

Frozen Heat: The Next Fossil Fuel

Harsh K. Anjirwala

Abstract— Future's frozen fossil fuel (Gas Hydrates) is ice like crystals where gas molecules, methane in most cases, are encaged in hydrogen bonded water lattices at high pressure and low temperature. Gas hydrates are significant resource of natural gas existing both on-shore buried under the permafrost and off-shore buried under oceanic and deep lake sediments. Gas hydrates were first discovered in oil industry when pipe lines carrying oil or gas got choked due to formation of an ice like material. Oil industry has to shell out a lot of money in order to clean the pipelines. so it is more of problem in oil & gas transportation industry, especially in colder regions. Hydrate formation is possible in any place where water exists with such molecules-in natural or artificial environments and at temperatures above and below 32°F when the pressure is elevated. We encounter conditions that encourage hydrate formation as we explore more unusual environments for gas and oil, including deepwater frontiers and permafrost regions. The idea of gas hydrate can be our future energy source struck much later. This paper consist identification , production and exploration technique of gas hydrates , problems facing in gas hydrates and problems in exploration tech such as subsidence,dissociation,etc.

Index Terms— Gas Hydrates, frozen fossil fuel,

I. INTRODUCTION

In a country like India where there exists a persistent widening gap between demand of natural gas and its supply, gas from gas hydrate may play a major role for mitigating this gap of demand-supply. Production from Indian oil and gas fields has been apparently decreasing with little reserve growth despite intensive exploration efforts by national and private oil companies. India gas hydrate resources are 1,894 trillion cubic metres, which is over 1,700 times as much as the proven natural gas reserves with the country of about 1.08 trillion cubic metres. To put the resource into perspective, India consumes 90 million standard cubic metres a day of natural gas. If the estimate gas hydrate reserves hold true, the energy source is infinite and can last several tens of thousands of years.

Natural gas hydrates have been the object of considerable research in recent years, because of the trouble they have caused in the natural-gas and naturalgasoline industries. Natural gas hydrates are white crystalline compounds of water and gas, which, under pressure, exist at temperatures considerably above the freezingpoint of water. Because of

the relatively high temperatures at which the hydrates exist, they become a nuisance in highpressure gas operations where water is present, since their formation causes partial or complete plugging of valves and pipes. From a practical standpoint, the trouble incident to hydrate formation has been

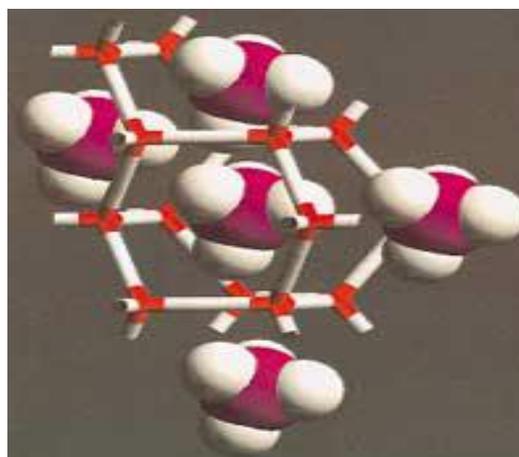
solved by dehydration of the gasbefore it enters the plant or pipe line, or by other remedial measures.

Hydrates are considered a nuisance because they block transmission lines, plug blowout preventers, jeopardize the foundations of deepwater platforms and pipelines, cause tubing and casing collapse, and foul process heat exchangers, valves, and expanders. Common examples of preventive measures are the regulation of pipeline water content, unusual drilling-mud compositions, and large quantities of methanol injection into pipelines. We encounter conditions that encourage hydrate formation as we explore more unusual environments for gas and oil, including deepwater frontiers and permafrost regions.

