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# Anton Bruun Memorial Lecture

# Gas-Hydrates – a Potential Source of Energy from the Oceans

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### ANTON FREDERICK BRUUN

ANTON FREDERICK BRUUN was born on the 14th of December 1901 as the oldest son of a farmer, but a severe attack of polio in his childhood led him to follow an academic, rather than agrarian, career. In 1926 Bruun received a Ph.D. in zoology, having several years earlier already started working for the Danish Fishery Research Institute. This association took him on cruises in the North Atlantic where he learned from such distinguished scientists as Johannes Schmidt, C.G. Johannes Petersen and Thomas Mortensen.

Of even more importance to his later activities was his participation in the *Dana* Expedition's circumnavigation of the world in 1928-1930, during which time he acquired further knowledge of marine animal life of the sea, general oceanography and techniques in oceanic research.

In the following years Bruun devoted most of his time to study the rich *Dana* collections and to the publication of his treatise on the flying fishes of the Atlantic. In 1938 he was named curator at the Zoological Museum of the University of Copenhagen and later also acted as lecturer in oceanology.

From 1945-1946 he was the leader of the *Atlantide* Expedition to the shelf areas of West Africa. This was followed by his eminent leadership of the *Galathea* Expedition in 1950-1952, which concentrated on the benthic fauna below 3,000 m and undertook the first exploration of the deep-sea trenches, revealing a special fauna to which he gave the name "hadal".

The last decade of Bruun's life was devoted to international oceanography. He was actively involved in the establishment of bodies like SCOR, IACOMS, IABO, and the IOC and was elected IOC's first chairman in 1961.

His untimely death a few months later, on 13 December 1961, put an end to many hopes and aspirations.

In 1962, the former US Presidential yacht *Williamsburg* was converted into a research vessel and renamed Anton Bruun in honour of the great scientist. The *Anton Bruun* took part in the International Indian Ocean Expedition (1959–1965) and, in the late 1960's, circumnavigated the globe in one of the last great exploratory expeditions of modern oceanography.

### THE BRUUN MEMORIAL LECTURES

This series of lectures is dedicated to the memory of the noted Danish oceanographer and first chairman of the Commission, Dr Anton Frederick Bruun. The "Anton Bruun Memorial Lectures" were established in accordance with Resolution 19 of the Sixth Session of the IOC Assembly, in which the Commission proposed that important inter-session developments be summarized by speakers in the fields of solid earth studies, physical and chemical oceanography and meteorology, and marine biology.

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Operational Oceanography — a perspective from the private sector by Ralph Rayner. IOC Bruun Memorial Lectures, Paris, UNESCO, 2003. (*Technical Series*, 58).

### TWENTIETH SESSION OF THE ASSEMBLY, 29 JUNE - 9 JULY 1999

Ocean Predictability, by John Woods. In: IOC Bruun Memorial Lectures, Paris, UNESCO, 2000. (*Technical Series*, 55).

### NINETEENTH SESSION OF THE ASSEMBLY, 2 - 18 JULY 1997

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# Gas-hydrates – a Potential Source of Energy from the Oceans

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Born on 28 June 1942 in Moradabad (U.P.), India, Dr Harsh Gupta had his education at the Indian School of Mines (B.Sc.(Hons), M.Sc. and A.I.S.M) and University of Roorkee (Ph.D.). Currently Dr Gupta is a Secretary to Government of India looking after the Department of Ocean Development. Among the important positions held earlier include Director, Centre for Earth Science Studies, Trivandrum (1982-87); Vice-Chancellor, Cochin University of Science & Technology (1987-90); Adviser, Department of Science & Technology, Govt. of India, New Delhi (1990-92) and Director, National Geophysical Research Institute, Hyderabad (1992-2001). Earlier he was a Research Scientist at the University of Texas at Dallas (1972-77) and an Adjunct Professor (1977-2001). Dr Gupta has published over 130 research papers in International Journals, written 3 pioneering books all published by Elsevier Scientific Publishing Company, Amsterdam and edited over 15 volumes.

