GAS HYDRATE - INVESTIGATIONS OF THEIR VARIOUS PROPERTIES

[1]Amandeep Singh Wadhwa

[1]*Department of Mechanical Engineering, UIET, Sector-25, Panjab University, Chandigarh-160025*
*Email: aman_wadhwa77@rediffmail.com*

ABSTARCT:
As a result of geophysical researches in non-conventional energy sources in the earth in recent years, the discovery of large gas hydrate accumulations in terrestrial permafrost regions of the Arctic and beneath the sea along the outer continental margins of the world's oceans creates the interest of gas hydrates as a possible energy resource. Gas-hydrates are crystalline form in which gases (mainly methane) are observed to be 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). According to the U.S. Geological Survey, the worldwide amount of carbon bound in gas hydrates is conservatively estimated to total twice the amount of carbon to be found in all known fossil fuels on Earth. Gas hydrates, also known as clathrates, are frozen, crystalline solids comprising gas molecules contained within a lattice of water molecules. The most common form of gas hydrate is methane hydrate, but other gas molecules include ethane, propane, butane, iso-butane, pentane, nitrogen, carbon dioxide and hydrogen sulphide. Natural gas hydrates are being studied worldwide as transport manufactured materials as they are more suitable for large-scale transport of natural gas over long distances than liquefied natural gas. A main component of hydrate deposits is methane hydrate formed from water and methane molecules so the hydrocarbon gas mixture contains >99% methane. The main aim of this paper is to investigate the various thermal and physical properties of gas hydrates that are the outcome of the experiments performed.

1. INTRODUCTION

Hydrates are the members of the class of compounds labeled "clathrates" after the Latin "clathratus" meaning, "To encage". All hydrate structures have repetitive crystal units composed of asymmetric, spherical "cages" of hydrogen-bonded water molecules. Each cage contains at most one guest (gas) molecule held within the cage by dispersion forces. There is no chemical union between the gas and water molecules. The water molecules that form the lattice are strongly hydrogen bonded with each other and the gas molecule interacts with water molecules through van der Waals type dispersion force.

Gas-hydrates are 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). The issue of gas hydrate geology was initiated in 1969 when the discovery "Property of natural gases to occur in the solid state and to form the gas hydrate fields in the Earth's crust" was registered (the authors: V. G. Vasilyev, Yu. F. Makogon, F. A. Trebin and A. A. Trofimuk). By that time the gas hydrates have not practically been observed in natural conditions, but possibility of their discovery stimulated the interest of geologists in this unusual object. In accordance with the paradigm formed, first, the gas hydrates in submarine environment form mainly from authigenic and biogenic gas: second, all generating biochemical catagenetic gas which enters the gas hydrate formation zone stabilizes in hydrates; third, the gas hydrates within both offshore and onshore stability zones are universally distributed and occur as continuous layer which caps the free gas. These notions served as a basis for the suggestions concerning the giant reserves of natural gas (primarily, methane) in hydrate form in the World ocean basins and in the terrestrial Arctic, which exceeds total hydrocarbon resources all over the Earth.

The phase diagram Fig. 1 of gas-hydrates shows the zone of where hydrates are stable within few hundred meters below the sea bed.
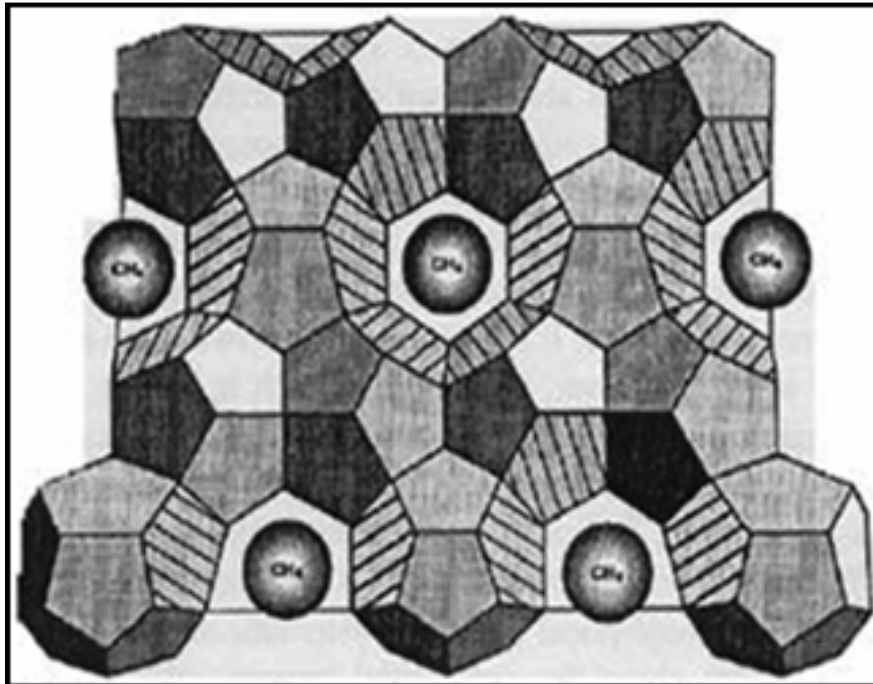
Fig. 1: Structure of gas-hydrates in which methane molecules are caged in hydrogen bonded water molecules (Kvenvolden, 1998). Cages are both exposed and covered.

