

Methane Clathrate: General Idea and Overview

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Abstract - The demand for energy has grown significantly over the past few years and to meet the ever increasing demand, we have increased the rate of power consumption by amping up the extraction of energy from their respective sources. This has caused the drying up of the current major sources of energy to the heavy industries or powerplants, thus requiring an alternate source of energy which can be utilized once the major sources such as Oil, Natural Gas, Coal, etc. get diminished. Renewable sources of energy such as solar energy, wind energy, tidal energy, geothermal energy etc. are being researched upon for maximum exploitation but the main problem of these sources is that they are very inefficient and are clearly not enough to support the demands of larger industries and powerplants which seem to exponentially grow with time. Thus, the renewable energy sources although less harmful to the environment than the non-renewable counterparts, are still not the viable alternate option. A solution to the above deadlock may be the compound Methane Clathrate; a complex molecule found beneath the oceanic beds which is essentially methane gas trapped in a single molecule of water under high pressure which can be released after extraction and can be harnessed as a source of energy since it is less environment deteriorating than the non-renewable sources and is more efficient than the renewable ones. This paper investigates the underlying potential of the compound and gives a basic idea of the whole relatively unexplored resource and its prospect for future.

Key Words: Methane Clathrate, Non-renewable energy, Renewable energy, Geothermal energy, Oceanic sediments

1. INTRODUCTION

Clathrates or Hydrates are ice-like solids with water as the host molecule and any gas or liquid as the guest molecule which is entrapped inside the hydrogen bonded "cages" of water molecule. Low molecular weight gases such as oxygen, hydrogen, nitrogen, methane, carbon dioxide and noble gases such as argon, krypton, xenon are capable of forming hydrate at suitable temperatures and pressures. Most hydrate structures require high pressure and low temperature for their existence with the exception of chlorine hydrate that can remain stable at room temperature and normal atmospheric pressure. On disintegration, the hydrate structure breaks down and

releases the innate water or ice(if the temperature is below the freezing point) and the guest gas.

Methane Clathrate ($4\text{CH}_4 \cdot 23\text{H}_2\text{O}$) is a compound formed when a large number of methane molecules coalesce together and get trapped inside a water molecule under low temperature and high pressure to form an ice-like substance. Such conditions are commonly found at a few metres of depth below the waterbodies or beneath the permafrost or in deep ocean sediments where methane clathrates exist naturally and is called as gas hydrate stability zone(GHSZ). A single cubic metre of methane clathrate can release upto 164 cubic metres of methane and its holding quantity is estimated at about 250,000-700,000 trillion cubic feet of methane gas over the globe, thus it is undoubtedly a resource with a high potential that needs much attention from the geological and chemical perspective. Almost 95% of methane present in methane clathrates is a result of organic decay of biological plants and animals. It is found in abundance in the sub-oceanic surfaces, beneath the arctic permafrost or below the sediments along the coastal parts of any continent. Other than the oceanic deposits, methane hydrates are also formed during natural gas transport operations when liquid water gets condensed in presence of methane at high pressures which is an undesirable process since it causes blockages in pipelines and causes deterioration of machinery and mechanical parts. Measures are taken to prevent the formation or break down the previously formed clathrate molecules by adding anti agglomerators or inhibitors to the flow regime[7].

2. STRUCTURE

With the help of techniques such as X-ray diffraction, Nuclear Magnetic Spectroscopy, Raman Spectroscopy and Neutron diffraction possible at the existing conditions of methane clathrate, scientists and researchers have been able to actively study and understand the structure of the crystalline compound and the structures have been broadly classified in three types:

2.1 S-1 structure

This variety is the most common type of clathrate found in the world and is usually formed by smaller guest molecules of size less than 0.5 nm. It has two types of cavities, simply put; a small cavity and a large one and

according to the sizes, the smaller molecule occupies the smaller cavity and vice versa. There are two small cavities which are Pentagonal Dodecahedral(512) almost spherical in shape and six large cavities of tetradecanedral geometry having two opposite hexagonal faces and twelve inner pentagonal faces. This 12 Å cubic structure has 46 water molecules and can show transition to S-2 or SH structure under compression. Shown mainly by methane, ethane, carbon dioxide etc [1,2]