Dr Harsh Gupta has been very deeply involved with investigations related to oceans. He has participated in the India Ocean Expedition Programme and in detailed investigations of regional crustal structure of the Bay of Bengal and Arabian Sea and later, as the Director, Centre for Earth Science Studies (1982-87), Trivandrum, pioneered efforts to generate wave atlas of the west coast of India.

He was the leader of the 3rd Indian Scientific Expedition to Antarctica (1983-84), which established a permanent base for India in a record time. This station fulfilled a very urgent scientific requirement of the country by setting up of a permanent seismic and a permanent GPS station.

In recent years, at the National Geophysical Research Institute, he has initiated work on Gas Hydrates in the Exclusive Economic Zone of India. Another landmark work by him in identifying locations where bottom simulating reflectors occur has helped in identifying zones of gas hydrate occurrences. Dr Gupta is internationally known. He is the founder President of the Asian Seismological Commission, Bureau Member of the International Union of Geodesy and Geophysics (IUGG) and Councillor of the International Union of Geological Sciences (IUGS). Earlier, he has been the Chairman of IASPEI/ UNESCO/ICL Working Group on Seismology and Related Sciences in Africa as well as Bureau Member and Chairman of several Committees of the International Lithosphere Programme.

Dr Gupta has been a visiting Professor at University of Paris Sud, Paris, France; University of Texas at Dallas, USA and University of Hamburg, Germany. He has also been a visiting scientist at US Geological Survey and Adviser/Consultant to UNESCO, IAEA and Commonwealth Science Council on several occasions. He is a Fellow of the Indian National Science Academy (INSA), National Academy of Science, Third World Academy of Sciences (TWAS) and several other academies.

# **NTRODUCTION**

Gas-hydrate, also known as clathrate, occurs worldwide in the oceanic and polar sediments where temperature is low enough and pressure is sufficiently high to crystallize the methane into gashydrates. The study of gas-hydrates has attracted the attention of the scientific community worldwide because of their widespread occurrences and potential energy content. It is estimated to be twice the amount of total fossil fuel energy reserves of world. **G**as-hydrates are ice-like crystals in which low molecular weight hydrocarbons (mainly methane) reside in cages of hydrogen-bonded water molecules (Fig.1) and are formed at elevated pressure and low temperature when gas concentration exceeds the solubility limit (Sloan, 1990; Kvenvolden, 1998). They occur worldwide in oceanic sediments of outer continental margins both active and passive; in deep water sediments of inland lakes and sea; and in polar sediments on continents and continental shelves. They are mostly confined to the shallow sediments where thermobarometric conditions are suitable for the existence of gas-hydrates. Gas-hydrates have attracted the attention of the scientific community because of their widespread distribution; potential as future energy resources; possible role in climate change and submarine geo-hazard; and their relationship with fluid flow in accretionary wedges.

**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.



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To meet the overwhelming demand of energy for a country like India, we look for an alternate source of energy. Gas-hydrates appear to be a good candidate as a clean fuel. A large amount of methane is stored in the vast deep-water regions of the Indian continental margins in the form of gas-hydrates and underlying free-gas. The estimated global reserves of methane locked in gas-hydrates are of the order of  $20x10^{15}$  and  $1x10^{13}$ cubic metre in the deep offshore and permafrost regions respectively (Kvenvolden, 1998). A total reserve of gas in the form of gas-hydrates and underlying 'free-gas' is estimated to be of the order of 40-120 trillion-metre cube in the Indian continental margins up to a water depth of 2,000 metres (Makogon, 2000). Since destabilization of gas-hydrates causes global warming and submarine geo-hazard, this nonconventional source of energy needs to be explored and exploited very systematically and properly without affecting the environment.

