

# INVESTIGATIONS OF GAS HYDRATE AS A NON CONVENTIONAL SOURCE OF FUEL - THEIR RESOURCE POTENTIAL AND PERSPECTIVES OF THEIR EXPLORATION

<sup>1</sup>Amandeep Singh Wadhwa

<sup>1</sup>Department of Mechanical Engineering, UIET, Sector-25, Panjab University, Chandigarh-160025  
Email: aman\_wadhwa77@rediffmail.com

## ABSTARCT:

There are a lot of geophysical and non-conventional material science engineering related researches in recent years in the field of deepwater drilling and the hermetic recovery of longer cores of bottom sediment. Gas-hydrates are the crystalline form in which gases (mainly methane) are trapped within a framework of hydrogen bonded water molecules (Kvenvolden, 1998). They form at elevated pressure and moderately cooled temperature, and occur worldwide in two distinct regions of permafrost and outer continental margins (Sloan, 1990). Natural gas hydrates occur worldwide in Polar Regions normally associated with onshore and offshore permafrost, and in sediment of outer continental margins. It is further observed that total amount of methane present in gas hydrates nearly doubles both the non-recoverable and recoverable fossil fuels. Also the Gas-hydrates can also be obtained from the actual and inferred distribution of gas hydrate in the marine sediments. Numerous finds of GH presence in sediments were discovered at water depths ranging from 500 to 5500m. Gas hydrate distribution has been found to occur in different regions of the World Ocean basins including India. In this present paper investigation of the gas hydrate geology, their accumulations and methods which should be preferred for the detection of gas hydrate accumulations has been discussed.

## 1. INTRODUCTION

Gas hydrates are ice-like crystalline compounds formed from mixtures of water and suitably sized 'guest' molecules and stable under low temperature and high-pressure conditions. Guest molecules in natural hydrates are either methane or a mixture of components comprising natural gas. Typically, they are found in sediments within a few hundred meters of the seafloor, in water depths of around 500m depending on seabed temperature, gas composition, and geothermal temperature gradient. An increase in the system temperature and/or a reduction in the system pressure could result in gas hydrates dissociation, and production of water and gas. As gas hydrates store large quantities of gas, their dissociation will result in the release of large amounts of gas. Gas hydrates are created when water and gas combine to form a crystalline substance that looks like an ice. They are nonstoichiometric crystalline compounds that belong to a group known as Clathrates. A Clathrate is simply a structure in which water molecules under certain conditions bond to form an ice like cage that encapsulates a gas molecule known as guest molecule. Gas hydrates are formed when water molecules attach themselves together through hydrogen bonding and form cavities which can be occupied by single gas molecule or volatile liquid molecule. The presence of gas or volatile liquid inside the water network thermodynamically stabilizes the structure through weak Vander Waals forces. The naturally occurring hydrates contain mostly methane as a guest molecule and are called methane hydrates (methane locked in ice). Another important type of gas hydrate is carbon dioxide hydrate.

## 2. OCCURRENCE (Sources and availability)

Methane hydrates are formed at low temperature and high pressure and are found in sea floor sediments and permafrost where methane originates from the decomposition of living things. They can be scattered through several hundred meter depths and at various concentrations. The gas hydrates being evaluated by ORNL

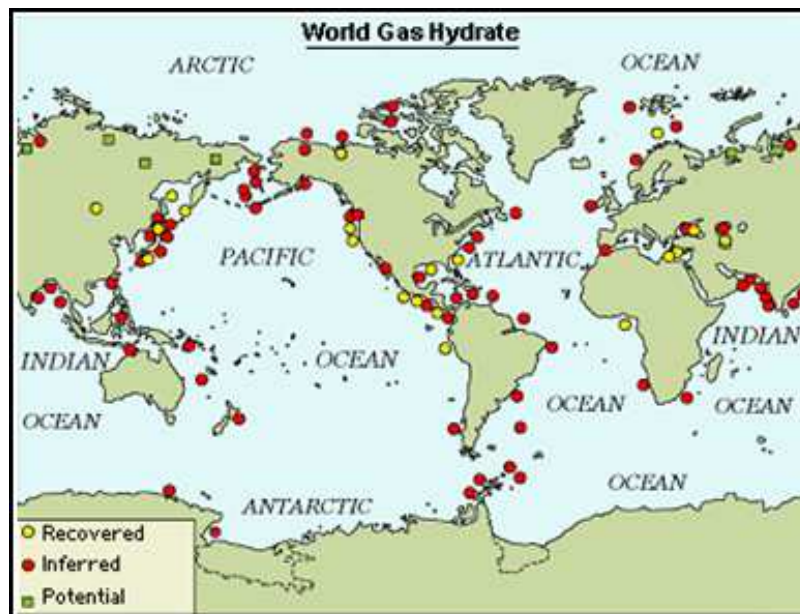
researchers are methane hydrates and carbon dioxide hydrates. The world-wide interest in the gas hydrates is due to the fact that natural gas hydrates is one of the most promising non-conventional source of fuel. Investigations for gas hydrates are multidisciplinary and attract specialists from chemistry, geology, engineering and ecology as elaborated below:

- ✚ Chemistry - fundamental aspects, source of basic information for other fields of interest
- ✚ Geology - non-conventional source of fuel, investigation of the permafrost and marine sediments
- ✚ Engineering –non-conventional source of fuel gas industry, gas transportation
- ✚ Ecology - greenhouse effect.