2.2 S-2 structure

S-2 structure is mainly formed by larger molecules(0.5 - 0.75 nm size). This variety also has two types of cavities viz 16 smaller cavities of distorted pentagonal dodecahedral geometry and 8 larger hexadecahedral cavities having 4 hexagonal faces and 12 pentagonal faces. The 17.3 Å structure has 136 water molecules and is mainly shown by larger hydrocarbons such as propane, isobutane etc. Due to repulsions within the structure, it is less stable than S-1 structure and sensitive to changes[1,2]

2.3 S-H structure

S-H structure requires both large and small molecules to remain stable and displays hexagonal symmetry. It has 34 water molecules distributed in 3 different types of cavities viz. 3 small 512 cavities, 2 medium irregular dodecahedral cavities and 1 large icosahedral cage. The dodecahedral cavity has 3 square, 6 pentagonal and 3 hexagonal faces as the name suggests and the icosahedral cavity has 12 pentagonal and 8 hexagonal faces. The presence of these many cavities allows much large molecules(7.5-9 Å) to form the clathrates. Mainly formed by a combination of methane-neohexane, methane-cycloheptane, etc [2]



Figure 1: Structure 1, 2 and H respectively

(Image Courtesy: Sa Fakharian)

3. PROPERTIES

Since the clathrate crystalline molecule represents ice closely, the properties are compared with pure ice in the table below[3]:

Table -1: Properties of Methane clathrates

Property	Ice	S-1 structure	S-2 structure
Number of water molecules	4	46	136
Density (Kg/m ³)	916	912	940
Dielectric constant(0°C)	94	58	58
Refractive index (638 nm, -3°C)	1.3082	1.3460	1.35
Young's Modulus at -5°C (Order of 10 ⁹ in Pa)	9.5	8.4	8.2
Poisson's Ratio	0.33	0.33	0.33
Bulk Modulus	8.8	5.6	-
Shear Modulus	3.9	2.4	-
Thermal Conductivity(-10°C)	2.23	0.47 - 0.51	0.49 - 0.53
Heat Capacity(J/Kg.K)	3800	3300	3600

4. METHODS OF EXTRACTION

Research projects are being carried out since 1995 when the idea of methane clathrate existing as an insidious source of energy was much nascent and the technology required to detect and explore the concentration zones or Gas Hydrate Stability zones was not much developed. The general principle of extraction is to destabilize methane clathrates(existing at low temperature and high pressure), for which we must either increase the temperature or decrease the pressure which makes the structure unstable and releases the guest methane. The major processes employed in the extraction process are :

4.1 Thermal Extraction

This method involves the pumping of heated water or brine solution at about 80-90 degree celsius through a well into the gas hydrate deposits. This stream of fluid reaches the methane deposits at a temperature lower than the inlet temperature due to losses since the deposits are present at around 100-1000m below the surface so care has to be taken to minimize the losses or compensate for the same. The fluid stream on reaching the deposits causes destabilization of the crystal structure which ultimately causes breakdown of the clathrate releasing the trapped methane gas in large quantities which is drawn up through the well. An example where this thermal extraction method was used is the experimental testing of the Mallick site in the Mackenzie Delta of Canada that promised heavy quantity of clathrates due to subzero temperatures and high pressure environments in winters. The test was successful in drawing out 470 m³ of methane gas over 5

days in total. This method is not much economically viable since it expends energy in heating the extraction fluid and pumping it into the deposits so should be used only when the quantity of hydrates present is high which can easily overcome the energy spent[1,5,6]

4.2 Depressurization

This method involves lowering of pressure in the methane hydrate deposit layers which is done by drilling through the overlying sediment or draining out the water present on top of the deposit layers. Water or sediments present on the deposits maintain a steady pressure on the clathrate deposits and when removed result in sudden lowering of pressure causing the cage structure to break and release innate methane gas. This method was tested on the Nankai trough region off the coast of Japan for a week that yielded significant amount of methane. This method is economically cheaper than the thermal method but has the drawbacks of causing environmental hazards, being a slow process and instances of ice formation routinely that can plug the entire system creating a blockage overall[1,6].