Figure 2: Sample of methane hydrate from the Gulf of Mexico. Methane hydrates can look like ice or packed snow but break down at atmospheric conditions, releasing nearly 160 times their own volume of methane gas. (Source : Photograph by W.J. Winters, U.S. Geological Survey)

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

S.No.	Methane Quantity, m^3	Year	References
1.	$5x10^{15} – 2.5x10^{16}$	1977	Trofimuk et al.
2.	$7.6x10^{18}$	1981	Dobrynjn et al.
3.	$3.1x10^{15}$	1981	McIver
4.	$4x10^{16}$	1988	Kvenvolden, claypool
5.	$1x10^{16}$	1988	Makogon
6.	$2.1x10^{16}$	1988	Kvenvolden
7.	$2.1x10^{16}$	1990	Mac Donald
8.	$2.6x10^{16} - 1.4x10^{17}$	1994	Gornitz, Fung
9.	$2.3x10^{16} - 9.1x10^{16}$	1995	Harvey. Huang
10.	$1x10^{15}$	1995	Ginsburg, Soloviev
11.	$7x10^{15}$	1996	Holbrook et al.
12.	$1.5x10^{16}$	1997	Makogon
13.	$2x10^{15} – 2x10^{16}$	1997	Dickens et al.
14.	$2x10^{14}$	1999	Soloviev, Ginsburg

II. STUDY OF THERMAL PROPERTIES OF GAS HYDRATE

Gas hydrates are crystalline solids in which molecules of a "guest" species occupy and stabilize cages formed by water molecules. Similar to ice in appearance (fig.3), gas hydrates are stable at high pressures and temperatures above freezing (0°C). Methane is the most common naturally occurring hydrate guest species. Methane hydrates, also called simply "gas hydrates," are extremely concentrated stores of methane and are found in shallow permafrost and continental margin sediments worldwide. Brought to sea-level conditions, methane hydrate breaks down and releases up to 160 times its own volume in methane gas.

A. Measurements of Thermal Properties

Thermal properties of pure methane hydrate were studied in the laboratory. The formation technique uses a highly reproducible method developed by USGS (Stern and others, 2000, 1996) in which granular ice is packed into the sample chamber of a pressure vessel (fig. . The vessel is then pressurized with methane gas, slowly heated to allow the ice to convert to hydrate, and finally compressed to compact the methane hydrate around the centrally located thermal probe. Thermal properties were measured by warming the sample with a heater wire in the thermal probe while measuring the temperature change with a centrally located thermal sensor. The methane stored in gas hydrates is of interest and concern to policy makers as a potential alternative energy resource and as a potent greenhouse gas that could be released from sediments to the atmosphere and ocean during global warming. In continental margin settings, methane release from gas hydrates also is a potential geohazard and could cause submarine landslides that endanger offshore infrastructure. Gas hydrate stability is sensitive to temperature changes.

To understand methane release from gas hydrate, the U.S. Geological Survey (USGS) conducted a laboratory investigation of pure methane hydrate thermal properties at conditions relevant to accumulations of naturally occurring methane hydrate. Prior to this work, thermal properties for gas hydrates generally were measured on analog systems such as ice and non-methane hydrates or at temperatures below freezing; these conditions limit direct comparisons to methane hydrates in marine and permafrost sediment.

Three thermal properties, defined by Briaud and Chaouch (1997), are estimated from the experiments :

Thermal conductivity, λ: if λ is high, heat travels easily through the material.

Thermal diffusivity, κ: if κ is high, it takes little time for the temperature to rise in the material.

Specific heat, *cp*: if *cp* is high, it takes a great deal of heat to raise the temperature of the material.

International Journal of Research in Advent Technology
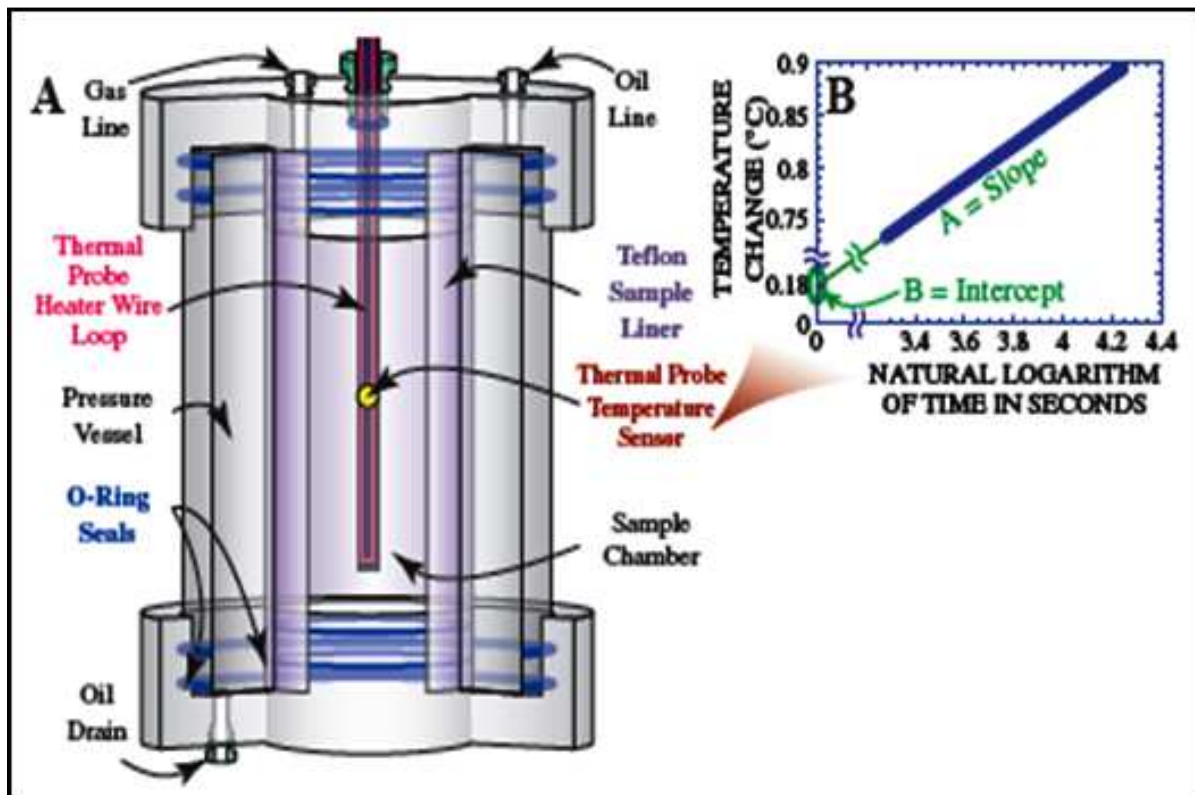
Figure 3: Schematic diagram of the thermal properties pressure vessel. Cylindrical hydrate samples that are 13.3 cm long by 4.1 cm in diameter are formed around a needle probe (enlarged to show detail). (*B*) Thermal properties are estimated from the slope and intercept of the straight-line fit (green line) to the sample's temperature change in response to heat from the heater wire (overlapping blue circles, showing every tenth data point).

