

Natural Gas Hydrate as an Upcoming Resource of Energy

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Abstract

With increasing energy demand and depleting energy resources, gas hydrates may be seen as a fuel for future and can meet energy requirements of future generations. Methane gas hydrates is source of methane gas which is found in crystalline ice like structure in permafrost regions and under the sea in outer continental margins. It is purposed that total amount of carbon in the form of methane hydrates is almost double the carbon content in all the fossil fuel reserves put together. Like several other countries, India has also started a national gas hydrate programme for focused exploration and possible exploitation of this important natural gas resource. This review article briefly takes up the issues related to understanding of methane hydrates, their origin, occurrence, energy potential and their exploitation techniques.

Keywords Gas hydrate; Methane clathrate; Carbon content; Energy resource

Introduction

Gas hydrates were discovered by Sir Humphrey Davy in 1881; he observed that water and chlorine can form a crystalline substance under certain conditions of temperature and pressure and it was called it chlorine hydrate. Later in 1930's, it was found that solid gas hydrate formed in the oil and gas transmission pipelines in the U.S. were accountable for the clogging of pipelines. After this, gas hydrate was seen as a nuisance. Today gas hydrates are considered as one of the potential resource of methane and it is also called as fuel of the future. Gas hydrates (clathrate) are solid and nonstoichiometric crystalline compound consisting of water called host molecules and low molecular weight hydrocarbons gases called guest molecules. Water molecule arranges itself in a cage like formation which encapsulates a gas molecule. At low temperature and high pressure condition, guest and host interact with each other through Van der Waal's interaction and stabilize the structure; there is no chemical bonding between them. When the guest molecule is methane, it is called methane hydrate. It is found worldwide in the oceanic and polar sediments where suitable conditions of temperature and pressure are found. Thermodynamically, hydrate formation is favoured at high pressure, low temperature and low salt concentration [1, 2]. Such conditions can exist in ocean-bottom sediments at water depths below 500 m [3]. Gas hydrates constitute a tremendous reserve of natural methane in the earth [4, 5]. For example, 1 m³ of hydrate disassociates at atmospheric temperature and pressure to form 164 m³ of natural gas plus 0.8 m³ of water [3]. With the help of pressurization, gas hydrates remain stable at temperatures up to 291 K. Density of gas hydrate is 0.79 kg/L [6].

The worldwide organic carbon in the gas hydrates is estimated to be roughly about 10000 X 10¹⁵ grams which is almost double the carbon content in total fossil fuel (crude oil, natural gas and coal) reserves of the world. The comparison of the sources of global organic carbon is shown in Figure 1.

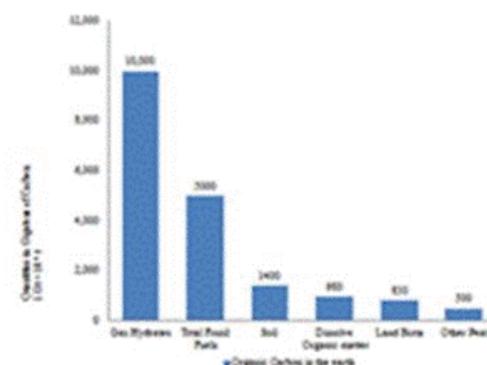


Figure 1: Comparison of sources of global organic carbon on the earth [7].

Historical Perspective

The history of natural gas hydrates has developed over three key periods as described below:

Period I: Hydrate as a Laboratory Interest

As discussed above, natural gas hydrates were accidentally discovered by Sir Humphrey Davy in 1800's [8]. Since then, gas hydrates remained an academic curiosity for almost five decades. Scientists experimented to identify all of the compounds which can form hydrates and their physical and chemical properties. By the end of the 19th century Villard [9,10] observed that hydrocarbons like methane, ethane, propane etc. can form hydrates. First tabulated results were recorded by de Foucard [11], a collaborator of Villard.