II. BASIC STRUCTURES

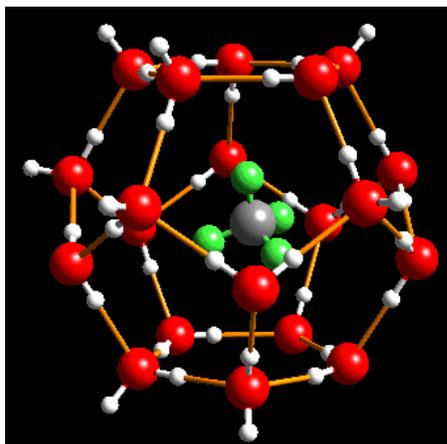
Hydrates normally form in one of two small, repeating crystal structures, shown in Fig. 1. The two hydrate structures are formed from a basic 'building block' water cavity that has 12 faces with 5 sides per face (5 12). Linking the vertices of the 5 12 cavi-ties results in Structure 1, with interstices of large cavities composed of 12 pentagons and 2 hexagons (5 12 62). Linking the faces of the 5 12 cavities results in Structure 2, with interstices of large cavities composed of 12 pentagons and 4 hexagons (5 12 64). Details of structure are given in a recent monograph.

Structure 1, a body-centered cubic structure, forms with natural gases containing molecules smaller than propane; consequently Structure 1 hydrates are found in situ in deep oceans with biogenic gases containing mostly methane, carbon dioxide, and hydrogen sulfide. Structure 2, a diamond lattice within a cubic framework forms when natural gases or oils contain molecules larger than ethane but smaller than pentane; Structure 2 represents hydrates that commonly occur in production and processing conditions, as well as in the cases of gas seeps in shallow ocean environments. The newest hydrate, Structure H, is neglected in this overview; it is yet to be found outside the laboratory .



Structure1

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Structure 2

Inside each structure cavity resides a maximum of one of the eight guest molecules. The cavity occupied is a function of the size ratio of the guest molecule within the host cavity. To a first approximation, the concept of "a ball fitting within a ball" is the key to understanding many hydrate properties. Much more certainty exists with respect to the molecular structure of hydrates than to the kinetic mechanism of hydrate formation; hydrate kinetics are currently at the forefront of research.

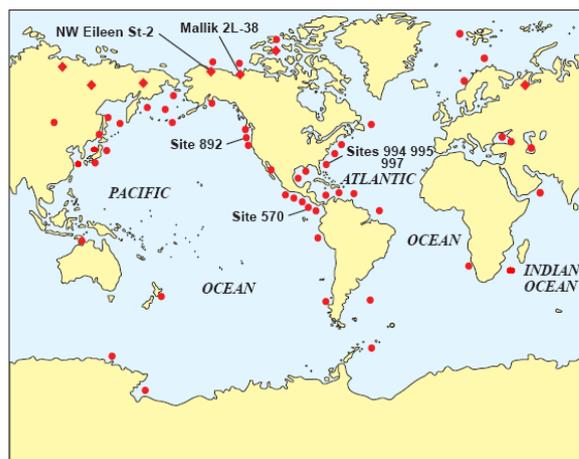
III. EVIDENCE FOR GAS HYDRATE

Three kinds of evidence have been used to identify the presence of natural gas hydrate--geological, geochemical, and geophysical. Geological evidence includes sediment properties, stratigraphic relationships, gas-migration pathways, and, most importantly, the actual recovery and description of gas-hydrate samples. Pore fluid chemistry and gas compositions (molecular and isotopic) are important aspects of gas-hydrate geochemistry. Finally, geophysical evidence includes data from seismic reflection profiling, seismic refraction-wide angle reflection studies, vertical seismic profiling, and various kinds of well-logging. Seismic reflection profiling is especially valuable for accessing the areal extent of gas-hydrate deposits. Much of the geophysical evidence for oceanic gas hydrate is based on observations of Bottom-Simulating Reflectors (BSRs) on marine seismic records. These anomalous reflections result from the acoustical difference between hydrate-bearing sediments within the hydrate-stability zone (HSZ) and non-hydrate bearing, gassy sediment below the HSZ (Shipley et al., 1979).