Although some research has been carried out in past little is known about their location, formation, decomposition or actual quantities of methane hydrates. These naturally occurring hydrates contain mostly methane and the amount of organic carbon entrapped in hydrate exceeds all other reserves (fossil fuels, soil, peat and living organisms). However, national and international research and exploration over the last 20 years by various governmental and industrial entities have resulted in general agreement that methane hydrates should be evaluated as a potential primary energy source for the future.

Natural gas hydrate occurs worldwide in oceanic sediment of continental and insular slopes and rises of active and passive margins, in deep water sediment of inland lakes and seas, and in polar sediment on both continents and continental shelves. In aquatic sediment where water depth exceeds 300m and bottom water temperature approach 0 degree celcius, gas hydrate is found at sea floor to sediment depths of about 1100m. In polar continents region, gas hydrate can be present in sediments at depth between about 150m and 2000m. Thus natural gas hydrate is restricted to the shallow geosphere where its presence affects the physical and chemical properties of near – surface sediments.

During its 113.5-day voyage, the expedition cored or drilled 39 holes at 21 sites (one site in the Kerala-Konkan Basin, 15 sites in the Krishna-Godavari Basin, four sites in the Mahanadi Basin and one site in the Andaman deep offshore areas), penetrated more than 9,250 meters of sedimentary section, and recovered nearly 2,850 meters of core. Twelve holes were logged with logging-while-drilling (LWD) tools and an additional 13 holes were wireline logged.



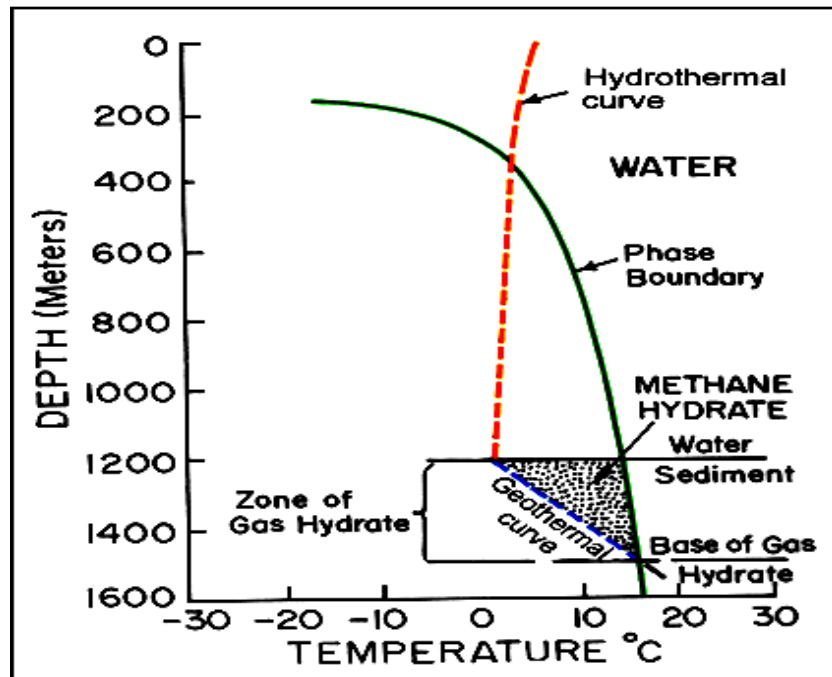


Fig. 1 : phase diagram for submarine gas-hydrates stability field showing the zone of occurrences of gas-hydrates deposit (Sloan, 1990).

