

METHANE HYDRATES IN MARINE SEDIMENTS — UNTAPPED SOURCE OF ENERGY

*Pratima Jauhari **

ABSTRACT

Existing largely in the form of a crystalline, frozen mixture of methane and water under low temperature and high pressure, methane hydrates are now looked upon as an untapped source of hydrocarbon energy) Methane production from hydrates can contribute low cost natural gas to partially fulfil domestic demand, play a greater role in power generation and transportation because of increasing choice for cleaner fuels and reduced CO₂ particulate, sulphur oxides and nitrogen oxides production. Areas of rapid hemi-pelagic sediments are favourable for the accumulation of considerable amounts of organic detritus where methane is produced by bacterial degradation of organic matter buried under below the sea floor, by thermogenic 'cooking' of organic matter or by the dissociation of hydrates. Several countries including India have started active research programmes on methane hydrates, and it is expected that if advanced technologies for converting the natural gas to liquid fuels can be scaled up, gas could replace oil as the next source of transportation fuel.

Seismic reflection and geochemical methods are the most important approaches for identifying gas hydrates in marine sediments. In addition to their potential as energy resources, their influence on the stability of sea floor is well recognised. When disturbed by activities such as drilling, or when massively disturbed by natural causes, their influence on global climate could be significant. A long term research and development effort will be required to turn this potential resource into gas reserves while developing technologies to conduct safe petroleum operation in hydrate areas, and defining the role of methane hydrates in global climate.

*National Institute of Oceanography, Goa.
(NIO Contribution No, 3663)*

Journal of Indian Ocean Studies, Vol. 9 No. 1 April 2001

Introduction

Known as a formidable nuisance in oil and gas pipelines for clogging the lines, methane hydrates are now looked upon as a promising alternate resource of energy. Natural gas is expected to play an important role in power generation and vehicular transportation because of the increasing pressure for cleaner fuels and reduced CO₂, particulate, sulphur oxides and nitrogen oxides production. Methane production from hydrates can contribute low cost natural gas for domestic demand. Recent studies by the US Geological Surveys have conservatively estimated the deposits of methane hydrates worldwide to represent an untapped source of hydrocarbon energy. These amounts to twice the quantity found in all known fossil fuels on earth (Cruickshant & Masutani, 1999). In addition to its economic importance, methane is a powerful greenhouse gas which, molecule for molecule, is about 25 times more potent than CO₂ in its radiation effect (Kiehl *et al.* 1987). This is especially pertinent now because the world faces the prospect of global warming. The fields of gas hydrates can have diameter of few kilometres to several tens of kilometres (Mienert & Posewang, 1999). One cubic metre of gas hydrate absorbs about 163 cubic metres of free gas, thus containing an extremely large amount of gas. Though all the gases except hydrogen, helium and neon form gas hydrates, methane is the dominant gas in gas hydrate which generally comprises 99.9% of the total hydrocarbons, and hence the name 'methane hydrate'.

Hydrates are naturally occurring solids of a special category called the inclusion compounds' in which a molecule of a chemical compound gets trapped within a molecule of another component without forming any chemical bonds between them. "Clathrate" is one of the inclusion compounds in which the molecule to be caged in fits into special voids of another molecule and can be released only by the decomposition of the compound. If the host molecule is water, it is called "clathrate hydrate" or hydrate and if the guest molecule is a gas then the term "gas hydrate" is used (Singh & Singh, 1999).

Occurrence

Interest in methane has recently increased with the discovery of enormous methane deposits off the continental margins. These vast reservoirs, buried deep within the marine sediments, exist largely in the form of a crystalline, frozen mixture of methane and water known as methane hydrate (Kvenvolden, 1988) formed under low temperature and high pressure. They occur naturally in such areas where methane and water can combine under appropriate

conditions of temperature and pressure. These conditions are found, in the Arctic regions of permafrost, in deep water basins adjacent to continental shelves, and in deep ocean basins where the sediment thickness is at least one kilometre (Cruickshant & Masutani, 1999). Equally important to note is the occurrence of gas hydrates in outer continental margins in both the continental settings of divergent and convergent margins (Subramanyam, 1998).