The temperature change is linear when plotted as a function of the natural logarithm (ln) of time, as shown by the overlapping blue circles plotting every tenth data point in figure 2B. The sample's thermal properties are calculated from the slope and intercept of the straight-line fit through the data (A and B, respectively, along the green line in fig.) (Waite and others, 2006). These measurements are repeated over a range of pressures and temperatures.

B. Thermal Property Results

Equations for calculating thermal conductivity, thermal diffusivity, and specific heat in methane hydrate are given in table 1 (Waite and others, 2007).

Measurements of thermal properties are used in models that can predict changes that methane hydrates undergo during their recovery as a resource or their potential dissociation during warming. Because hydrates displace either ice (permafrost settings) or water (marine settings or beneath permafrost)comparing thermal properties of methane hydrate to those of ice and water helps gauge the extent to which a host sediment's thermal properties are altered by the presence of methane hydrate.

Thermal conductivity, λ: The thermal conductivity of water is approximately equal to that of methane hydrate, so the thermal conductivity beneath permafrost or in marine settings is essentially independent of methane hydrate content. Methane hydrate is generally found in abundance below, rather than in, permafrost, but the presence of methane hydrates in ice-dominated permafrost can measurably increase the geothermal gradient because the thermal conductivity of ice is approximately four times that of methane hydrate.

Thermal conductivity of gas hydrate is one of the more important physical properties relevant to drilling, logging, and gas production from natural gas hydrate reserves, however, it is not easy to make direct measurement of thermal conductivity of gas hydrate due to its ephemeral nature at earth surface conditions.

III. EXPERIMENTAL METHODS

A solid gas hydrate in Section 164-994C-31X-6 was used for measurement of thermal conductivity. The size of the sample was approximately 20 mm x 10 mm x 5 mm. The sample was cut plane to fit the plate probe of a specially designed apparatus to measure thermal conductivity of small samples at elevated pressure. The measurement system is shown in Figure4 . This system has two types of probes for a hot-wire method, a plate probe and a needle probe. We used the plate probe because the sample was hard. The apparatus was cooled to -30ºC, then the sample was inserted and pressurized at 12 MPa for 4 hr before measurement. We measured three times at the same temperature every 4 hr. The data were reported as the average of these three measurements.
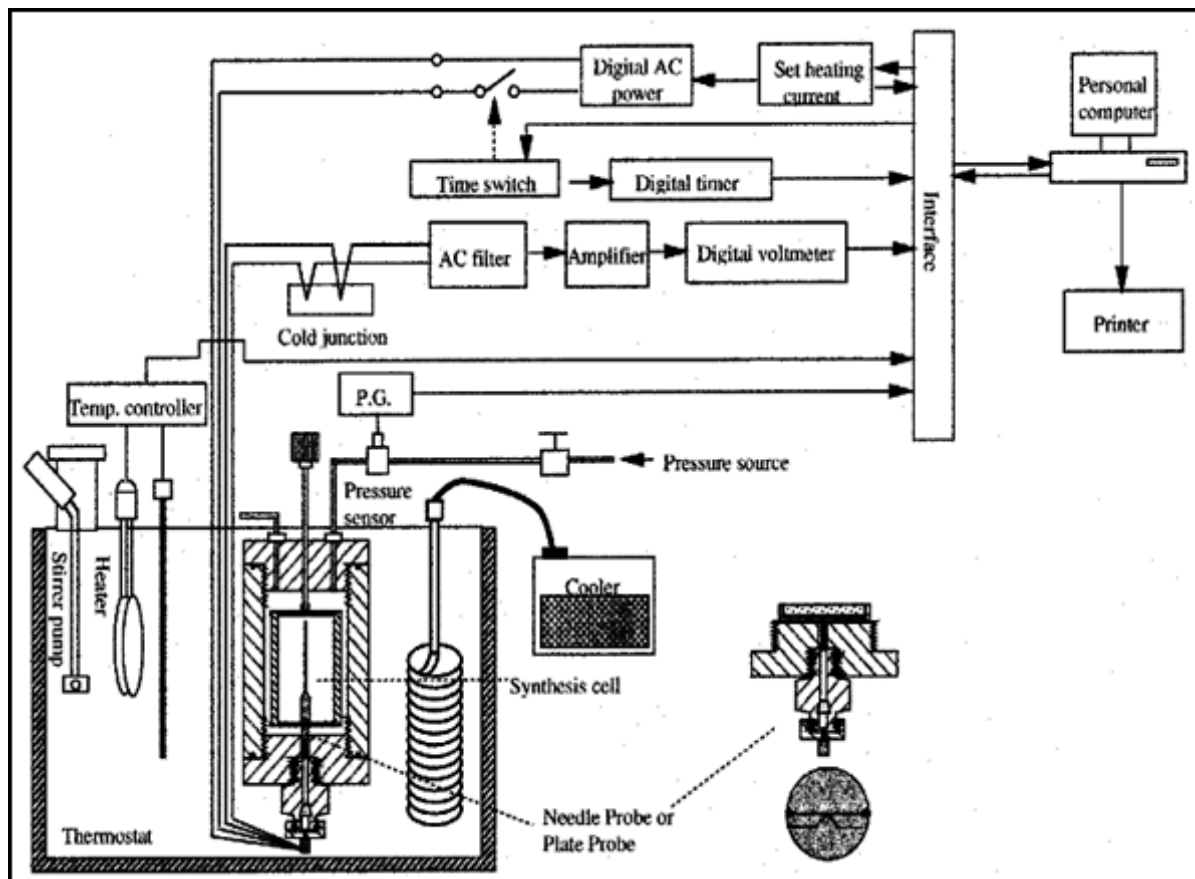