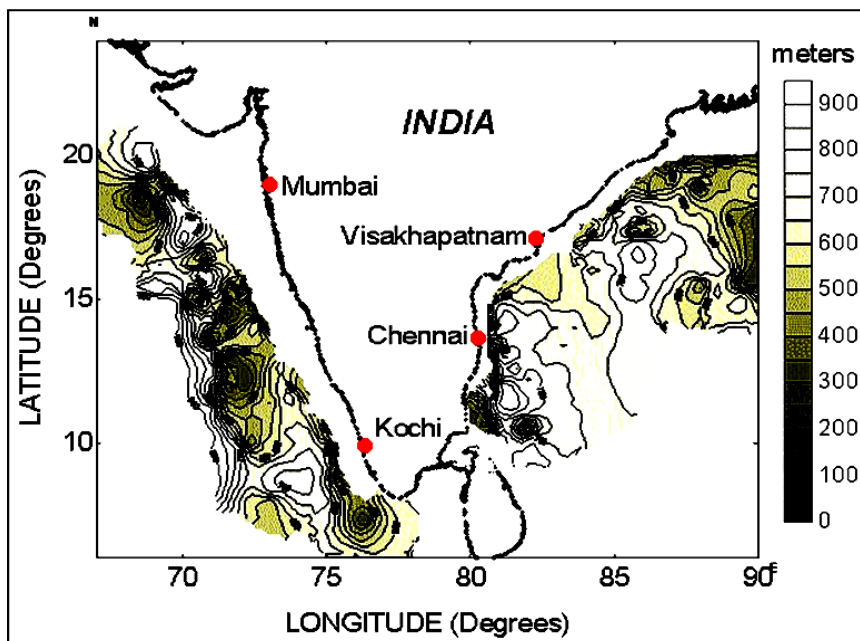


Fig. 2 : Thickness variation of gas-hydrates stability zone in offshore regions of India (Hanumantha Rao et al., 1998).

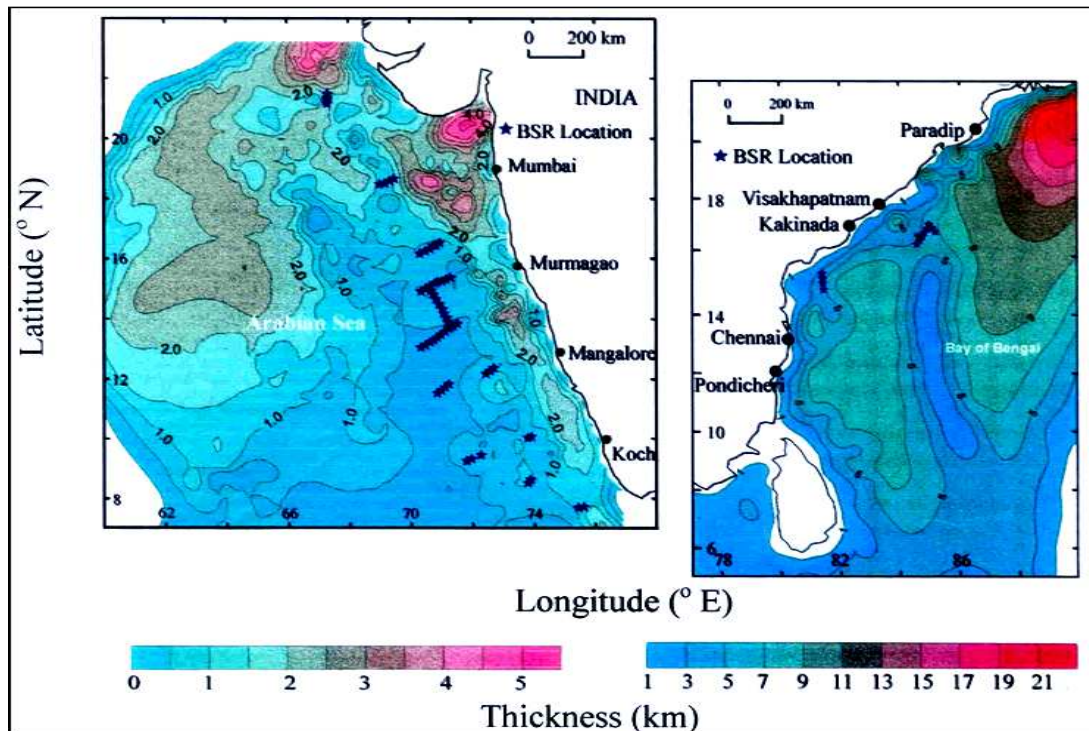


Fig. 3: Map showing BSR locations and sediment thickness distribution in (a) western offshore and (b) eastern offshore regions of India. (Gupta et al., 1998).

Table 1: GLOBAL ESTIMATION OF METHANE CONTENT IN GAS HYDRATES OF THE OCEAN

S.No.	Methane Quantity (m <sup>3</sup> )	Year	References
1.	$5 \times 10^{15} - 2.5 \times 10^{16}$	1977	Trofimuk et al.
2.	$7.6 \times 10^{18}$	1981	Dobrynjn et al.
3.	$3.1 \times 10^{15}$	1981	McIver
4.	$4 \times 10^{16}$	1988	Kvenvolden, claypool
5.	$1 \times 10^{16}$	1988	Makogon
6.	$2.1 \times 10^{16}$	1988	Kvenvolden
7.	$2.1 \times 10^{16}$	1990	Mac Donald
8.	$2.6 \times 10^{16} - 1.4 \times 10^{17}$	1994	Gornitz, Fung
9.	$2.3 \times 10^{16} - 9.1 \times 10^{16}$	1995	Harvey. Huang
10.	$1 \times 10^{15}$	1995	Ginsburg, Soloviev
11.	$7 \times 10^{15}$	1996	Holbrook et al.
12.	$1.5 \times 10^{16}$	1997	Makogon
13.	$2 \times 10^{15} - 2 \times 10^{16}$	1997	Dickens et al.
14.	$2 \times 10^{14}$	1999	Soloviev, Ginsburg