Period II: Hydrate as an Issue to the Natural Gas Industry

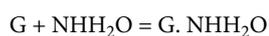
In 1930's it was found that solid gas hydrate formed in the oil and gas transmission pipelines in the U.S. were accountable for the clogging of pipelines. After this, gas hydrate was seen as a nuisance. The first such example responsible for blocking the pipes due to gas hydrate was provided by Hammerschmidt [12] in 1934. Hammerschmidt in 1939 [13] invented the first algorithm for calculating the amount of methanol to inhibit the formation of natural gas hydrates. Many Researchers [14] examined the effects of several chloride salts on hydrate formation and noticed that these salts inhibit gas hydrate formation.

Period III: Hydrate as a Untapped Energy Resource

About 60 years ago natural gas hydrates were located for the first time as gas hydrate deposit in Siberia. Since then they are seen as potential fossil fuel reserves. Makogon [15] provided the background on the up to date sole continuous gas production in the Messoyaka field, Siberi from natural gas hydrates. After that it was recognized that the low temperature and high pressure conditions is the necessity for the hydrate formation which should present extensively around the globe, under the deep oceans and in permafrost region. The occurrence of gas hydrates in oceanic sediments was first estimated on the basis of seismic observations [16, 17]. In 1992, the Ocean Drilling Programme was started intentionally identifying for hydrate deposits, and samples were brought to the surface for further investigation [18]. During the last decade the efforts of research and development in the field of gas hydrates has resulted into the discovery of occurrence of gas hydrates in the continental margin areas [19].

Hydrate Fundamentals

Natural gas hydrates are stable at a moderate to high pressure of the order of 1-30 MPa and at low temperature (-5°-20° C). The methane found in the marine sediments is either biogenic [20] or thermogenic [21] or mixture of these two. Clathrates are formed as per the following reaction:-



G is the guest molecule which is 90 – 99% methane in a natural gas hydrate sample. The most common guest molecules could be methane, ethane, propane, n-butane, carbon dioxide etc. of which methane occurs most plentifully in natural hydrates [22]. nH is the hydration number, which is average number of water molecules per guest molecules in a unit cell of crystalline gas hydrate compound and it can be used for calculating the number of water molecules in the unit cell of a particular structure of gas hydrate. For a stable gas hydrate crystal, hydration number lies between 5.66 to 17; a lower hydration number will lead to higher saturation of gas in the sample.

Structure of Gas Hydrates

With the help of X-ray diffraction methods von Stackelberg [23, 24] provided the information of the detailed structure of gas hydrates. Van der Waals and Platteeuw [25] gave the basis for calculating gas hydrate phase equilibria. Parrish and Prausnitz in the 70ies of last century [26] was the pioneer to provide additional assumptions on the occupation of the cages to gas mixtures including natural gases and they also provided the first computer executable algorithm.

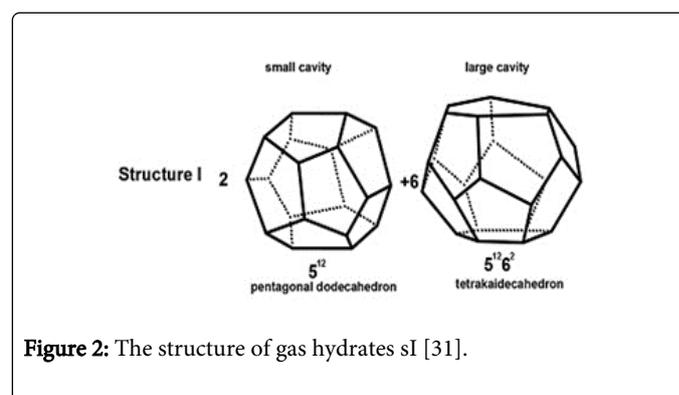
The structures I and II were first explained by von Stackelberg, structure H was invented by Ripmeester et al [27]. Pure methane forms structure I, if less than 0.1% propane is added than the structure changes to structure II, being formed by pure propane [28].

Three types of methane hydrate structures have been reported in natural sediments known as sI, sII and sH hydrate. All the three hydrate structure has a cage of water molecule enclosing methane known as pentagonal dodecahedron.