Figure 4: Schematic diagram of thermal conductivity measurement system for gas hydrate and freshwater ice.

Results of the measurement are shown in table 2 and figure 4 along with the value reported by Sloan (1990). Thermal conductivity of the Blake Ridge gas hydrate ranges between 0.553 and 0.314 W/(m·K) for temperatures between -30ºC and 10ºC. The conductivity values decrease with temperature from -30º to 0ºC, then abruptly increase by 0.2 W/(m·K) at 0ºC. This abrupt increase was probably caused by the release of liquid water; the higher thermal conductivity of water increased the thermal conductivity of the system.

Table 2: Results Of Measurements Of Thermal Conductivity Of Gas Hydrates Of Blake Ridge.

Temperature (° C)	Thermal conductivity (W/[m·K])
-30	0.553
-20	0.500

-15	0.476
-10	0.386
-5	0.350
0	0.523
5	0.422
10	0.314
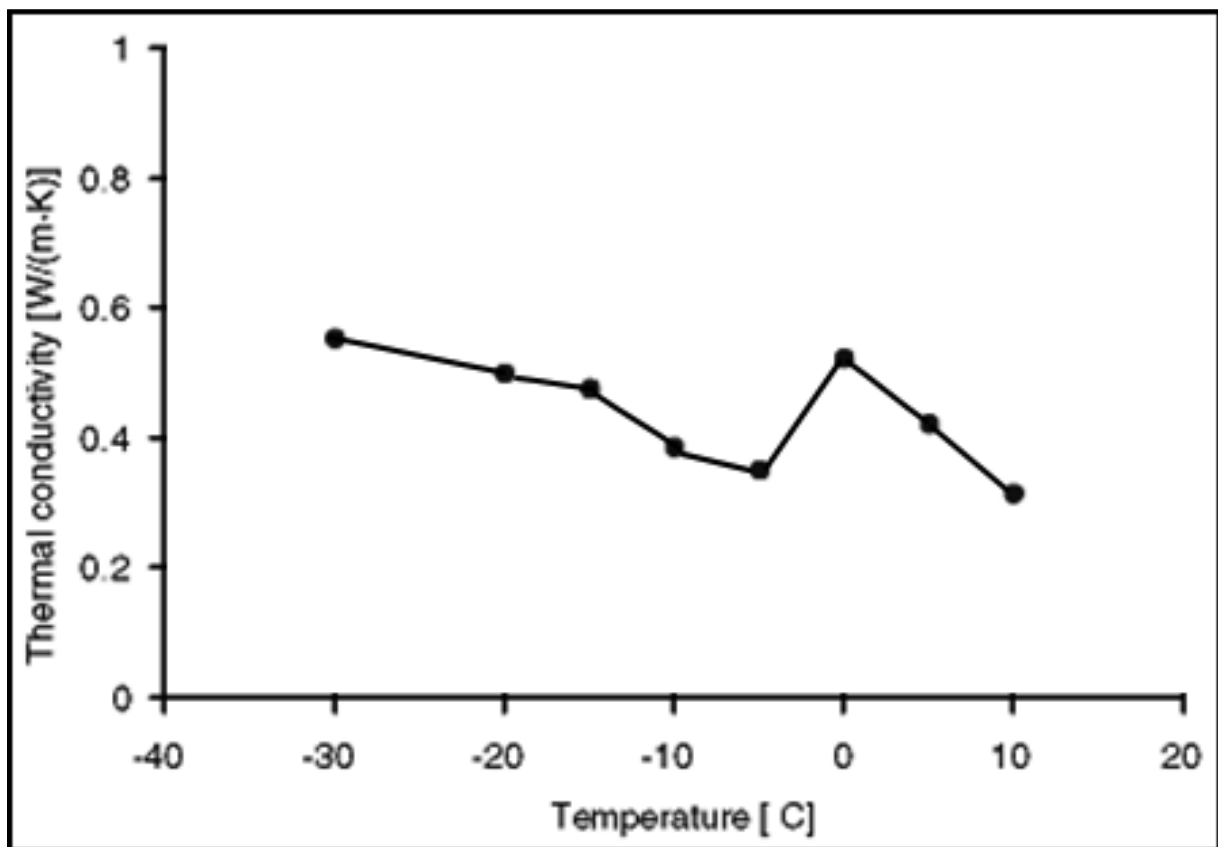
Figure 5: Relationship between thermal conductivity of gas hydrate and temperature.

Thermal diffusivity, κ: Because the thermal diffusivity of water is about half that of methane hydrate, hydrate-bearing sediment can change temperature more rapidly than water-bearing sediment. This characteristic presents a potential geohazard for petroleum production from deepwater production sites overlain by hydrate-bearing layers (fig.). If high-temperature hydrocarbons in the wellbore dissociate hydrate in the surrounding sediment, the strength of the sediment decreases, potentially causing well failure or localized submarine landslides.