The presence of gas-hydrates over a large area can be detected efficiently by inexpensive seismic measurements. Associated with the base of gas-hydrates stability field is the bottom simulating reflector (BSR) that mimics the shape of seafloor and has large amplitude and opposite polarity compared to the seafloor reflection event (Fig.2). The presence of gas-hydrates is indicated in an area by mapping the BSR. Since the BSR is a physical boundary and not a lithological contact, it cuts across the underlying dipping strata. Blanking or reduction of amplitude on seismic section above the BSR can also be used as a marker for gas-hydrates. This may be employed to quantify hydrates. Care is to be taken whether the blanking is due to the cementation by hydrates or due to the homogeneity of lithology. For example, very good blanking in the Blake Ridge area (Shipley et al., 1979) should have produced very high seismic velocity. But the sonic log (Holbrook et al., 1996) exhibits moderate increase in seismic velocity against the background trend. It is therefore inferred that in the Blake Ridge area, the observed low energy in the seismic signals is due to homogenization of sediments, and the BSR is caused primarily due to the presence of free gas..

Pure hydrates have much higher seismic velocity and resistivity compared to the normal oceanic sediments within the stability zone. So, the presence of gas-hydrates above the BSR increases the seismic velocity or resistivity. The increase depends on the concentration and distribution of gas-hydrates. Whereas, even a small amount of 'free-gas' lying below the hydrated sediments decreases the velocity considerably (Fig.2). Therefore, the velocity function (derived from the traveltime tomography of the ocean bottom wide-angle seismic data or waveform inversion of multichannel or ocean bottom seismic data) and resistivity function (derived from the dipole-dipole resistivity sounding data) provides vital information for the quantitative assessment of gashydrates and/or 'free-gas'. A concerted effort is required to translate the velocity or resistivity 'buildup' against the background trend above the BSR in terms of concentration of gashydrates. The velocity 'drop' can be utilized to quantify the amount of 'free-gas' underlying the BSR.

The methane in gas-hydrates may be genetically related to biogenic or thermogenic origin. Methane hydrates in

continental margins are mostly biogenic due to very high organic carbon flux and sedimentation rate. Various mechanisms have been proposed for the formation of gashydrates (Sloan, 1990; Kvenvolden, 1993). One theory suggests that the gas-hydrates are part of pre-existing gases in reservoir. Another theory suggests that gas-hydrates are formed by upward migration of 'free-gas' in the zone of hydrate stability field.

An updated global inventory reports 77 places where the presence of gas-hydrates has been inferred from geophysical,

**Fig.2** Left: velocity 'increase ' in the hydrated sediments above the BSR and 'drop' in free-gas bearing sediments below, Right: BSR showing large amplitude, opposite polarity seismic event w.r.t seafloor reflection.



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geochemical and geological evidences, and natural gas-hydrates recovered from 19 places worldwide (Paul & Dillon, 2001). A special mention should be made of the Blake Ridge in the Atlantic Ocean of US continental margin and the Nankai Trough of the Japan continental margin (Henriet & Mienert, 1998; Ginsburg & Soloviev, 1998) where samples of gas-hydrates have actually been recovered during deep sea drilling programmes. Samples of gas-hydrates have also been recovered from the permafrost regions in the Messoyakha gas field of western Siberia, Lake Baikal (Makogon, 1981), Prudhoe Bay oil fields of Alaska (Collet et al., 1988) and more recently in the Mackenzie Delta of Canada (Dallimore et al., 1999).

Several offshore parameters like bathymetry, sediment thickness, rate of sedimentation, sea bottom temperature, total organic carbon content, etc. (Subrahmanium et al., 1999) indicate conducive environment for the formation of gas-hydrates in the shallow sediments in the vast continental margins of India. The Indian National Geophysical Research Institute (NGRI) has prepared a theoretical map of gas-hydrates stability field in the Indian offshore (Rao et al., 1998), which serves as a depth window within which features of gas-hydrates could be searched.

NGRI (Gupta et al., 1998) has visually scrutinized more than 50,000 line-km of single channel analog seismic records and indicated promising sites for the occurrences of gas-hydrates along the offshore regions of India (Fig.3).