Gas hydrates have caught the attention of the industry in 1930s when it was realised that the long distance oil and gas transmission pipelines in the USA were being clogged by the formation of gas hydrates within the pipelines. To overcome this problem, researches were done on the composition and structure of gas hydrates and thus gas hydrates studies became important for the future (Desa, 2000). The presence of natural gas hydrates in marine sediments was speculated by Makogon *et al.* (1973), and a few years later the first natural gas hydrates were discovered by the deep-sea drilling of the sea floor during DSDP leg 66 (Shipley & Didyk, 1981). These were then dredged from the surface sediments of the Caspian Sea. Since then the occurrence of these has been repeatedly reported as submarine gas hydrates. According to United States Geological Survey (USGS), two very small areas along north and south Carolina coast, lying in apart of the Bermuda Triangle contain gas equivalent to about 70 times the annual gas consumption of the USA. As much as 200,000 trillion cubic feet (Tcf) of methane may exist in the hydrate systems of the US permafrost regions and in the surrounding waters which is hundreds of times greater than the estimated conventional US gas resource base of 1,400 Tcf. Even if actual reserves prove to be only a small fraction of these estimates, methane hydrate production could alter the US and world pattern of energy supply and consumption,

Japan was the first country to establish a national hydrate research program in 1995. India, in 1996 was the second nation to establish a gas hydrate research program under the auspices of the Oil Industry Development Board of India. Japan has set up the first drilling campaign in 1997, specifically designed for the hydrate and related issues such as methane generation and flux carried out by the international scientific Ocean Drilling Programme (ODP) on the Black Plateau 9 USA.

Formation

Areas of rapid hemipelagic sediments are favourable to accumulate considerable amounts of organic detritus and preserve them from oxidation

by rapid burial under the seafloor so that it is converted into abundant methane by bacterial activity within the sediments (Singh & Singh, 1999). Methane is produced biogenically by bacterial degradation of organic matter buried under the sea floor. Microbes in marine sediments are thought to consume methane that diffuses upward, before it can escape into oxygenated waters (Delong, 2000). The gas can also be produced by thermogenic "cooking" of organic matter or by the dissociation of hydrate (Vogt *et al.*, 1999). After the generation of methane, its transportation in the sediment can take place through various means such as the movement of pore-water containing dissolved gas, free gas flow and molecular diffusion. When the ascending methane molecules reach a favourable subsurface — thermobaric conditions (i.e. hydrate stability zone), the formation of hydrate takes place within the pore spaces of the sediments in the presence of water molecules. The biogenic methane formation can occur both *in situ* within the hydrate stability zone (HSZ) and beneath the zone. Thermogenic methane, on the other hand, has to move upwards from depth into the HSZ (Ginsburg, 1998).

Signatures

The results of numerous material studies show that the occurrence of these hydrates is related to fluid discharge sites such as gas seeps, vents, mud volcanoes and the like suggesting that methane inflow must be resupplied at a minimum rate for sea-floor gas hydrate to form and be stable (Egorov *et al.* 1999). Many known gas seep areas and mud volcanoes are characterised by the formation of authigenic carbonates. In the Gulf of Mexico, which is the best studied area, the association of bacterial mats, gas hydrates and authigenic carbonates in the same seep area has been noted repeatedly (MacDonald *et al.* 1994).

The value of gas in the gas hydrate of a given prospect depends on five parameters: (i) geographic area of the hydrate stability zone, (ii) reservoir rock thickness, (iii) effective porosity, (iv) hydrate concentration within the sediment pores and, (v) hydrate gas yield. No direct method exists to calculate the possible amount of hydrates in the sediments due to the lack of knowledge of their actual distribution in the sediments and how they modify the sediment bulk moduli (Subramanyam, 1998).

Identification

Seismic reflection and geochemical methods are the most important approaches for identifying the gas hydrates. The presence of natural

submarine gas hydrates is commonly inferred from seismic reflection data (Hyndman & Spence, 1992). The base of stability zone for gas hydrates is geophysically identified by the occurrence of a bottom simulating reflector (BSR). The BSR is a reflection at the boundary between the high-velocity gas hydrate cemented sediments and the underlying low-velocity gas bearing sediments. Whereas compressional velocity values of 1700-2400 m/s indicate free gas in the pore space (Posewang & Mienert, 1999). It is suggested that high reflection polarity reversal a large reflection coefficient and increasing sub-bottom depth with increasing water depth are the different criteria which characterise a BSR. The BSR mimics the shape of the seafloor, often cuts the dominant stratigraphy and is characterised by a high, reversed-polarity event. In addition to BSR, the amplitude blanking and velocity inversions are the other geophysical means of identifying the fields of gas hydrates.

Research needs

A large, long term R&D effort is required to turn the potential hydrate resource into gas reserves while developing technologies to assure safe petroleum operation in the hydrate areas:

- Where methane hydrates are located and in what quantities?
- How natural gas can be economically produced from methane hydrate deposits?
- The role methane hydrates play in global carbon balances and atmospheric methane.
- The potential impacts of hydrates on conventional hydrocarbon operations.
- The impact of hydrate deposits on the submarine landslides and sediment collapse features (sea floor stability).