In 1993 we discovered the first evidence of structure H hydrate in nature at a similar water depth near Jolliet Field. This rare hydrate forms "cages" large enough to hold molecules much bigger than methane. For example, hydrates at Jolliet Field contained abundant iso-pentane, a big, branched-chain hydrocarbon molecule with five carbon atoms. We are excited by the real possibility of discovering other, previously unknown types of hydrate

crystals in our natural laboratory, the Gulf of Mexico. It is no accident that unusual gas hydrates were discovered near Jolliet Field, a site now occupied by a huge oil platform. Oil and gas continually migrate from great depths in the earth's crust toward the gulf floor. Some of the oil and gas is trapped below the sea bottom, but much migrates toward the seafloor where hydrates form. For this reason, natural oil and gas seeps and their associated hydrates are studied as a guide to the presence of subsurface fields.

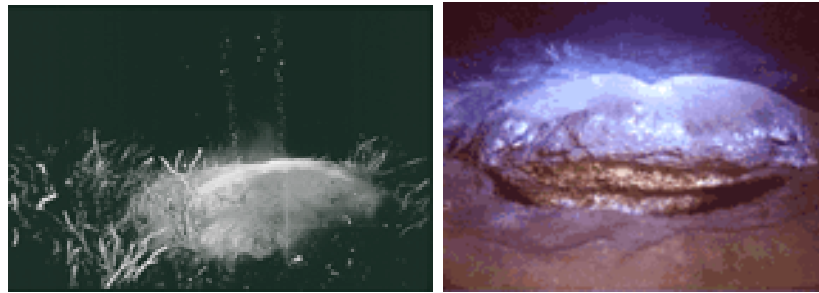


Fig. 4

Figure 4 shows the serene hydrate environment colorful mats of bacteria blanket sediment over and around a hydrate mound, surrounded by tendril-like tubes of chemosynthetic worms.

Free hydrocarbon gas bubbles out of the sediment to begin its 540-meter ascent to the sea surface. This mound of gas hydrate grew large enough to break free of the seafloor's surface. Sediment still drapes the top of the mound but on its underside the hydrate burrows of ice worms lie exposed.

#### Oceanic Surveys

The Deep Sea Drilling Program (DSDP), which was extended in 1985 as the Ocean Drilling Program (ODP), stimulated an interest in hydrates. Russian research suggested that they could occur at a depth of a few hundred meters below the seabed in deep water areas. Geophysicists simultaneously identified what was known as the Bottom Simulating Reflector (BSR) on deepwater seismic surveys (Markl 1970, Shipley 1979). It was soon assumed that the BSR marked the occurrence of hydrates, trapping free gas below, and several Joides sites were designed to investigate them. These sites were planned by universities not oilmen, although the latter were called in to advise on safety on the PPSP panel (I was one of them during the first half of the 80s). A total of 625 sites were drilled by the Glomar Challenger between 1963 and 1983 under the auspices of the DSDP, (see Figure 1), but it was ruled not to drill through the BSR to avoid any blow out.

#### Solubility of methane in seawater

Minshull.1989 wrote: ""The stability of gas hydrate depends not only on the pressure and temperature conditions but also on the concentration of natural gas present in the sediment, which must exceed the solubility of gas in seawater"". Many graphs have been published on the stability of hydrates versus pressure and temperature, but complete graph of the solubility of methane in deepwater is lacking, save one graph of solubility of methane in water sediments in Bonham (1978) (figure 5). It shows a drastic increase of solubility of methane with pressure explaining the lack of giant gasfields in HPHT conditions.