Analysis of large offset Multi-Channel Seismic (MCS) and/or wide-angle ocean bottom seismic data will provide more



**Fig.3** BSR locations on the sediment thickness map in western (left) and eastern (right) offshore of India (Gupta et al., 1998).

detailed information about the identification and quantification of gas-hydrates and/or free-gas. Fig. 4 shows a clear structural image of BSR in the Makran accretionary prism (Arabian Sea) with its aerial extent derived from MCS data using the advanced seismic data processing software. To provide very accurate velocity variation across the BSR, Sain et al. (2000) applied a sophisticated waveform inversion to the seismic data at two Common Depth Point (CDP) locations, namely CDP 4375 and CDP 4400. The results reveal an unusually thick 'free-gas' zone (~200-350 m) underlain by ~160 m thick hydrated sediments, comparable only to the sonic log results of Ocean Drilling Programme (ODP) leg 164 at Blake Ridge sites (Holbrook et al., 1996). It is estimated that the reserves from the Blake Ridge area alone can meet the natural gas requirement of the whole USA for the next 300 years. This implies the tremendous energy potential of gas-hydrates.

**Fig.4** Full waveform inversion results at CDPs 4375 and 4400, (b) Seismic section for the Makran accretionary prism (Sain et al., 2000).



Concerted efforts are required to acquire, process and interpret new seismic data; generate drillable prospects; test and assess the amount of gas-hydrates and 'free-gas'; establish recovery mechanism; develop plan for commercial production and transportation, etc.

# **FUTURE OF EXPLORATION AND EXPLOITATION**

Till date not much is known about the nature and distribution of gas-hydrates. No suitable technique is available for quantitative assessment of gas-hydrates. It is felt necessary to carry out various geological, geochemical and geophysical analyses systematically for the identification and quantification of gashydrates for evaluating the resource potential. Here are described some of the important studies and techniques to demarcate the zones of gas-hydrate occurrences and to quantify the amount of gashydrates and the underlying free-gas. Standard processing of MCS data can produce clear structural image of BSR without any reliable velocity information. Whereas traveltime tomography of first arrivals and wide-angle reflection from BSR acquired by ocean bottom seismometers gives a good velocity image with poor structural information. A simultaneous use of MCS and wide-angle seismic data (Katzman et al., 1994; Korenaga et al., 1997) produces a 2-D or 3-D average velocity model that describes the BSR configuration along with the velocity variation within the hydrated sediments. Since the BSR is a good conversion point, converted waves recorded by ocean bottom seismometers (OBS) also provide good constraint on the depth of BSR. The traveltime tomography of wide-angle ocean bottom seismic (both P- and S-wave) data is a powerful tool to delineate 2-D and/or 3-D velocity structure, and hence to demarcate the prospective zones of gas-hydrates and/or 'free-gas' bearing formation. The detailed velocity tomogrammes also reveal features such as faults that help in understanding the tectonic processes for the accumulation of gas in a particular geological set up, and hence to understand the mechanism for the formation of gas-hydrates.

The nature of distribution of gas-hydrates in the pore spaces of sediments is not fully understood. Two end-member models of gas-hydrate distribution are: (i) non-contact model in which hydrates are located in the pore voids without appreciable grain contacts; and (ii) contact model in which hydrates are connected and surround the grains as shown in the bottom part of Fig.5. Based on modelling using rock-physics, Ecker et al. (1998) and Carcione & Trinivella (2000) showed that the

ratio of P-wave and S-wave seismic velocity above the BSR to that below the BSR for the above two models vary with gashydrate saturation in completely different ways (Fig.5). So, both P- and S-waves seismic data are required to understand the nature of distribution of hydrates, and thus four-component (4-C) OBS data acquisition is very much required for quantitative assessment of gas-hydrates and/or 'free-gas'.

BSRs, being strongly reflective, and with high stratigraphy, pose problem in exploring deeper layers from the conventionally acquired MCS data. This is similar to the problem encountered in imaging subvolcanic Mesozoic sediments, which can be alleviated by using wide-angle seismic data (Jarchow et al., 1994; Sain et al., 2002). Therefore, OBS data play an important role in delineating the structure lying below the BSR. In order to improve the seismic image, pre-stack depth migration (Kirchoff method) of seismic data can be performed using the obtained velocity field derived from the OBS data.