The three important structures are explained as follows:

Structure I (sI): Structure I is cubic. There is a pentagonal dodecahedral (5^{12}) cage which is centered at the corners of the unit cell and in the centre of the cell a rotated dodecahedron is present. sI is formed by Pure methane forms sI hydrate and all large cages are occupied by it. CO_2 , also forms structure I. The Structure I includes of 2 small cages consisting of 12 pentagonal surfaces i.e. 5^{12} and 6 larger cages of again 12 pentagonal and two hexagonal surfaces i.e. $5^{12}6^2$ [29] which is shown in Figure 2.

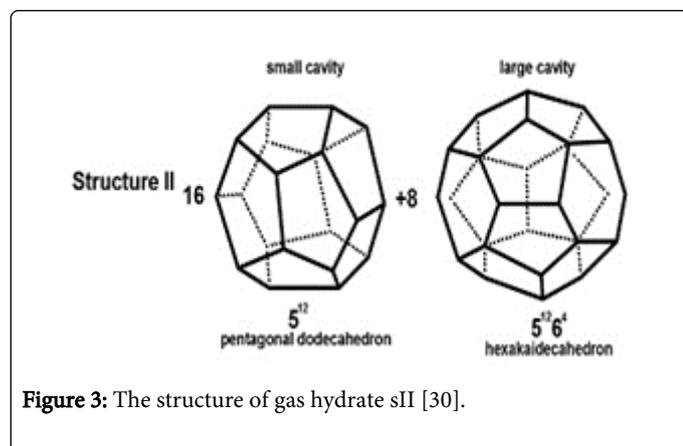
The unit cell consists of water molecules = $(2 \times 5^{12} + 6 \times 5^{12}6^2 = 46)$ [30].



Structure II (sII): Structure II is also cubic, in addition to common pentagonal dodecahedra, a large cage (hexakaidecahedral) made up of 12 pentagons rings and 4 hexagonal rings is also there. Large cage diameter in sI hydrate is slightly lesser than the large cage diameter of sII hydrate. Gases like ethane, propane, butane, natural gas forms sII hydrates which is shown in figure 3.

Structure II is made up of 16 small cages consisting of 12 pentagonal surfaces i.e. " 5^{12} " and 8 larger cages of again 12 pentagonal and four hexagonal surfaces i.e. $5^{12}6^4$

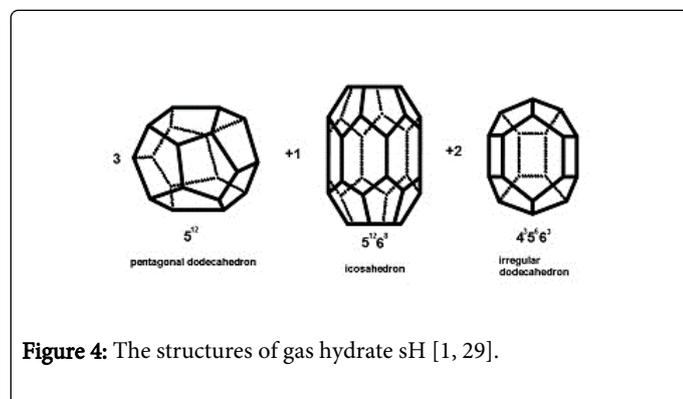
The unit cell consists of water molecules = $(16 \times 5^{12} + 8 \times 5^{12}6^4 = 136)$ [30].



Structure H (sH): It has hexagonal crystals having three pentagonal dodecahedron (5^{12}) cavities, two small irregular dodecahedron ($4^3 5^6 6^3$) cavities, one large icosahedron ($5^{12} 6^8$) cavity, and 34 water molecules per unit cell, and can accommodate larger molecules such as 2,2-dimethylbutane in the larger cavities only. Each icosahedron ($5^{12} 6^8$) barrel-shaped cavity is enclosed by six irregular dodecahedron ($4^3 5^6 6^3$) cavities around its central ring of six hexagons which is shown in fig 4.

