. *J Geophys Res* 112:B04304
- Merey S, Longinos SN (2018a) Does the Mediterranean Sea have potential for producing gas hydrates? *J Nat Gas Sci Eng* 55:113–134
- Merey S, Longinos SN (2018b) Numerical simulations of gas production from Class 1 hydrate and Class 3 hydrate in the Nile Delta of the Mediterranean Sea. *J Nat Gas Sci Eng* 52:248–266
- Merey S, Longinos SN (2018c) Investigation of gas seepages in Thessaloniki mud volcano in the Mediterranean Sea. *J Pet Sci Eng* 168:81–97
- Miller SL (1969) Clathrate hydrates of air in Antarctic ice. *Sci New Ser* 165(3892):489–490
- Motghare PD, Musale A (2017) Gas hydrates: drilling challenges and suitable technology, SPE-185424-MS
- PiNero E, Marquardt M, Hensen C, Haeckel M, Wallmann K (2012) Estimation of the global inventory of methane hydrates in marine sediments using transfer functions. *Biogeosciences* 10:959–975
- Pryor S, Barthelmie R (2010) Climate change impacts on wind energy: a review. *Renew Sust Energ Rev* 14:430–437
- Rhakmanov RR (1987) Mud volcanoes and their importance in forecasting of subsurface petroleum potential. Nedra, Moscow (in Russian)
- Riedel M, Hyndman RD, Spence GD, Chapman NR, Novosel I, Edwards N (2014) Hydrate on the cascadia accretionary margin of North America, AAPG Hedberg research conference
- Ribeiro Jr CP, Lage PLC., Modelling of hydrate formation kinetics: State of the art and future directions, *Chemical Engineering Science*, 2008,63(8): p.2007–2034
- Roos I, Soosaar S, Volkova A, Streimikene D (2012) Greenhouse gas emission reduction perspectives in the Baltic States in frames of EU energy and climate policy. *Renew Sust Energ Rev* 16:2133–2146
- Sanjairaj V, Iniyar S, Goic R (2012) A review of climate change, mitigation and adaptation. *Renew Sust Energ Rev* 16:878–897
- Saxton MA, Samarkin VA, Schutte CA et al (2016) Biogeochemical and 16S rRNA gene sequence evidence supports a novel mode of anaerobic methanotrophy in permanently ice-covered Lake Fryxell, Antarctica. *Limnol Oceanogr* 61:S119–S130
- Schiermeier Q (2008) Fears surface over methane leaks. *Nature* 455:572–573
- Sloan ED, Carolyn AK (2008) *Clathrate hydrates of natural gases*, 3rd edn. CRC Press, Boca Raton
- Sloan ED Jr (1991) *Natural gas hydrates*, JPT SPE technology today series, SPE 23562, pp 1414–1417
- Sloan ED Jr (2003) Fundamentals principles and applications of natural gas hydrates. *Nat Publ Group* 426:353–359
- Sloan ED Jr (1990) *Clathrate hydrates of natural gases*. Marcel Dekker Inc, New York, 641 pp
- Sloan ED, Koh CA (2007) *Natural gas hydrates: recent advances and challenges in energy and environmental applications*, AIChE
- Solomon S (2007) *Climate change 2007-the physical science basis: working group I contribution to the fourth assessment report of the IPCC*. Cambridge University Press, New York
- Tan CP, Freij-Ayoub R, Clennell MB, Tohidi B (2005) Managing wellbore instability risk in gas hydrate-bearing sediments, SPE 92960
- Thomsen L, Barnes C, Best M, Chapman R, Pirenne B, Thomson R et al (2012) Ocean circulation promotes methane release from gas hydrate outcrops at the NEPTUNE Canada Barkley Canyon node. *Geophys Res Lett* 39:L16605

- Watts N, Adger WN, Agnolucci P, Blackstock J, Byass P, Cai W et al (2015) Health and climate change: policy responses to protect public health. *Lancet* 386:1861–1914
- Wilcox WI, Carson DB, Katz DL (1941) Natural gas hydrates. *Ind Eng Chem* 33(5):662–665
- Yang J, Haixiong T, Zhengli L et al (2013) Prediction model of casing annulus pressure for deep-water well drilling and completion operation. *Petroleum* 40(5):2
- Yonghai G, Baojiang S, Wang Z et al (2008) Calculation and analysis of wellbore temperature field in deepwater drilling. *J China Univ Pet Ed Nat Sci* 32(2):58–62
- Zhang L, Zhang C, Huang H, Qi D, Zhang Y, Ren S, Wu Z, Fang M (2014) Gas hydrate risks and prevention for deep water drilling and completion: a case study of well QDN-X in Qiongdongnan Basin, South China Sea, *Petroleum Exploration & Development*
- Zhang XH, Lu XB, Chen XD et al (2016) Mechanism of soil stratum instability induced by hydrate dissociation. *Ocean Eng* 122:74–83
- Zhao J, Song Y, Lim XL, Lam WH (2017) Opportunities and challenges of gas hydrate policies with consideration of environmental impacts. *Renew Sust Energ Rev* 70:875–885