These studies in long term would also enable to have improved data on ocean and atmospheric thermal and chemical changes for use in global climate modelling and improved seismic and other geophysical tools for use by the petroleum industry.

Gas hydrates — other aspects

Little is currently known about the processes or volumes involved in global perturbation from gas hydrate decomposition on the sea floor. The stability of gas hydrate during global warming and the environmental consequences of a significant methane release are poorly understood.

Decomposition of gas hydrates may trigger mass wasting on the continental slopes by the liberation of gas trapped beneath the hydrates. Gas evolution in turn weakens the overlying sediments (Carpenter, 1981). Methane (CH₄) is an important greenhouse gas and submarine gas hydrates are a potential source of atmospheric methane. In the event of these gas hydrates being destabilised, excess pressure in the pore water builds up as a result of the release of gases which can cause a rapid release of gases from the ocean bottom into the ocean atmosphere. These processes often take place eruptively and leave their imprints on the ocean bottom in the form of craters. Large amounts of methane in the ocean bottom and in the global climate are of increasing scientific and economic importance for the understanding of the coupling mechanism between the lithosphere, oceanosphere and atmosphere (Mienert & Posewang, 1999).

The widespread occurrence of methane hydrates in the world oceans and seas, their ability to change from solid to gas when their natural equilibrium is disturbed and other characteristics have resulted in four distinct areas in which more information is urgently needed: (i) their potential as energy resource, (ii) their influence on the sea floor stability when disturbed by activities such as drilling, (iii) their influence on global climate when massively disturbed by natural cause, and (iv) their implications on indicated unique acoustic properties (Cruickshant & Masutani, 1999). For the extraction of methane from gas hydrates, three methods — thermal stimulation, depressurisation and solvent injection are being considered. Of these, depressurisation combined with hot water injection appears to be the most practical one where 'free gas' lies beneath the gas hydrates. However, much work is needed to document and field test to be carried out on these techniques for their commercial scale production.

Indian scenario

The Oil Industry Development Board of India, as part of its plan to boost natural gas resources has earmarked \$ 56 million for a programme of methane hydrates research to be carried out largely under the auspices of the Gas Authority of India (Cruickshant & Masutani, 1999). Increased international activity and significant spending in Japan and India point out their commercial production in not so very distant future. Studies have been initiated to investigate the prospects of gas hydrates in the Indian waters in 1996. Organisations like the National Institute of Oceanography (NIO), the National Geophysical Research Institute (NGRI), the Oil and Natural Gas

Commission (ONGC) and the Gas Authority of India Ltd. (GAIL) are looking forward to demarcate the signatures of gas hydrates bearing strata in deeper waters of the Bay of Bengal and the Arabian Sea, off the continental shelf of India. Based on the analysis of geoscientific data of the oceanic areas of the Bay of Bengal and the Arabian Sea, covered within the Legal Continental Shelf (LCS) of India, it has been found that the upper few hundred metres of sediment would, in all probability, have gas hydrates in very large quantities (Rastogi. *et al* 1999), as the thick sediments of the Bengal Fan and the Indus Fan would have provided adequate organic matter for the generation of methane in sufficient quantities (Rastogi *et al* 1999). Preliminary studies by the ONGC have shown that the areas off the coasts of the Krishna and Godavari river deltas and the Andaman & Nicobar islands are also likely to be the potential areas of gas hydrate accumulation (Singh & Singh, 1999). Along the western off shore, the topographic high and particularly their flanks, with thick sediments and associated faulting should be considered as potential zones for possible formation and occurrence of gas hydrates (Subramanyam, 1998). Considerable work has been undertaken at NIO, Goa to study these deposits in their geo-scientific relevance. The institute is considering to start a centre of gas hydrate research for exclusive studies on these resources.

Presently, the production of gas in India is around 58 million cubic metres per day and the demand is likely to increase to approximately 285 million cubic metres per day (Rastogi *et al.* 1999). To meet the growing demand, sustained efforts are required to look for other perspective areas. The high and rapid rate of sedimentation, particularly in the Bengal Fan is highly favourable for the formation of thick and massive gas hydrates (Rastogi *et al* 1999).

Future scenario

Japan, India, Canada, England, Brazil, Norway and Russia are currently having active research programmes on methane hydrates. Several of these countries are expected to propose cooperative work and research exchange. It is hoped that R & D efforts in the field of marine methane hydrates will get enough financial support so that a new, unconventional, untapped fuel resource could be developed to ensure adequate and affordable energy for the future (Desa, 2000). Many analysts believe that there will be a change from growth to decline in the oil production world wide in the early 21st century. If advanced technologies for converting the natural gas into liquid

fuels can be made profitable and scaled up, gas could replace oil as the next source of transportation fuel. Consumption of natural gas will increase in the 21st century and methane hydrates can contribute to a reliable, low cost domestic supply. In the near future, natural gas is expected to play a greater role in power generation and transportation because of increasing pressure for cleaner fuels and reduced CO₂, particulate, sulphur oxides and nitrogen oxides production.