The depth of hydrate stability in the earth can be obtained through a plot of the geothermal gradient and the hydrate thermodynamic stability envelope. Figure shows a hydrate envelope for methane above and below the permafrost and in ocean sediments. As discussed previously, when any amount of propane is added to the gas, the stability field will be appreciably broader. Verma *et al.*, 8 have shown that hydrates can denude lighter hydrocarbons from oil, thereby explaining instances of highly viscous "dead oil reservoirs" near the surface in permafrost regions.

IV. OCCURRENCE OF GAS HYDRATE

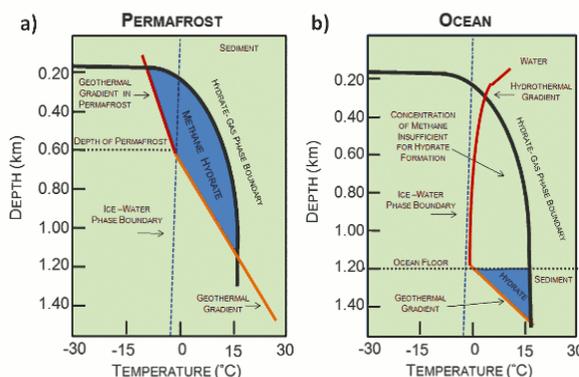
The geologic occurrence of gas-hydrates has been known since mid -1960s when gas hydrate accumulations were discovered in Russia. Natural gas-hydrates can be found in the deep marine sediments and permafrost, were the thermodynamic conditions of low temperature and high pressure allow gas-hydrate formation. Gas-hydrates are located in areas like North Slope of Alaska and Canada and as well as in offshore continental marine environments throughout the world including the Gulf of Mexico and the East and West Coast of the United States.



Source :- collett , 2002

V. THE HYDRATE PRESSURE-TEMPERATURE STABILITY ENVELOPE

Hydrates are formed at conditions of low temperature and high pressure as explained in figure. Figure a. and b. shows the hydrate stability zone both in permafrost and in oceanic sediments. The overlap of the phase boundary and temperature gradient indicates the extent of the gas hydrate stability zone (GHSZ). Gas hydrates are stable on ocean floor sediments at a depth of roughly 400 meters and in permafrost regions of depth approximately 200 meters. These figures are based upon hydrates which are formed by methane. If we consider other heavy natural gases like propane, iso-butane we can observe an increase in the depth of the hydrate stability zone due to the shift of the phase boundary line.



VI. APPLICATIONS IN THE PETROLEUM INDUSTRY

Inhibition/Dissociation. The four common means of inhibiting/dissociating hydrates are (1) removing one of the components, either the hydrocarbon or water; (2) heating the system beyond the hydrate formation temperature at a pressure; (3) decreasing the system pressure below hydrate stability at a temperature; and (4) injecting an inhibitor, such as methanol or glycol, to decrease hydrate stability conditions, so that higher pressures and lower temperatures will be required for hydrate stability. These techniques are called thermodynamic inhibition because they remove the system from thermodynamic stability by changes in composition, temperature, or pressure. As long as the system is kept outside thermodynamic stability conditions, hydrates can never form. A newer method, called kinetic inhibition, allows the system to exist in the hydrate thermodynamic stability region. Small hydrate nuclei are hindered from agglomerating to larger masses by means of new inhibitors. Kinetic inhibition is the focus of a substantial amount of current research, in both Europe and North America.

Pipeline and Platform Applications. When these problems occur, consequences can be formidable. Depressurization of deepwater pipelines to remove plugs frequently requires days of flow interruption. When flow is halted because of a plug in a pipeline, it is difficult to place heat at the precise plug site. The line is usually depressurized at each end of the plug. Depressurization decreases the hydrate formation temperature to below that of the environment, which enables the plug to be dissociated by ambient heat. After the plug is dissociated, a pig is used to clean the line.

For long gas and multi phase pipelines in cold, high-pressure conditions, insulation alone will not suffice to maintain a hydrate-free channel. Methanol is injected into the gas phase, which carries it to the site of free liquid water where methanol dissolves and provides hydrate inhibition. Because methanol is easily vaporized, but concentrates in free water, it is preferred over such other inhibitors as salts or glycols, which have lower vapor pressures. However, much of the methanol does not dissolve in free water and is lost in the gas or hydrocarbon liquid phase.