Reflection coefficient or amplitude versus offset (AVO) or angle modelling of large-offset seismic data is a powerful tool to understand the origin of BSR whether it is caused by hydrated sediments underlain by water saturated sediments or by partially hydrated sediments underlain by free-gas. Theoretical analysis (Carcione and Tinivella, 2000) indicates that the increase of free-gas saturation causes an increase in the near vertical negative reflection coefficients for a given concentration of gas-hydrates, and the negative values of reflection coefficients increase with increasing angles for non-contact model (Fig.6). For a given gas saturation, the normal incidence

**Fig.5** The ratio of P-wave velocity above the BSR to that below the BSR (light line), and of S-wave velocity above the BSR to that below the BSR (dark line) versus gas-hydrates saturation, and for two (left: contact and right: non-contact) end member deposition models (Ecker et al., 1998).



**Fig.6** Computed reflection coefficients from BSR for various concentrations of gas-hydrates of three fixed saturations of free-gas for contact (left) and non-contact models (Carcione and Tinivella, 2000).



reflection coefficients increase with the increase in concentration of gas-hydrates (Castagna and Swan, 1997). Analysis of AVO helps to understand the nature of distribution of gas-hydrates and/or free-gas.

BSR, in most low-frequency seismic sections, is a single negative pulse, almost the mirror image of the seafloor reflection event. This attribute may be useful in identifying BSR in western margins of India where bedding planes are parallel. The BSR reflection coefficient at vertical incidence decreases with increasing frequency. The frequency dependence of BSR amplitude is due to the BSR having a gradational velocity contrast with depth. If the thickness is less than one wavelength, the boundary appears as a sharp interface, but if the thickness is more than one wavelength, the boundary is observed as gradational. A thin gas layer may have a distinctive AVO frequency response. Such studies are important in determining the thickness of the gas-layer and concentrations.

Sophisticated waveform inversion of seismic data is a powerful tool to extract very accurate velocity variation across a BSR including the delineation of thin layers in which gas-hydrates and/or 'free-gas' naturally occur in the shallow sediments of outer continental margins and polar regions. There is a strong need to develop a 2-D waveform inversion of ocean bottom wide-angle seismic data to delineate the spatial distribution of gas-hydrates and/or 'free-gas' in a potential area.

Due to lack of precise relationship between seismic velocities of hydrated sediments and hydrates content, translation of velocity

increase and/or drop against the background trend in terms of concentration of hydrates and/or saturation of 'free-gas' has been a difficult task. To establish a theory between seismic velocities and concentration of hydrates in a porous medium, and its validation from the available drilled data is urgently required. Mostly, the three-phase time average semi-empirical relation (Lee et al., 1996) is used for quantification of gas-hydrates and/or free-gas, which cannot take into account the effects of anisotropy and sediment microstructures (nature of hydrate distribution in pore voids). Another problem of using this relation is that it cannot predict the S-wave velocity. As the effective medium theory (Jakobsen et al., 2000) has the potential to include all these effects and is capable of computing complete stiffness tensor for a transversely isotropic composite with several solid phases, pore water and gas, the theory can be invoked for a quantitative assessment of gashydrates and free-gas.

Deep towed acoustic/geophysics system (DTAGS) provides a very high resolution image and layer velocities that may result in improved structural detail of BSR (Rowe & Gettrust, 1993), and helps to understand the migration path of fluid flow.

To know the genesis of gas-hydrates, geochemical methods provide supplementary information. The molecular composition of hydrocarbon gases and isotropic composition of methane can distinguish between biogenic and thermogenic origin of gas-hydrates. Higher ratio of methane to higher molecular weight hydrocarbons or low concentration of  $\delta$ C13 indicate biogenic origin of methane. Generally, hydrate-BSR is formed where some processes (such as tectonic uplift, a change in bottom-water temperature or ongoing rapid sedimentation) have disturbed the thermal structure and caused the phase boundary to move upward relative to the sediments. Hydrates might, therefore, be present at places where no BSR (prime indicator of gas-hydrates) is observed on seismic section, but found while drilling.

An example is the Northern Cascadia margin. If a precise relationship between the hydrate saturation and seismic velocity can be defined for a given sediment type, then determination of seismic velocity may allow the detection and quantification of hydrates without the BSR. For this purpose, the seismic data should be of very large offset with respect to seafloor depth. Substantial amount of gas-hydrates has been found by drilling in Cascadia margin where no clear BSR was mapped. In the Bering Sea area, BSR is caused by 'diagenetic alteration of diatomaceous deposits' and on drilling, no gashydrates were found.