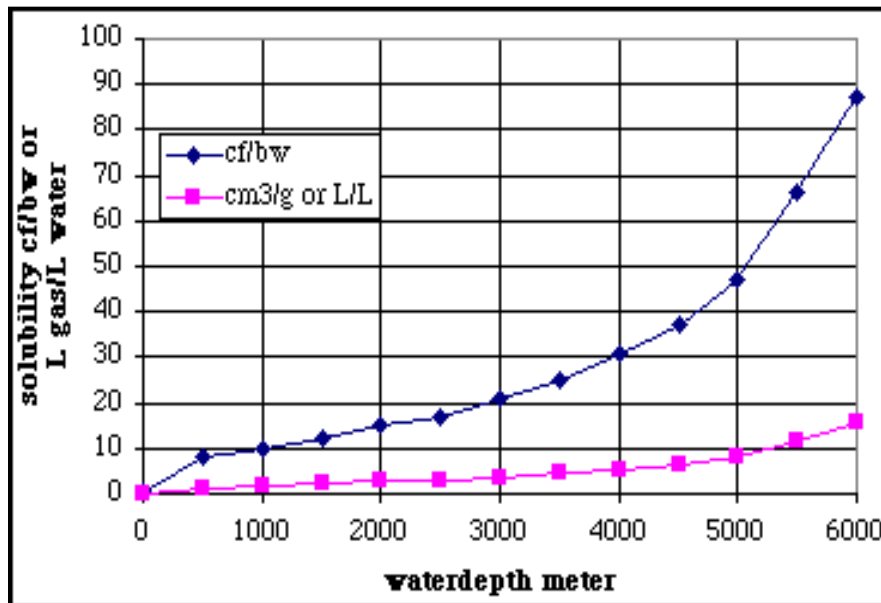


Fig. 5 Solubility of Methane in water (Source: Bonham 1978)

Du Rouchet 1980 mentioned that Makogon has drawn in 1971 a graph where the solubility of methane of 2L gas /L water for 70 bars decreases sharply to 0.4 L/L when converting into hydrate, but this theory of discontinuity of solubility was not kept in recent articles.

Methane hydrates are well known to the oil industry as a material that clogs pipelines and casing. They are also present in permafrost areas and in the oceans where the necessary temperature and pressure conditions for stability occur. Oceanic hydrates are mainly biogenic and different from thermogenic hydrates.

Claims for the widespread occurrence in thick oceanic deposits are unfounded. The thickest interval recovered from a total of 250 000 m of core from 2300 ODP/DSDP boreholes was one meter with an unknown extent. Mostly, they occur as dispersed grains and lamina. Indirect evidence from seismic reflectors (BSR), seismic direct hydrocarbon indicators, logs and free gas samples is unreliable and highly speculative.

BSR can have several origins, the most likely being the so-called free gas below the hydrate stability zone where gas is not trapped but has the same concentration as hydrate i.e. 1% of the porosity. Such dispersed hydrate cannot seal free gas as the porosity is 99% water.

Being a solid, methane in oceanic hydrates cannot migrate and accumulate in deposits sufficiently large to be commercially exploited. The published estimates of the size of the resource are highly unreliable and give flawed comparisons with conventional fossil fuels. There are other non-conventional sources of gas which are infinitely more reliably known and accessible than hydrates, yet remain uneconomic for the time being. The prospects for the commercial production of oceanic hydrates in foreseeable future are negligible. In short, they are a chimera.

The academic research dedicated to hydrates has brought more questions than answers. Hopefully the oil industry with the deepwater exploration will start to look more into the realities of oceanic hydrates outside their impact as a nuisance clogging pipelines.

Hydrates are basically of three types called Type I, Type II, and Type H. Other types of hydrates are known and proposed, but they are uncommon. The crystal structures of hydrates are three-dimensional and are quite complicated. The crystal structure of the hydrate, be it Type I, II or H, is not a single polyhedra.

#### Type I

- It is usually smaller molecules form Type I hydrates. Type I hydrate formers include: (1) methane, (2) ethane, (3) carbon dioxide, and (4) hydrogen sulfide
- Type I hydrates are made up of 8 polyhedral cages -- 6 large ones and 2 small. They are made up of 46 water molecules and thus have a theoretical composition of  $8X \cdot 46 \text{ H}_2\text{O}$  or  $X \cdot 5 \frac{2}{3} \text{ H}_2\text{O}$ , where X is the guest molecule.

#### Type II

- It is usually larger molecules form Type II hydrates. Type II hydrate formers include: (1) propane and (2) isobutane, however, (3) nitrogen, a relatively small molecule, also forms a Type II hydrate.
- Type II hydrates are made up of 24 polyhedral cages -- 8 large ones and 16 small. They are made up of 136 water molecules and thus have a theoretical composition of  $24 X \cdot 136 \text{ H}_2\text{O}$  or  $X \cdot 5 \frac{2}{3} \text{ H}_2\text{O}$ . If only the large cages are occupied, which is typical, then the theoretical composition is  $8 X \cdot 136 \text{ H}_2\text{O}$  or  $X \cdot 17 \text{ H}_2\text{O}$ .