As E&P operations move to regions of deeper water or lower temperature, much more methanol will be required and the issue of economics will receive more attention. One company estimated the 1988 cost of methanol inhibition in a North Sea pipeline to approach 1 % of the gross revenue. On another North Sea platform, the 1990 methanol injection costs exceeded \$2.5 million. Typical capital costs to prevent hydrates in a processing plant are 5 % to 8 % of the total plant cost. As a result of such economics, work is under way to find alternative and more economical means of inhibition.

VII. CLASSIFICATION OF HYDRATE DEPOSITS

Natural hydrate accumulations are divided into three main classes:

Class I—the class I accumulations are composed of two layers; the hydrate interval and an underlying two-phase-fluid zone with free (mobile) gas.

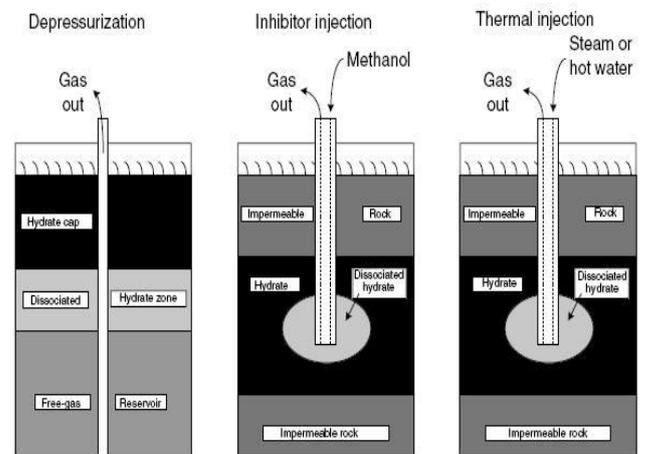
Class II — this consists of a hydrate bearing layer underlain by a one-phase layer of mobile water.

Class III — the class III accumulations are composed of a single zone, the hydrate layer with absence of underlying zones of mobile fluids.

Production methods: There are three main methods of hydrate dissociation: (a) Depressurization: In this method, a production well is drilled into the hydrate reservoir and a pressure difference is created between the wellbore and adjacent blocks. Pressure reduction frees the methane molecules from hydrate.

(b) Thermal stimulation method: In this technique heat is added to the reservoir at constant pressure. When the heat is added by, e.g., circulating hot fluids downhole, the temperature increases until the hydrate dissociation temperature is reached.

(c) Inhibitor injection method: In this method, injection of inhibitors (e.g. Salts, methanol, and e.t.c) shifts the pressure-temperature equilibrium leading to rapid dissociation of gas hydrate.



Source : - er. Oragui Charles Ogamegbunam , 2010

In-situ gas hydrate conversion into gas phase and the subsequent use of traditional natural gas recovery techniques are presently considered as basic development techniques. So far, four methods of gas hydrate dissociation to produce free gas have been made available:

- lowering reservoir pressure below equilibrium
- rising reservoir temperature above equilibrium
- injection of inhibitors to promote gas hydrate dissociation
- high-frequency field treatment

The choice of technology is based on particular reservoir conditions (i.e. the presence of free gas below the hydrate deposit) and the rate of hydrate overcooling (i.e. difference between the reservoir and equilibrium hydrate formation temperature). Costs of gas production and gas recovery need to be comparable with those for conventional gas fields.

Lowering reservoir pressure below equilibrium appears to be the most cost-effective technology of gas hydrates development so far. This method of hydrate development was first introduced in the Messoyakh gas field.

However, for those offshore hydrate deposits located in the young sediments - when hydrate itself serves as a binding

matrix - it would be generally impossible to lower reservoir pressure below equilibrium, since hydrate dissociation could cause seafloor instability.