Specific heat, c_p: Hydrate breakdown is an endothermic process, absorbing heat while the surrounding sediment cools. Because the specific heat of methane hydrates is about half that of water, hydrate-bearing sediment stores less heat which can then be made available to help fuel dissociation. When estimating the efficiency of hydrate dissociation, neglecting the reduced contribution of methane hydrates to the host sediment's specific heat results in an overestimate of the dissociation rate and, hence, the methane production rate.

International Journal of Research in Advent Technology

Available Online at: http://www.ijrat.org

Table 3: Equations for estimating thermal properties of methane gas hydrate (Waite and others, 2007).

Thermal property fit equations	
Temperature dependence ,(Pressure held at 31.5 MPa, 4,570 psi)	Temperature range
λ (W/m·K) = -(2.78 ± 0.05)·10^{-4}·T(°C) + (0.62 ± 0.02)	-20–17°C
*κ (m^2/s) = (5.04 ± 0.02)·10^{-5}/T(K) + (1.25 ± 0.05)·10^{-7}	1–17°C
	(274–290K)
cp (J/kg·K) = (6.1 ± 0.3)·T(°C) + (2,160 ± 100)	1–17°C
Pressure dependence(Temperature held at 14.4°C, 58°F)	
λ (W/m·K) = (2.54 ± 0.06)·10^{-4}·P(MPa) + (0.61 ± 0.02)	
κ (m^2/s) = (2.87 ± 0.08)·10^{-10}·P(MPa) + (3.1 ± 0.2)·10^{-7}	
cp (J/kg·K) = (3.30 ± 0.06)·P(MPa) + (2,140 ± 100)	

The T^{-1} dependence of the κ fit requires input temperatures in Kelvin

IV. EQUILIBRIUM DISSOCIATION EXPERIMENT

The pressure-temperature (P-T) stability conditions for the formation of methane hydrate have been determined on synthetic methane hydrate (e.g., Deaton and Frost, 1946; Yokoi et al., 1993); however, those of natural gas hydrate formed in marine sediments have not been measured, because natural gas hydrate samples have not been available for such an experiment. Considering that the environment of formation of natural gas hydrate is quite different from that of laboratory experiments, the P-T conditions for the three-phase equilibrium of natural gas hydrate may not be the same as that determined on synthetic gas hydrate.