#### Type H

- Type H hydrates are formed by larger molecules but only in the presence of a smaller molecule, such as methane. Type H hydrates only form in the presence of both the large and small molecules.
- Type H hydrates are made up of six polyhedral cages - 1 large, 3 medium and 2 small. The large molecule occupies the large cage and the small molecule occupies the small and medium cages. They are made up of 34 water molecules and have a theoretical composition of  $X \cdot 5 Y \cdot 34 \text{ H}_2\text{O}$  where X is the large molecule and Y is the small.
- Type H formers include: (1) 2-methylbutane, (2) methylcyclopentane, (3) methylcyclohexane, and (4) cyclooctane. It bears repeating, Type H hydrates only form if another, small molecule (such as methane) is present.

Hydrates are non-stoichiometric. A stable hydrate forms without all of the cages being occupied. The degree of saturation (the number occupied cages) is a function of the temperature and the pressure.

- For example, hydrogen sulfide forms a hydrate at 10°C and 290 kPa (50°F and 42 psia). At these conditions, the large cages are 98.1% full and the small ones only 93.8%. As a second example, carbon dioxide forms a hydrate at 5°C and 2230 kPa (41°F and 323 psia). At this temperature and pressure, the large cages are 98.6% full and the small ones only 78.2%. (Calculated with CSMHYD).
- Normal butane is an interesting, special case. On its own it does not form a hydrate, but in a mixture it can enter the hydrate if other hydrate formers are present.
- Molecules larger than n-butane do not form Type I or II hydrates. Some slightly larger molecules do form Type H hydrates.
- Highly soluble gases do not form hydrates, regardless of their size. For example, ammonia and hydrogen chloride do not form hydrates.

- Hydrates can form with either gases or liquids, provided the three criteria given earlier are met. There is a bit of a misconception that liquids cannot form hydrates. This misconception is partially fed by the use of the term "gas hydrates".

#### Hydrate Loci for Natural Gas Components

The figure below shows the hydrate loci for several components in natural gas.

At temperatures less than the loci and at pressure greater than the loci (i.e., to the left and above) are where hydrates will form.

For example, at 5°C and 1 MPa, hydrogen sulfide, ethane and propane form hydrates, whereas carbon dioxide, methane, and isobutane do not.

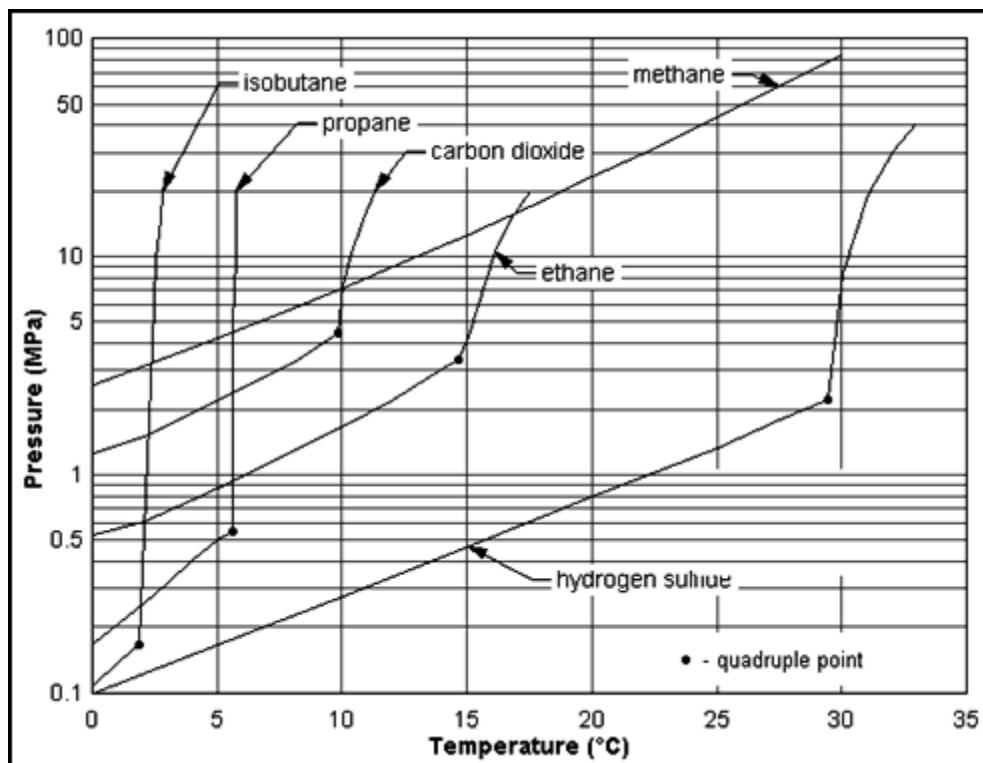


Fig. 6 Hydrate Loci for several components found in natural gas.

#### Inhibitors

The formation of hydrates can be inhibited in a manner similar to de-icing. Note, they do not prevent the formation of hydrates, they inhibit it. That is, for a given pressure, they reduce the temperature at which the hydrate will form.