4.3 Injecting a foreign species

As stated earlier, there are a few low molecular gases which can also form clathrates when met with required conditions of temperature and pressure. This method exploits the stated fact by injecting a certain gas molecule into the deposit layers that are capable of forming stable hydrate structures in that environment. The "foreign" molecule displaces the inner methane as guest due to formation of relatively more stable structure thus forcing the methane out of its cage. Gases like CO₂ and N₂ are capable of displacing methane and forming stable hydrates and are also readily available. The Ignik-Sikumi project in Alaska, carried out by Japan with the help of US employed this method by exchanging methane with carbon dioxide causing methane flow out of the bed at a constant rate over 2 weeks. This method is also extremely slow and environmental deteriorating but has a higher yield[1,5,6].

These methods have been practiced individually or intercombined to gain maximum results but have some or the other limitations which are always encountered. Although they have been successful to some extent, they cannot be stated as a commercial method for continuous extraction and still more exploring and research is called for. Model simulations and mathematical modelling of clathrate bed deposits is one upcoming method that requires attention. This theoretical analysis is done based on seismological data and survey results which is combined with mathematical relations to estimate quantity of resource available and properties that can help in the process of extraction. The combination of mathematical modelling

along with simulations and the above physical extraction processes might be a success later on in the future.

5. DEPOSITS OVER THE GLOBE AND ACTIVE SITES

Methane clathrates are discovered by the images and data collected by the bottom simulating reflector which essentially mirrors the seafloor by observing the seismic variations of the seabeds caused due to uneven sediment deposition and clathrate distributions. Exploration and extraction of gas hydrates from around the globe is usually a joint initiative between public and private sectors from multiple countries. For example, the Mallick exploration conducted on the coast of Canada was a joint initiative by India, Canada, USA and Germany. Mainly, the exploration studies for the gas hydrates deposition focus on five research areas viz. Exploration, Modelling, Field Testing, Development of extraction technology and Health & Environment safety assessment. Various exploration sites and experimental programs carried out by countries are listed below:

In India, a National Gas Hydrate Program (NGHP) was initiated by the Ministry of Petroleum and Natural Gas for exploration of gas hydrate deposits and research & developmental activities, in the year 1997. Kerala-Konkan belt has one site, Krishna-Godavari river belt has fifteen sites, Mahanadi river basin has four sites and Andaman Islands has one site for exploration. Most of the gas hydrate deposits in the Indian Ocean are in the Bay of Bengal region.

Japan launched the Methane Hydrate Exploitation Program - MH21 in July, 2001. Drilled gas hydrates in the Nankai trough area, offshore Japan. In March 2013 Japan confirmed the presence of Methane Hydrate off the coast of Shima peninsula. Joetsu-Noto Sea of Japan is also being searched for potential site for the deposits. Aichi Prefecture is the world's first production from seabed methane hydrates site located on the coast of Japan. Most of the methane hydrate deposits in the Sea of Japan are concentrated near the seafloor's surface, while sandy sediment layers are contained in the reserves of Pacific waters off the Atsumi Peninsula beneath the ocean floor.

Korea conducted marine geophysical surveys in the East Sea between 2000-04 mainly in the Ulleung Basin. Gas hydrate research coring and logging was done in the Ulleung Basin in 2007 (UBGH1). Gas hydrate research coring and logging expedition conducted July-September 2010 in the Ulleung Basin (UBGH2). Gas hydrate production testing in the Ulleung Basin in 2015.

China has examined the geologic occurrence of gas hydrates in the South China Sea. Shenhua area of the South China Sea GMGS-1 (2007) and the Pearl River Mouth Basin of the South China Sea GMGS-1 (2013) are the major gas hydrates sites around Chinese coast. China has conducted

Permafrost gas hydrate drilling and Testing in the regions of Qinghai-Tibet (2007, 2009, 2011) Mohe Basin (2011).

Canada has the Mallik exploration site on the Marine (offshore Pacific and Atlantic margin) and Arctic focus (Mackenzie Delta – Beaufort Shelf) areas of northern coast.