Falling reservoir temperature attributable to hydrate dissociation could become a limiting factor at high overcooling and hydrate saturation rates in the reservoir rock. It is well known that specific heat of gas hydrates dissociation is about 0.5 MJ/kg, which exceeds specific heat of ice melting. Assuming hydrate dissociation is substantial would imply that due to increased heat exchange with the surrounding rock, the pay zone will cool down to the equilibrium temperature of hydrate formation (which short-stops hydrate dissociation), or to the ice formation temperature (which leads to the sharp drop in reservoir rock permeability). Also, this process is complicated by the fact, that matrix rocks with over 60% hydrate content appear to be gas-tight.

Thus, to maintain stable gas hydrate dissociation within the porous media, one should provide continuous heat flow to the pay zone. This approach can offer new prospects for employment of thermal techniques for gas hydrate development. In 2001, the Gas & Gas/Condensate Fields Development Department of the Gubkin Oil & Gas University (Moscow) proposed several new technologies for gas hydrate deposits heat treatment, aiming to improve hydrocarbon recovery.

The first new technique of this sort is based on injection of a thermal liquid below impervious hydrate-bearing layer bottom.⁷ This implies the formation of a radioactive effluent underground storage below the impervious reservoir bottom. Such underground storage should comprise a cluster of horizontal/slanted wells to improve heat exchange efficiency "Smart wells" are highly recommended in this case.

Active life span for liquid radioactive waste should be "synchronised" with the lifetime of a gas hydrate field. The advantages of this thermal liquid are: production of vast amounts of heat and low operating costs. The main disadvantage is attributable to its high environmental risks associated with field development. Also, this technique implies the use of intensive heat exchange systems between the heat source (thermal liquid) and the reservoir, since natural heat exchange via impervious reservoir bottom is very slow.

The second thermal technique provides for construction of dual-head multi-hole wells for simultaneous production of gas from hydrate layer and heat-carrier injection into pay zone (see Figure 2).⁸ Hot water, gas, superheated steam, and other agents can be used as heat-carrier. Heat-carrier is injected into the reservoir via injection wells, and the produced dissociated gas is recovered from a producing well. The first stage of this technique ensures hydrate dissociation in the borehole vicinity, which produces an "artificial gas reservoir" with restored rock permeability, and the second provides for gas production from the reservoir using traditional techniques.

The simplest method for producing natural gas from hydrate deposits is centred on hot water injection into the reservoir. However, this technique would be only applicable when cumulative consumption of energy used for in-situ hydrate dissociation does not exceed the energy produced while burning the produced gas. This condition can be met by injecting cheaper thermal water produced from underlying seams.

(Source :- *Makogon, Yu.F. Hydrates of hydrocarbons.*, Tulsa, Pennwell Publishing Co., 1997)

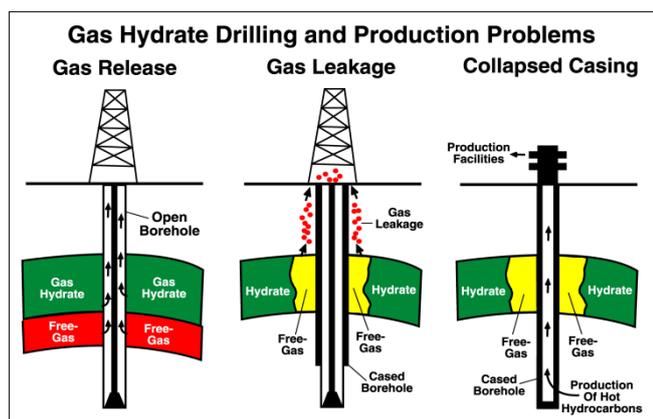
VIII. GAS HYDRATE CHALLENGES

- Environmental Challenges Damage to sensitive chemosynthetic communities The potential connection, between the gas hydrate reservoir and the earth's climate is little understood and the quantitative contribution of different elements in this complex loop needs to be established through further research. Lack of understanding between gas hydrate reservoir and the earth's climate could be an even bigger inhibitor on hydrate exploration than present low oil prices and lack of funding support for hydrate research. The balance may lie between mounting intensive campaigns on climate research and safety procedures on the extraction and use of gas hydrates. The possible short and long term impacts of large scale hydrate exploitation on the geological environment and global climate need to be studied to develop safe standardized procedures for exploration and production before attempting to exploit this resource. It is also necessary to systematically collect base line information on related environmental indicators and continuously monitor short and long term effects on them. Perturbations associated with exploiting methane hydrates need to be analyzed by careful modeling and techniques have to be developed to avoid or mitigate them.