One gas hydrate sample (Sample 164-997A-42X-3, 25-35 cm) was observed to contain a gray part and black part. The former was expected to contain gas and hydrate, and the latter one seemed to be mainly the host sediment. It is crucial for this experiment to develop the method to detect a slight increase in pressure caused by the dissociation of natural gas hydrate. Because the equipment used for this experiment was originally designed for synthesis of a large gas hydrate, the volume of the vessel was too big (630 mL) to detect the dissociation of a small amount of gas hydrate. Therefore, the volume of the vessel was reduced to 160 mL by putting stainless steel blocks inside). Consequently, the accuracy of temperature measurement was approximately ±0.5 K. The equilibrium conditions were obtained only by wrapping the gas hydrate sample in a vinyl bag
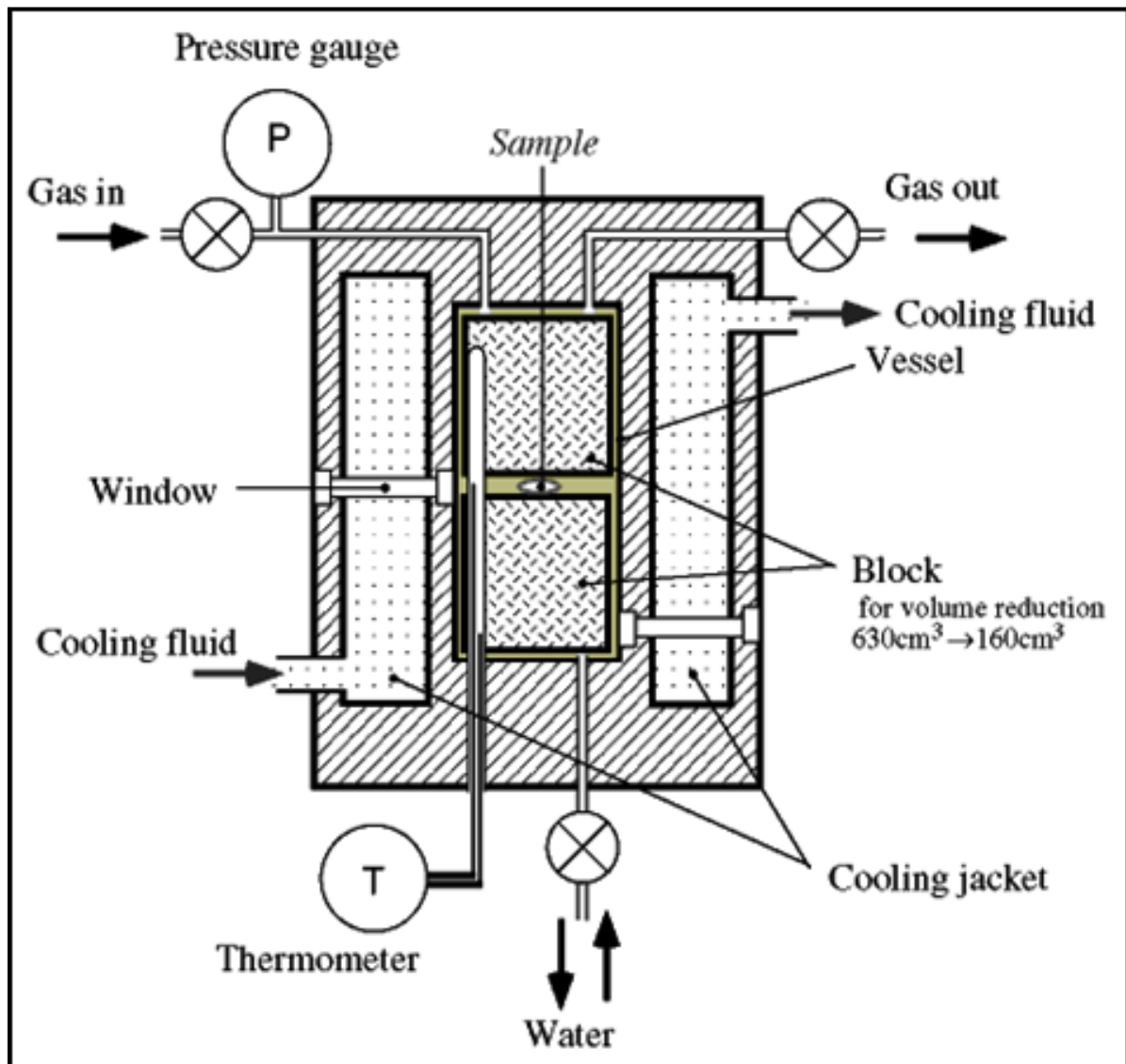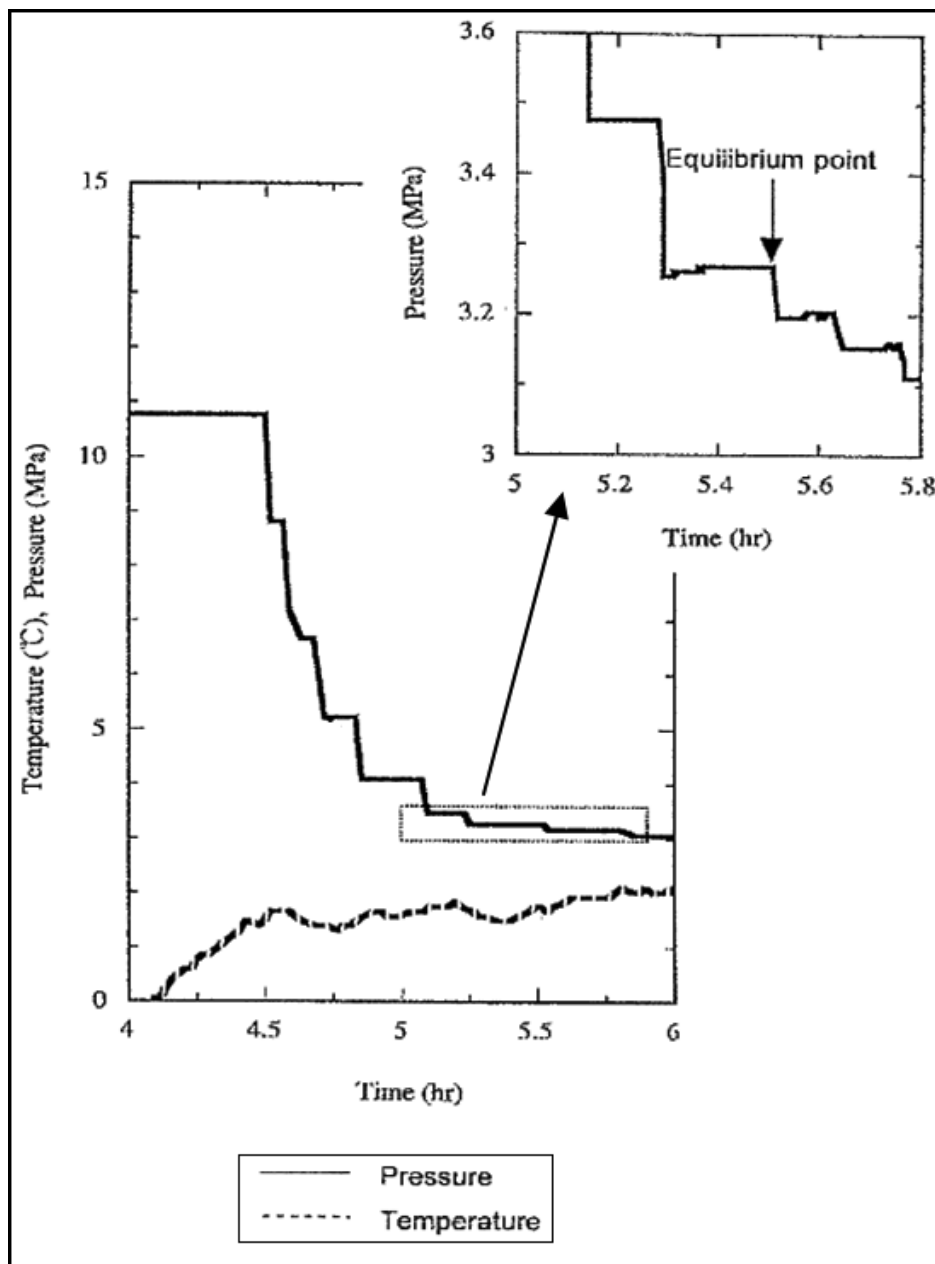
Figure 6: Equilibrium Dissociation Experiment

A 6.5 g of the frozen sample that consists of mixture of both a black part and a grey part was placed in a thin vinyl bag, and the bag was tightly sealed after the air in the bag was evacuated. The sample was placed in a pressure vessel and the remaining volume of the chamber was filled with nitrogen and water.

The temperature of the vessel was increased from 268 to 275 K by circulating coolant and the pressure was increased up to 11 MPa. This condition is well within the methane hydrate stability. Equilibrium dissociation was initiated by careful pressure release by 0.05 MPa steps at a temperature of 274.5- 275.0 K.Gas hydrate did not dissociate upon step-wise pressure release while the pressure was maintained within the stability condition. However, when the pressure decreased down to 3.25 MPa at a temperature of 274.5-274.8 K, a slight pressure recovery was recognized in a few minutes. This pressure increase is explained to reflect partial dissociation of gas hydrate. The pressure finally attained constant value of 3.27 MPa in 15 min. These P-T values (3.27 MPa and 274.7K) are considered to be a close approximation of the three-phase equilibrium conditions of the Blake Ridge gas hydrate.