The mere presence of an inhibitor does not assure that a hydrate will not form. There has to be a sufficient amount of inhibitor present.

Common inhibitors include: (1) alcohols, (2) glycols, and (3) ionic salts (including common salt).

#### Combating Hydrates

There are three ways to combat the formation of hydrates:

The use of inhibitors, particularly methanol. The application of heat. Dehydration - removing enough of the water from the stream such that a hydrate will not form. In the natural gas industry, methanol is usually the method of choice. High pressure pumps are used to inject methanol into process lines and equipment. Methanol costs required to combat hydrates in typical gas fields may be tens of millions of dollars annually.



The Hammerschmidt equation provides a method for rapidly estimating the temperature depression in the hydrate formation due to the presence of an inhibitor:

$$dT = 2335W/(100M - MW)$$

$dT$  = temperature depression, deg F

$W$  = weight per cent inhibitor

$M$  = molar mass (molecular weight) of inhibitor (g/mol)

= 32.043 for methanol

For example, a 25 wt% solution of methanol will effect the following temperature depression:

$$dT = 2335(25)/[(100)(32.043) - (32.043)(25)]$$

$$= 24.3 \text{ deg F}$$

$$= 13.5 \text{ deg C}$$

Therefore you would expect a hydrate to form at a temperature about 24 Fahrenheit degrees (or 13.5 Celsius degrees) less than in pure water. (Note: this is a temperature difference, so you do not merely convert 24.3°F to -4.8°C)

From the diagram shown earlier, at 1.5 MPa the ethane hydrate forms at about 10°C. From the Hammerschmidt equation the hydrate formation temperature at 1.5 MPa in a 25 wt% solution of methanol would be about -3.5°C.

The Hammerschmidt equation is limited to inhibitor concentrations of about 25 wt%. Errors on the order of 5 to 10% can be expected when using this equation.

### Volume of Gas in Hydrate

The following are the properties of the methane hydrate:

density: 913 kg/m<sup>3</sup>

molar mass (molecular weight): 17.74 kg/kmol

methane concentration: 14.1 mole per cent

- this means there are 141 molecules of methane per 859 molecules of water in the methane hydrate

From this information we can determine the volume of gas in the methane hydrate.

From the density, 1 m<sup>3</sup> of hydrate has a mass of 913 kg.

Converting this to moles  $913/17.74 = 51.45$  kmole of hydrate, of which 7.257 kmoles are methane.

The ideal gas law can be used to calculate the volume of gas when expanded to standard conditions (15°C and 1 atm or 101.325 kPa)

$$V = nRT/P = (7.257)(8.314)(15+273)/101.325 = 171.5 \text{ m}^3[\text{std}]$$

Therefore 1 m<sup>3</sup> of hydrate contains about 170 m<sup>3</sup>[std] of methane gas.

For those who prefer American Engineering Units, this converts to 1 ft<sup>3</sup> of hydrate contains 170 SCF of gas - not a difficult conversion. And 1 ft<sup>3</sup> of hydrate weighs about 57.0 lb.

By comparison, 1 m<sup>3</sup> of liquid methane (at its boiling point 111.7 K or -161.5°C) contains 26.33 kmol, which converts to 622 m<sup>3</sup> of gas at standard conditions.

Alternatively, 1 m<sup>3</sup> compressed methane at 7 MPa and 300 K (27°C) (1015 psia and 80°F) contains 3.15 kmol or 74.4 m<sup>3</sup>[std] of methane gas.

To store 25,000 m<sup>3</sup>[std] (0.88 MMSCF) of methane requires about 150 m<sup>3</sup> (5300 ft<sup>3</sup>) of hydrates. This compares with 40 m<sup>3</sup> (1400 ft<sup>3</sup>) of liquefied methane or 335 m<sup>3</sup> (11,900 ft<sup>3</sup>) of compressed methane.

### 3. PROBLEMS OF EXTRACTION OF GAS HYDRATES

Conventional methods of natural gas extraction from gas hydrates involve heating and/or depressurizing the gas hydrates in order to release the natural gas. However, there are two major problems with these conventional methods. First, they require a large amount of energy to be added to the system, resulting in a high cost of extraction. Second, they destabilize hydrate formations because both depressurization and heating cause the hydrate to melt. This can lead to the destabilization and/or collapse of sediments that contain hydrates and other nearby subterranean formations. Because gas hydrates are usually extracted near oil and natural gas deposits, such instability can result in problems with the extraction of oil and natural gas. Amount estimated and comparison with other fossil fuels. The estimated amount of natural gas in the gas hydrate accumulations of the world greatly exceeds the volume of all known conventional gas resources. While gas hydrates hold great potential as an "environmentally-friendly" fuel for the 21st Century, the technical challenges of realizing them as a resource are substantial. Additional research is required to understand and develop new techniques to