Technical Challenges

- Hydrates decompose releasing hydrocarbons as a gas when removed from low temp/high pressure environment.
- Gas hydrate, flow assurance and system implications Methane hydrate contains methane in concentrations up to 160 times its volume. Gas hydrates are solids with densities greater than those of typical fluid hydrocarbons and this has practical implications for flow assurance and the safety thereof. However, of more immediate concern to the natural gas industry is the fact that methane hydrate also can form within pipelines under certain pressure and temperature conditions, forming a solid or semi-solid mass that can slow or completely block gas flow. While the problem is particularly serious for producers moving gas from offshore wells to onshore processing facilities, methane hydrates can also be found in many other elements of the network of gas storage facilities and transmission pipelines.
- Seismic analysis of hydrate deposits is developed to point where we can predict with reasonable accuracy the location and concentration of some hydrate deposits. More needs to be done to improve the quantification of the deposit and also to locate hydrates that are not in conventional horizontal deposits. Collecting pressure core samples for testing and verification of hydrates is needed.

- Developing a recovery scheme compatible with a permafrost environment
- Tailoring existing production technologies and equipment for use in hydrate production.
- Drilling and completion (stimulation) technology development. Drilling for recovery of methane from the hydrate is a challenging task because of the characteristics of the hydrates especially, its unstable nature with change in pressure temperature conditions. Hydrates may dissociate during the process of drilling and initiate a process of uncontrolled gas release and site subsidence. Well completion for hydrate production has not been addressed. Some of potential problems are sand control and hole stability.



Source :- USGC.

- Reservoir models have been developed and limited testing completed. However, more tests and data on reservoir properties and performance is required before acceptance of model predictions. More production test will be required to gain confidence in models. Integration of field production testing data with numerical simulation.
- Hydrate recovery will in all probability involve forced dissociation, which will involve significant demand for heat. Supplying and managing this heat and maintaining an artificial thermodynamic balance that allow the controlled dissociation of hydrate and the safe recovery of methane will probably prove the key to commercialization.

IX. CONCLUSION :-

Natural gas hydrate is a global phenomenon now receiving international attention. It occurs worldwide but is restricted to two environments--in polar continental and deep water (mostly on outer continental and insular margins) sediment of the shallow geosphere. An inventory of global occurrences shows 77 places in which the presence of gas hydrate is inferred by geophysical, geochemical, and geological methods. This inventory includes 23 places where samples of the substance have actually been recovered. Details concerning individual gas-hydrate occurrences and the global implications of gas hydrate are discussed at a new world-wide-web (www) site (<http://walrus.wr.usgs.gov/globalhydrate>). The potential amount of methane in global gas-hydrate occurrences is very large, with current estimates converging at about 10

exagrams of methane carbon. Interest in gas hydrate is increasing because of its potential as (1) an energy source, (2) a factor in climate change, and (3) a submarine geohazard. This new web site has been created to help facilitate global gas-hydrate research.

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I am studying in third year of b.tech petroleum engineering. I got 90% in 12th standard and my current CGPA is 8.5. I am active member of Society of petroleum engineers (SPE), society of exploration geophysicist (SEG), EAGE, Petrotech, etc. I was event management head in college's technical fest last year. Currently i am technical head of SEG STUDENT CHAPTER PDP. I presented paper on "UNDERGROUND COAL GASSIFICATION" in technical fest of college and presented paper and poster on "DRILLING" in SPE PDP FEST. I did summer internship at ONGC, ANKLESHWAR. I am working on one project name: "MATHEMATICAL MODEL FOR SOLUTION OF SUBSIDENCE DURING DRILLING". I have learnt two software" MATLAB" and " RISK - ASSESMENT OF PETROLEUM RESERVS" .