USA has conducted Arctic permafrost gas hydrate testing on Alaskan North Slopes. Gulf of Mexico is also a prime spot for finding out gas hydrate deposits in North America[4]

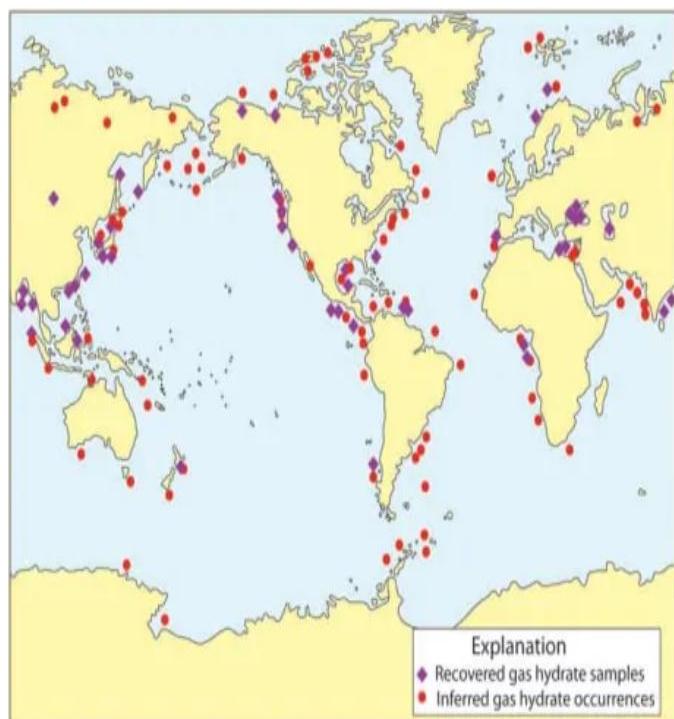


Figure 2: Methane Clathrate deposits over the globe

(Image courtesy: Timothy Collett, US Geological Survey USGS)

6. APPLICATIONS

Apart from the primary application of being used as a source of energy due its enormous quantity of entrapped methane which when released could generate tremendous energy, there are also some secondary applications:

6.1 Carbon dioxide capture and storage

Carbon dioxide that is present in the atmosphere can be absorbed efficiently by methane clathrate. There is an IPCC report which displays the statistics that post industrial era, carbon dioxide emissions must be reduced to a large extent i.e; around 45 % by 2030. To do this, methane clathrate can be used extensively. Carbon dioxide has molecules which are nonpolar and can form hydrates in a formula of $\text{CO}_2 \cdot n\text{H}_2\text{O}$. A unit cell which is formed by

the aforementioned hydrates consists of two small cages and six large cases. Here, n is the hydration number and the large cells are filled in a preferential order because of their size which is favored by carbon dioxide. Carbon dioxide, nitrogen and hydrogen along with methane itself in a particular form are the major gas components for a flue gases, fuel gases and biogases. All these gases have the ability at specific thermodynamic conditions to form hydrates. For temperatures from 0-10 degrees celsius, the phase equilibrium pressure of carbon dioxide hydrate is at an extremely lower pressure than those of the other hydrates formed by hydrogen and nitrogen. CO_2 gas is generally discharged after meeting the stringent discharge requirements from the industries and thus can be trapped in clathrates which can be stored in a location to prevent global warming by the greenhouse effect of carbon dioxide emissions. Research indicates that the hydrates can safely be stored in depleted gas refineries in northern alberta, canada, etc. The subsequent decomposition of the above mentioned clathrates produces a stream of CO_2 rich gas[1]

6.2 Desalination

Freshwater demand has grown consistently in the recent years but the corresponding supply has not grown as much. To rectify this, desalination of seawater technologies have been proposed, especially in places without groundwater like the middle east. Desalination is the removal of excess salts from seawater or brackish water to make it suitable for drinking or irrigation. There are many desalinization techniques currently in use such as reverse osmosis, freeze thawing, distillation, membrane separation, etc. Methane clathrate can be used for desalination techniques and the process is basically a freezing approach. In this process, an electrolyte solution such as seawater is contacted with a hydrate forming agent at proper conditions of temperature and pressure. The water molecules gather around the clathrate molecules and salt along with other impurities are filtered out from the structure making the water free of the undesired impurities. The hydrate crystal can then be mechanically separated and removed from the brine and decomposed to potable water[1]

7. PROBLEMS AND HAZARDS

Apart from the technical problems related to the extraction, which are a major headache for scientists and researchers, there are also some crucial environmental hazards associated with it:

7.1 Global warming/climate change

The most worrying situation regarding clathrates is that a warming of climate could cause rapid decomposition of hydrates causing accumulation of greenhouse gases into the atmosphere. The melting of ice glaciers and increase in overall temperature, both on land and waterbodies is

evident in the environmental reports over the years and increase in temperature, as we have seen earlier is a destabilizer for methane clathrate. This increase in temperature would then cause more hydrate dissociation leading to an endless vicious cycle occurring as a chain reaction. However, the most alarming problem is not the decomposition of the clathrates themselves, it is the release of methane in the atmosphere. 15% of global methane, is estimated to be trapped in methane hydrate deposits. Under normal breakdowns, the CH₄ molecules generally remain trapped or even if they migrate, they will recombine to form the original clathrate. But for the chain reaction like conditions, due to excessive warming of climate, the methane molecules may reach the surface of the earth and further into the atmosphere causing damage to the environment. Since we already know that methane is a greenhouse gas that is even more hazardous than CO₂ and the other pollutant, it is a real threat if such a chain phenomenon is triggered by any climatic changes[1,8].

7.2 Seafloor Destabilization

Seafloor destabilization is simply put, a disturbance or variation in the natural shape or flat structure of the seafloor and the process of destabilization occurs continuously and has been occurring throughout the years due to deposition of biological sediments over the parts of seafloor. But this type of destabilization is natural and innocuous causing no particular harm. Threatening variety of seafloor destabilization may occur due to extraction of the hydrates. Development of slope failures that are in the proximity of wells that are used extensively for production in gas wells is alarming. The continental slope that is located nearby is also at a risk of instability. The atlantic ocean, parts of the pacific, the gulf of mexico, northwestern parts of the arctic ocean and the Indian Ocean near the new zealand and australia are all active drilling and experimenting sites thus "danger" zones. Human activities such as drilling and bore channelling during extraction experiments that affect hydrate-bearing sediments may also cause seafloor failure. This destabilization may have certain adverse geological impacts such as seafloor collapse or disturbance in tectonic plates which may cause earthquakes, tsunamis, landslides and other natural disaster. Seafloor failure that is caused by inaccurate or excessive mining for clathrates deposits is a large problem today and it must be prevented or lessened to some degree in order to avoid further sediment destabilization[1]

8. CONCLUSION

Given the profundity of methane clathrate, both by quantity and potential; and the current scenario of energy crisis, it is important to understand the potential of this resource and hence direct more attention and research to it than it is being given now. Keeping in mind the applications and probable hazards of this resource, it is

clear that this resource has two very stark opposite consequences; first, it has the potential to strengthen the energy sector which is crucial to our current scenario and the second consequence would be that it has the power to destroy the environment altogether by releasing tremendous quantities of methane as a chain reaction into the atmosphere and we clearly know that methane is a greenhouse gas and is responsible for global warming. Thus it is to be understood that this resource needs to be handled or exploited very meticulously and with due care taken so that it does not create a havoc to the environment. This paper cogently summarizes the general characteristic properties of methane clathrate as a useful resource and discusses the future applications of this compound as a source of energy.

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REFERENCES

- [1] Hassanpouryouzband, A., Joonaki, E., Farahani, M. V., Takeya, S., Ruppel, C., Yang, J., . . . Tohidi, B. (2020). Gas hydrates in sustainable chemistry. *Chemical Society Reviews*, 49(15), 5225-5309. doi:10.1039/c8cs00989a
- [2] Ripmeester, J. A., Tse, J. S., Ratcliffe, C. I., & Powell, B. M. (1987). A new clathrate hydrate structure. *Nature*, 325(6100), 135-136. doi:10.1038/325135a0
- [3] Gabitto, J. F., & Tsouris, C. (2010). Physical Properties of Gas Hydrates: A Review. *Journal of Thermodynamics*, 2010, 1-12. doi:10.1155/2010/271291
- [4] International Gas Hydrate Research. (2014, March 12). Retrieved August, 2020, from https://www.energy.gov/sites/prod/files/2014/04/f14/International_Review_USGS_Collett%5B1%5D.pdf
- [5] Extraction "World Ocean Review. (n.d.). Retrieved August, 2020, from <https://worldoceanreview.com/en/wor-3/methane-hydrate/extraction/>
- [6] Production of gas from methane hydrate. (n.d.). Retrieved August, 2020, from <https://www.mh21japan.gr.jp/english/mh21-1/3-2/>
- [7] Gas Hydrates. (n.d.). Retrieved August, 2020, from <https://www.energy.gov/fe/science-innovation/oil-gas-research/methane-hydrate>
- [8] Ruppel, C. D. (2018). Gas hydrate in nature. Fact Sheet. doi:10.3133/fs20173080