quantify their distribution in nature. Depressurization and thermal heating experiments at the Mallik site were extremely successful. The results demonstrated that gas can be produced from gas hydrates with different concentrations and characteristics, exclusively through pressure stimulation. The data supports the interpretation that the gas hydrates are much more permeable and conducive to flow from pressure stimulation than previously thought. In one test, the gas production rates were substantially enhanced by artificially fracturing the reservoir. So how big a deal is this as compared to other fossil fuels energy sources? Gas hydrates reserves estimates vary quite a bit. But some of the estimates are pretty high. There may be twice as much energy in gas hydrates than in all other fossil fuels combined. The technology may take between 10 and 15 years to develop, but will help us tap gas hydrate reserves, estimated to be "more than double the known reserves of fossil fuel," said C.N.R.Rao, Founder and Honorary President of the Jawaharlal Nehru Centre for Advanced Scientific Research, and A.Kuznetsov, Director, Institute of Inorganic Chemistry, in Russia. Interest in hydrate E&P has soared in recent years because of growing evidence that more hydrocarbon exists in hydrate deposits than the combined oil, gas and coal reserves worldwide. According to the U.S. Energy Information Agency in its just-released Natural Gas 1998: Issues and Trends, "Recovery of only 1% of hydrates would more than double the domestic gas resource base." A report from Ocean Drilling Program Leg 164, which investigated the huge Blake Ridge offshore the Carolinas, estimated U.S. methane hydrate reserves at 200,000 Tcf. That really puts gas hydrates in the big leagues because there is an enormous amount of fossil fuel energy stored in coal. There is orders of magnitude more natural gas in hydrates than in conventional natural gas reserves. The estimate was refined in 1997 to a more conservative 200,000 trillion cubic feet. Even this lower estimate is significant when compared to the 1,400 trillion cubic feet in the nation's conventional gas reserves. On a world-wide basis, it is estimated that methane hydrate reserves are 400 million trillion cubic feet, compared with 5,000 trillion feet in known gas reserves. Well, there may not be enough hydrocarbons available to bring on global warming from conventional fossil fuels reserves. But if the technology to extract methane gas hydrates can be made cost-effective then humanity might need to refrain from using as much fossil fuel as it can burn. In one science fiction novel whose title escapes me (anyone remember the story?) some event (nukes exploded on the ocean floor by accident or by terrorists?) caused all the gas hydrates to come to the surface and this caused an enormous hot house effect that melted all the ice and let loose massive hurricanes (or am I mixing up different science fiction novels? they all blend together after a while). The point here is that it would be a bad thing if all the gas hydrates came to the surface in an uncontrolled manner. They constitute a pretty large amount of hydrocarbons.

As a source for natural gas, hydrate today is about where coal bed methane was 15 years ago, says Michael Max, a hydrate expert formerly with the Naval Research Laboratory in Washington, D.C. "Coal bed methane was a classic, unconventional gas play," with more than a few doubters, Max says. "Now it supplies around eight percent of the U.S natural gas supply. We think hydrate has a similar trajectory."

Natural gas from hydrates may well become a much higher percentage of the total energy mix if oil field production starts to decline within 10 years as some predict.

The gas hydrate resource could exceed 60 million trillion cubic feet of gas -- almost 5,000 times the conventional natural gas resource. That number is also 730,000 times annual gas consumption for the globe -- which equaled 82 tcf in 1998.

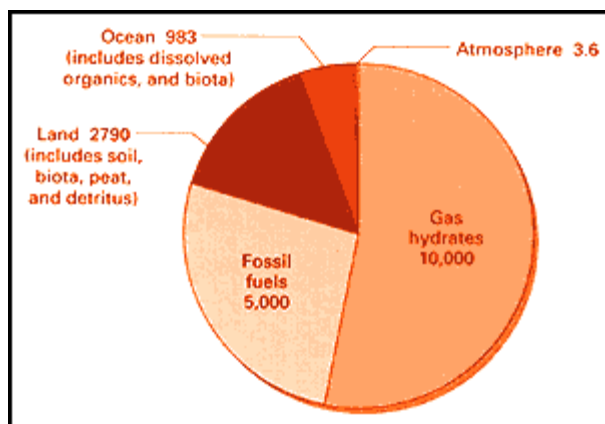


Fig. 7

In terms of carbon, gas hydrates seem twice as massive as all other fossil fuels -- coal, gas and oil -- combined. And while nobody suggests all this stuff could be extracted at a reasonable price, even a tiny percentage could make a big difference in our energy future.

With little notice outside the oil patch, gas hydrates have grabbed the attention of fossil-fuel analysts. "I know, oil companies know, governments know that [today's oil and gas] game will be over in 20 to 30 years," says Sassen, who directed geochemical research for three major oil companies. "If you going to change the planetary infrastructure before the lights go out, you've got to start thinking about gas hydrates now."

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