The Structure H made up of 3 small cages consisting of 12 pentagonal surfaces i.e. 5^{12} and 6 larger cages of again 12 pentagonal and 1 hexagonal surfaces i.e. $5^{12} 6^8$.

The unit cell consists of water molecules = $(3 \times 5^{12} + 2 \times 4^3 5^6 6^3 + 1 \times 5^{12} 6^8) = 34$. [1,33,34].



Classification of Gas Hydrate Accumulation

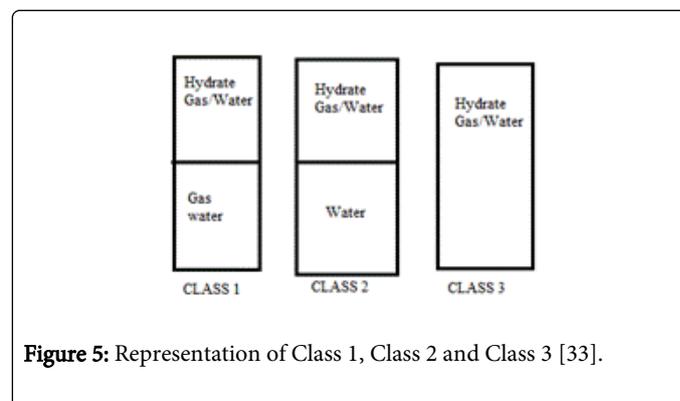
Natural occurring hydrate reservoir varies both in terms of geologic structure & thermodynamic conditions.

Gas hydrate deposits have been classified into four major classes:

- Class-1: These are made up of two layers – the hydrate layer and beneath two phase fluid zone containing free gas and liquid water which is shown in fig 5. Class I type of hydrates are referred as “Hydrate capped gas reservoirs” [31].
- Class-2: This is made up of two zones i.e. hydrate layer overlying the zone of mobile water zone.
- Class-3: Hydrate deposits comprise of a single zone of hydrate interval and characterized by the absence of beneath zone of mobile fluids.

- Class-4: Hydrate deposits are referred to oceanic accumulations and includes disperse, low saturation hydrate deposits (< 10%) which fall short of confining geologic strata [32].

They are classified into following categories as shown in figure 5 below:



Energy Potential of Gas Hydrates

Methane is the major constituent among other hydrocarbon gases in sediments [34, 35]. According to the United State of America’s department of energy, if only one percent of the methane in the hydrates could be obtained, it would be more than the two times of the current domestic supply of United States of America’s of natural gas [36, 37]. The energy potential of methane hydrates is higher than that of the other unconventional sources [38].

The current techniques for exploiting methane from gas hydrates are discussed as per follows:

Current Techniques of Extraction of Gas from Natural Gas Hydrates

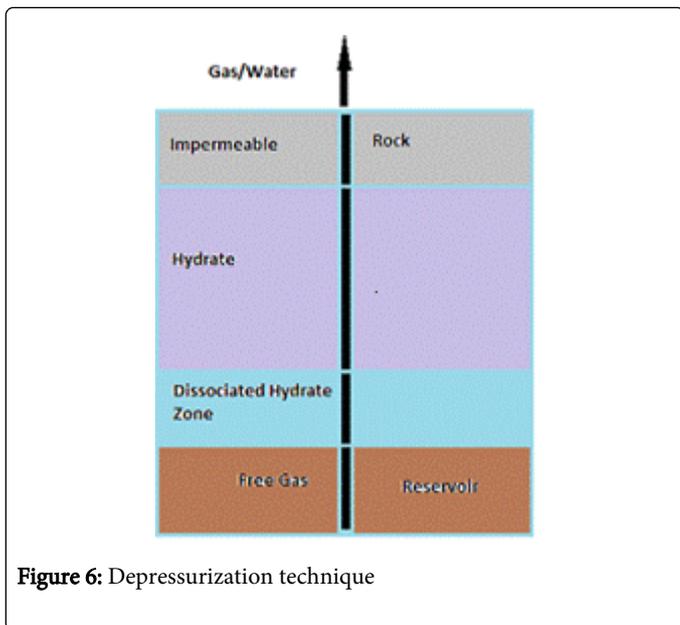
Methane is the major constituent in the natural gas hydrate sediment [39]. Methane hydrates are considered a major future potential source of hydrocarbon [40].