Since well-bedded sediments reduce the permeability compared to the deformed accreted sediments, inhibiting vertical fluid and methane flow, hydrates may be present in well-bedded slope basins. Alternatively, hydrates may be present but tectonic subsidence and sediment deposition in the basin slope results in downward movement of the base of the stability field. Detailed seismic interval velocity data and seafloor electrical resistivity data suggest that hydrates indeed may be present above the base of stability field. A new technique of dipoledipole electrical profiling system (consisting of a single transmitter and a series of electrical receivers, towed on the sedimented floor) developed by the University of Toronto can be useful to obtain resistivity-depth information. The high resistivity anomaly compared to the background indicates the presence of gas-hydrates.

Globally, gas hydrates occur at tectonically active margins. Therefore, geophysical data like gravity and magnetic surveys may help to indicate the geological areas suitable for gashydrates exploration using seismics.

Study of gravity coring up to sufficient core-length and water samples are useful proxies for gas-hydrates – values of total organic carbon (TOC) in % and analysis of absorbed gas into lighter to higher hydrocarbon are proxies for gas-hydrates. Carbon isotopic study of methane contained in the samples indicate origin of methane either biogenic or thermogenic. Reduction of salinity (or chloride anomaly) in the pore water extracted from portions of core against the value in normal seawater is another proxy for the occurrences of gas-hydrates. The microbial study — cell count of methanotropic, sulphate and nitrate reducing bacteria isolated from sea sediment samples — is a measure of bacterial activity of these three indicator microbes.

There exists a strong lithological control on gas-hydrate occurrences as evidenced by well log interpretations and core samples in the Malik well of the Mkenzie Delta. It is observed that gas-hydrates occurred within coarse grained, sandy sediments that were typically interbedded with non-hydrates or very low gas-hydrates content, fine grained silty sediments (Dallimore et al., 1999).

Commercial production of gas from gas-hydrates lying in the deep-water regions is a distant prospect and is not expected in the near future, as the exploitation technology is far from established. Basically, three methods can be considered: (i) thermal stimulation in which the temperature is increased through heating so that hydrates break into water and gas and the gas is recovered; (ii) depressurization in which the pressure is lowered by pumping out gas at the base of the hydrate that causes dissociation of hydrates into gas; and (iii) inhibitor injection where a dissociating agent like methanol is injected into the hydrated sediments that leads to the destabilization and releases gas from hydrates (Holder et al., 1984). With the fast growth of the technology, it is expected that the technique for commercial production of methane from below the gas-hydrates will be developed soon.

Gas from the Messoyakha gas-hydrates field in Western Siberia in the permafrost region has been exploited commercially (Makogon, 1981). Similar strategies can be adapted to the marine environment.

# **CONCLUSIONS & REFERENCES**

Identification and quantification of gas-hydrates and/or 'freegas' in the shallow sediments of outer continental margins have many important implications on economy, environment and thermal modelling. The most important implication of studying gas-hydrates is its economic aspect as a tremendous amount of energy is stored within and below the hydrated sediments. The energy content is estimated to be twice the amount of total fossil fuel reserves. As methane is a greenhouse gas, release of the same from the dis-association of the gas-hydrates may cause global-warming. Hence exploration and quantification of gashydrates are very much required for evaluating the resource potential and hazard assessment. Proper exploitation of methane at one hand can meet the ever-increasing demand of energy and on the other hand will reduce the environmental and submarine geo-hazard. As the depth of BSR depends on pressure-temperature conditions, mapping of BSRs over the continental margins also helps in preparing a heat flow map or to derive thermal structure without any well data. There are several technical problems in extracting and producing gas from gas-hydrates at this moment. There is a strong need to prepare suitable strategies to assess the resource potential before exploitation. A concerted effort is required to study the gas-hydrates in a scientific manner systematically, and efforts in this direction are on throughout the world.

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