A long term research and development effort will be required to turn this potential resource into gas reserves while developing technologies to assure safe petroleum operation in hydrate areas, and defining the role of methane hydrates in global climate.

References

- Carpenter, G. 1981. Coincident sediment slump/ clathrate complexes on the US Atlantic Slope. *Geo-Marine Letters*, Vol. 1, pp. 29-32.
- Cruickshank, M.J. & Masutani, S.M. 1999. Methane hydrate research and development. *Sea Technology*, Vol. 40, No. 8, pp. 69-74.
- Delong, E.F. 2000. Resolving the methane mystery. *Mature*, Vol. 407, pp. 577-579.
- Desa, E. 2000. *Submarine methane hydrates — Potential fuel resources of the 21st century*. Workshop on Mineral Resources of the International Seabed Area . Kingston, Jamaica. 26-30 June 2000.
- Egorov, A. V, Crane, K., Rozhkov, A.N. & Vogt, P. R. 1999. Gas hydrates that outcrop on the seafloor: stability models. *Geo-Marine Letters*, Vol. 19, pp. 68-75.
- Ginsburg, G.D. 1998. Gas hydrate accumulation in deep water marine sediments. In: Henriot, J.P. and Mieneit. J. (eds). *Gas hydrates : Relevance of world margins stability and climatic change*. Geological Society London, special publications, No. 137, pp, 167-175
- Hyndman, R.D. & Spence, G.D. 1992. A seismic study of methane hydrate marine bottom simulating reflectors. *Journal of Geophysical Research*, Vol. 97, pp. 6683-6698.
- Posewang J. & Mienert, J. 1999. High-resolution seismic studies of gas hydrates west of Svlabard. *Geo-Marine Letters*, Vol. 19, pp. 150-156.
- Kiehl, J.T. & Dickinson, R.E. 1987. *J.Geophys. Res.*, Vol, 92, pp. 2991-2998.
- Kvenvolden, K.P. 1988. *Chemical Geology*, Vol. 71, pp. 41-51
- Makogon. Yu F., Trofimuk, A. A., Tsarev, V.P. & Cherskiy, N.V. 1973. Opportunity formation of gas hydrate seals of natural gases in near bottom zone of the seas and oceans. *Geology & Geophysics*, Vol. 4, pp. 3-6.
- Mienert, J. & Posewang, J. 1999. Evidence of shallow and deep-water gas hydrate destabilizations in north Atlantic polar continental margin sediments. *Geo-Marine Letters*, Vol. 19, pp. 143-149.

- Posewang, J. & Mienert, J. 1999- The enigma of double BSRs: Indicators for changes in the hydrate stability field? *Geo-Marine Letters*, Vol. 19, pp. 157-163.
- Rao, Hanumantha, Reddy Y., Ramesh Khanna, S. I., Rao, T.G., Thakur, N.K. & Subrahmanyam!, C. 1998, Potential distribution of methane hydrates along the Indian Continental margins. *Current Science*. Vol. 74, pp. 466-468.
- Rastogi, A., Deka, B., Budhiraja, I.L. & Agrawal, G.C. 1999. Possibility of Large Deposits of Gas Hydrates in Deeper Waters of India. *Mar. Geores. and Geotech.*, Vol. 17, pp. 49-63.
- Shipley, T.H. & Didyk, B.M. 1981. Occurrence of methane hydrates offshore southern Mexico. In : Watkins, J.S., Moore J.R. *et al.* (Eds). *Initial Reports deep Sea Drilling Project Leg 66*. Washington, D.C., US Government Printing Office, pp. 547-556.
- Singh, A., & Singh, B.D. 1999. Methane Gas: An unconventional energy resource. *Current Science*, Vol. 76, pp. 1533-1545
- Subrahmanyam, C, Reddi, S.I., Thakur, N.K., Rao, Gangadhar & Sain, Kalachandd. 1998. Gas hydrates - A synoptic view. *Jour. Geol. Soc. India*, Vol. 52, pp. 497-512
- Vogt, PR., Crane K., Sundvor, E., Hjelstuen, B.O., Gardner. J., Bowles, F, & Cherkasher, G. 1999. Ground - Truthing 11 to 12 kHz side-scan sonar images in the Norwegian - Greenland Sea: Part II: Probable diapirs on the Bear Island fan slide valley margins and the Vering Plateau. *Geo-Marine Letters*, Vol. 19, pp. 11-130.