Current techniques of extraction of gas from natural gas hydrates are depressurization, inhibitors injection and thermal stimulation (Moridis et al. 2004[41]). The difficulty in exploiting this resource is that it is not manageable by conventional gas and oil recovery techniques [42] Different mechanisms have been put for making unconventional gas hydrates source economical [43,44].

The four techniques which are used for the extraction of methane from the natural gas hydrates are illustrated as per following:

Depressurization:

It is an extraction technique in which drilling of hole into the layer of hydrate is involved which reduces the pressure beneath the hydrate equilibrium initiating an endothermic process (i.e. absorbing heat from the surroundings) which results in to release of methane gas from the hydrate flowing up the pipe [45, 46 ,47]. The dissociation continuous until equilibrium is maintained at the lower temperature. Depressurization is advantageous because it is a most economical method and low energy consumption. It is assumed that free gas can be obtained by drilling hole down the natural gas hydrate as shown in figure 6:-

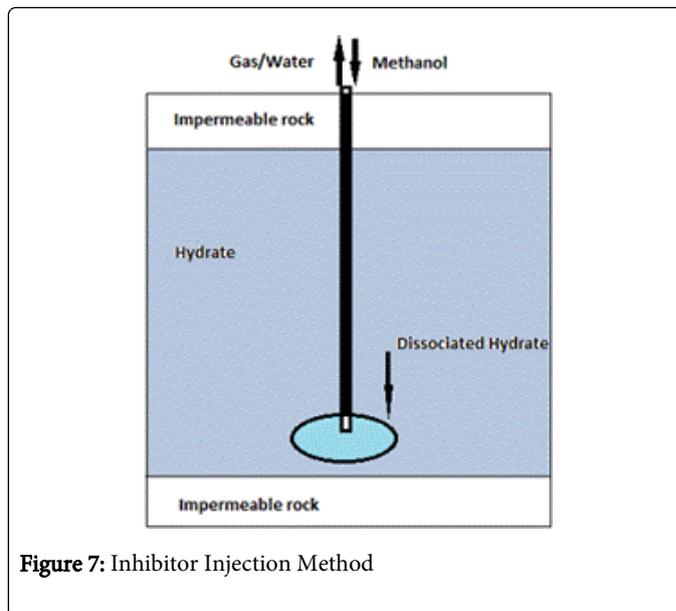


This technique is applicable for hydrates only in polar regions beneath the permafrost where the free gas is found to be present under the hydrate stability zone. Numerical simulation for producing the gas via this technique also studied [41]. The gas production rate is found to depend on function of both well pressure and reservoir temperature [48]. This method is most promising where gas occurs in a closure below the hydrate cap [49].

Specific heat of gas hydrate dissociation is about 0.5 MJ/Kg which is more than specific heat of ice melting. Due to increased heat exchange, reservoir zone temperature falls to equilibrium temperature of hydrate formation which stop the dissociation. So, the solution lies in discovering a technology which can maintain a stable gas hydrate dissociation within the porous media. This method is most economical till now for production of gas from gas hydrates.