Figure 7: Pressure and temperature change during gas hydrate dissociation experiment.
(Source : http://www-odp.tamu.edu/publications/164_SR/chap_02/ch2_f17.htm)

As shown in figure 6 the three-phase equilibrium condition of the Blake Ridge hydrate is almost the same as the equilibrium condition of pure methane hydrate in pure water, with an error of about 0.5 K. As documented by the discrepancy between BSR and BGHS, the apparent phase boundary condition of methane hydrate in the Blake Ridge sediment is a few degrees lower than that of the pure methane hydrate in pure water or in seawater; however, the three-phase equilibrium condition as determined on recovered solid methane hydrate samples does not greatly differ from the experimental data (e.g., Deaton and Frost, 1946).

International Journal of Research in Advent Technology
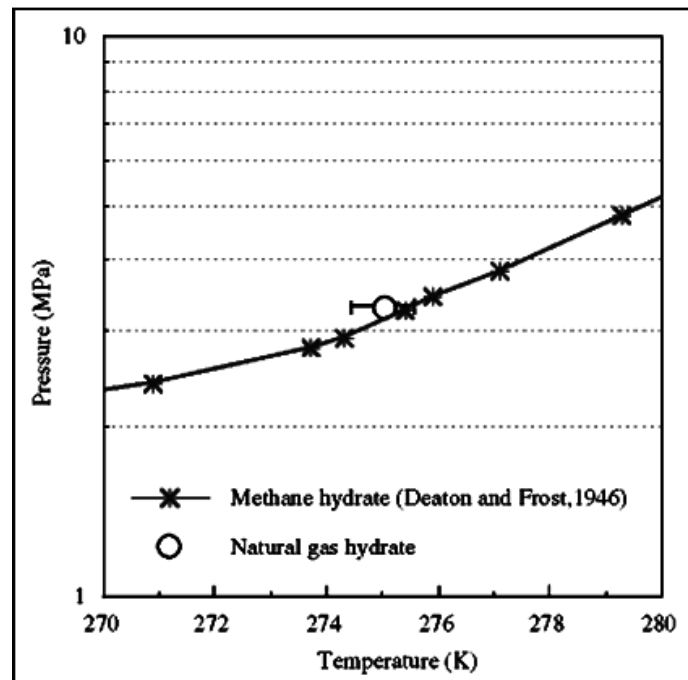
Figure 8: The P-T condition of equilibrium dissociation of the Blake Ridge gas hydrate plotted on the diagram of synthetic methane hydrate.

V. PHYSICAL PROPERTIES OF GAS HYDRATES

Table 4: Physical Properties of Hydrates and Ice (Source : Stephen Prensky, 1995)

Summary of published values for properties of ice and pure gas hydrates (modified from Davidson, 1983).		
Property	Ice	Hydrate
Dielectric constant at 273 K	94	=58
NMR rigid lattice 2nd moment of H_2O protons(G^2)	32	33 ± 2
Water molecule reorientation time at 273 K (µsec)	21	=10
Diffusional jump time of water molecules at 273 K (µsec)	2.7	>200
Isothermal Young's modulus at 268 K (10^9Pa)	9.5	=8.4
Speed of longitudianl sound at 273 K, velocity (km/sec), transit time (µsec/ft)	3.8 80	3.3 92
Velocity ratio Vp/Vs at 272 K	1.88	1.95
Poisson's ratio	0.33	=0.33
Bulk modulus (272 K)	8.8	5.6
Shear modulus (272 K)	3.9	2.4
Bulk density (gm/cm^3)	0.916	0.912
Adiabatic bulk compressibility at 273 K 10^{-11}Pa	12	=14
Thermal conductivity at 263 K (W/m-K)	2.23	0.49 ± 0.02

HAZARDS OF GAS HYDRATES

(1) Drilling into gas hydrate could result in sudden dissociation and hence collapse of sediment supporting the drill stem.

(2) Perturbations of the sea floor due to gas hydrate exploration could lead to tsunamis, large oceanic waves that bring catastrophic damage to low-lying coastal area.

(3) Methane released from gas hydrates could result in global warming and world climate change.

(4) Clogging of pipelines due to hydrate formation can also take place.

(5) Faults, fractures, earthquakes and submarine landslides pose danger to mankind.