Inhibitor Injection

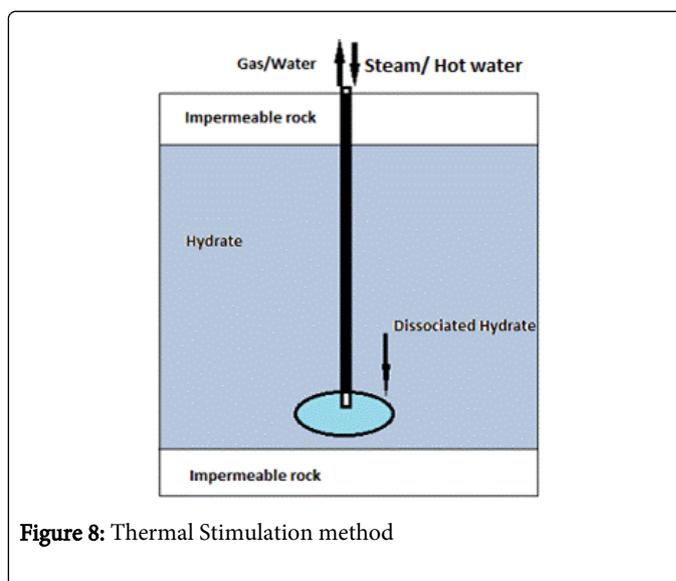
It is a technique to abolish the creation of hydrates. In this technique injection of a chemical inhibitor is employed to hydrates which disturb the gas hydrate equilibrium condition beyond the thermodynamic stability of the gas hydrate zone. The chemical inhibitor like methanol decreases the dissociation temperature [50, 51] and thus hydrates decompose to free gas and water. The common thermodynamic organic inhibitors are methanol, monoethylene glycol, diethylene glycol. Dissolved salts such as NaCl, CaCl₂, KCl. Schematic representation of Inhibitor Injection is shown in figure 7:-



Chemical inhibition injection method needs admirable porosity and moreover cost of various chemicals makes it an expensive technique. This method is like putting salt on icy road. This technology is used for inhibiting gas hydrates in pipelines. There has been experimental evidence for the gas production from methane hydrate in porous sediment by injecting ethylene glycol solutions [52].

Thermal Stimulation

It is an extraction technique which makes use of steam injection, hot brine solution, fire flooding and cyclic steam injection etc. which raises the temperature of the local reservoir outside the hydrate region. The rise in temperature will cause the dissociation of the hydrate, thus releasing free gas which can be collected. The methane obtained can then be pumped to the surface of the seafloor via drilling another hole [51]. Schematic representation of the Thermal Stimulation is shown in figure 8:-



Tang et al., [53] states that the efficiency of the method is directly proportional to the latent heat of the brine solution, the rate at which the solution is injected and initial hydrate saturation.

Global Efforts

Various country like India, USA, Canada, Japan, Germany etc. have put various effects in the locating and exploiting this vast source of energy. India has successfully completed Nation Gas Hydrate Programme NGHP-01 and about to start NGHP-02. The field testing of gas hydrate is done in North Slope Alaska, Mallik site located in Mackenzie Delta, Northwest Territories of Canada, and Nankai Trough in Japan. The details of NGHP and various field testing are explained as follows.

Recently, Shyi-Min Lu [54] has explained the global effort put up by various countries such United States of America, Japan, Canada, China, India and Taiwan for the development of gas hydrates. It is mentioned in the review that Japan could be the first country to develop methane hydrates and can start commercial mass production in the eastern Japanese Nankai Trough prior to 2018 according to Japan's Methane hydrate R&D programme MH-21. Taiwan is also planning Methane hydrate exploration with the co-operation of countries like Germany and U.S. and can go for commercial production as soon as 2026. As per the global consumption and proven resources of fossil energy sources in 2012 conventional gas and oil can be only used for about another 57 years[55]. So, in the light of above circumstances many countries are joining hand together in order to exploit this untapped resource of energy.

Conclusions

A tremendous amount of methane is stored in the gas hydrates which can supply the energy requirements energy requirements of the world for centuries if exploited properly. Pilot scale production test have been completed in permafrost region and in marine gas hydrate deposit to test the possible gas recovery technology from hydrate bearing reservoir. From the NGHP Expedition it was evident that the gas hydrates are distributed in the Krishna-Godavari, Mahanadi and Andaman off shores. Various lesson have been learnt from the field trial for gas production from gas hydrate in Alaska North Slope Site, Mallik Site, Nankai Trough, if the experience gained from these trial is understood and applied properly then it can help in designing a novel technology for the exploitation of this natural novel resource of energy. It is expected that the dream of taking energy from fire in the ice will be a reality very soon. However, there is a strong need to prepare a suitable technology for exploiting this untapped energy resource.

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