(6) Methane gas is a greenhouse gas and has high heating effect and its release from hydrates into the atmosphere at expense of oxygen also endangers life.
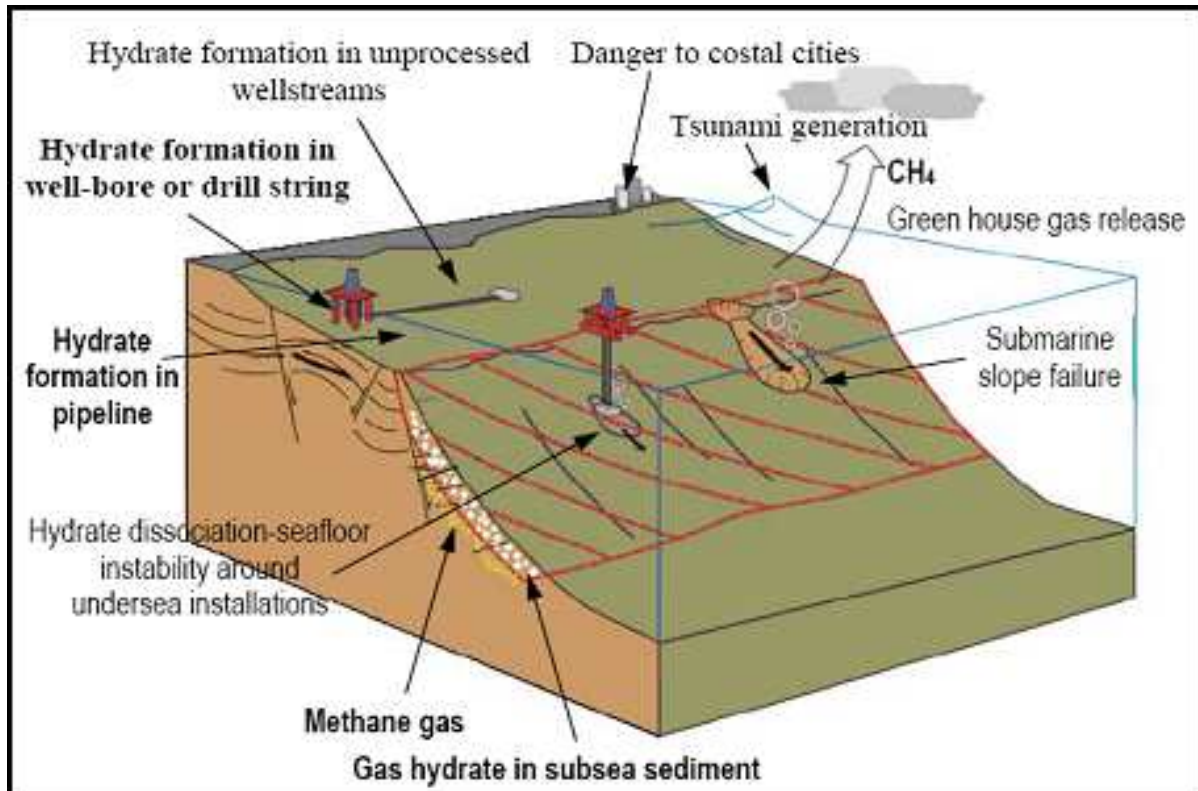

Figure 9: Hazards of Gas Hydrates

REFERENCES

[1] Gupta, H. K., et al., 1998. Analysis of single channel seismic data from the continental margins of India for exploration of gas hydrates. NGRI Technical Report, No. NGRI-98-LITHOS-221

[2] Hannumatha Rao, Y., Reddi, S. I., Khanna, R., Rao, T. G., Thakur, N. K., and Subrahmanyam, C., 1998. Potential distribution of methane hydrates along the Indian continental margins. Current Science, 74,466-468.

[3] Kvenvolden, K. A., 1998. A primer on the geological occurrence of gas hydrate. In Henriet, J. P. and Mienert, J. (eds) Gas hydrates: Relevance to the World Margin Stability and Climate Change. Geological Society, London, Special Publications, 137, 9-30.

[4] Velocities for hydrate-bearing sediments using weighted equation. Journal Geophysical Research, 101,2Q347-20358.

[5] Sain, K., Minshull, T. A., Singh, S. C., and Hobbs, R. W., 2000. Evidence for a thick free gas layer beneath the bottom-simulating reflector in the Makran accretionary prism. Marine Geology, 164,3-12.

[6] Masters C.D., Root D.H., Attanasi E.D. World resources of crude oil and natural gas. - Proceedings of the 3-th World Petroleum Congress, New York, 1991, pp.51-64.

[7] Ginsburg G.D., Soloviev V.A. Submarine gas hydrate estimation: theoretical and empirical approaches. - 27th Offshore Technology Conference, Houston, Texas, 1995, pp.513-518.

[8] MacDonald G.T. The future of methane as an energy resources. Annual Reviw of Energy, v.15, 1990, pp.53-83.

[9] McIver R.D. Gas hydrates. In: Meyer R.F., Olson J.C., eds., Long-term energy resources. Boston, Pitman, 1981, pp.713-726.

[10] Modelevsky M.S. Global resources of oil and gas. – Oil and Gas Geology, 5, 1989, p.51-55

[11] Soloviev V.A., Ginsburg G.D., Ivanova G.A. Submarinnoe gazogidratoobrazovanie i potentsial'nye gidratonosnye oblasti Mirovogo okeana (Submarine gas hydrate formation and gas hydrate prone regions of the Ocean), Report 903, VNIIOkeangeologia, St.Petersburg, 1988, 163 p. (in Russian).

[12] Harvey L.D., Huang Z. Evaluation of the potential impact of methane clathrate destabilization on future global warming. J.G.R., v.100, No.D2, 1995, pp.2905-2926

[13] Makogon Yu.F. Hydrates of Hydrocarbons. PenWell Books, 1997, 482 p.

[14] Kvenvolden K.A. Methane hydrate - a major reservoir of carbon in the shallow geosphere. - Chemical Geology, v.71, 1988, pp.41-51.

[15] Ecker, C., Dvorkin, J., and Nur, A., 1998. Sediments with gas hydrates: Internal structure from A YO. Geophysics, 63, 1659-1669.

[16] Trofimuk A.A., Cherskiy N.V., Tsarev V.P. The role of continental glaciation and hydrate formation on petroleum occurrences. In: Meyer R.F., ed., Future Supply of Nature-made Petroleum and Gas. New York, Pergamon Press, 1977, pp.919-926.

[17] Lee, M.W., Hutchinson, D.R., Collet, T.S. and Dillon, W.P., 1996. Seismic

[18]S loan, E.D., 1990. Clathrate Hydrate of Natural Gases, Marcel Dekker, New York.

[19] Makogon, Y.F., 2000. Geological and technology aspects of natural gas-hydrates. Proc. ofSPG-2000, New Delhi, India, Feb23-25, p.199-205.