

## Oceanic methane hydrates: Untapped fossil-fuel reservoirs

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Years ago, oil explorers had only a superficial idea about the existence of a solid form of natural gas known as methane hydrate, and much less, about its geological mode of occurrence. Prospectors came to know about its existence in the 1930s, their natural occurrence was first noticed in Siberian gas field in the 1960s and in other regions of oceanic and terrestrial environment, by the 1970s. Thanks to intensive explorations undertaken by oceanographers and oil geologists, during the last ten years, many occurrences around the world have come to light. Today, hydrate reserves are supposed to hold more fossil fuel energy than is present in conventional oil, gas and coal deposits.

Methane ( $\text{CH}_4$ ), the most common form of natural gas associated with petroleum deposits, is gaseous at room temperature and atmospheric pressure but under high pressure (>50 atmospheres) and low temperature (<7°C), it combines with water molecules to form an icy-white compound called methane hydrate  $\text{H}_4 \cdot 5.75 \text{H}_2\text{O}$  (also called methane clathrate hydrate). In nature, such high pressure and low temperature conditions are prevalent in areas of permafrost (both offshore and onshore) and ~30–~2000 m beneath sea floors (300–500 m below sea-level), on the outer continental margins and shelves<sup>1,2</sup>, depending upon the surface temperature of the ocean in the region. While this forms the upper limit, the stable lower limit for the hydrates is controlled by the geothermal gradient. The latter increases with depth, where the hydrate becomes unstable, dissociates and accumulates as free gas. According to K. A. Kvenvolden<sup>3,4</sup> of US Geological Survey, methane-to-water ratio is 1:6, in an ideally saturated compound, and its stability is governed by prevailing interrelation among temperature, pressure and composition (presence of other gases and impurities in water).

The origin of methane gas is not clearly known, though it is believed to be essentially due to microbial reduction of carbon dioxide derived from

organic matter that got buried along with sediments in many of the off-shore basins. This view is supported by molecular composition of the hydrocarbon gases and isotopic ( $\delta^{13}\text{C}$ ) composition of methane. Also, when such organic matter gets buried to greater depths and experiences higher temperatures in the range 80°–150°C, it gets transformed to gaseous hydrocarbon<sup>5</sup>, a thermogenic type.

The conversion of methane to methane hydrate is believed to take place during sedimentation within the hydrate stability zone; as the hydrate layer thickens and deepens, its bottom inevitably subsides into higher temperature zone where the hydrate becomes unstable and dissociates into gas. Conversely, ascending pore fluids may supply gaseous methane (believed to be mostly thermogenic) for hydrate formation, as they pass through hydrate stability region<sup>6,7</sup>. These methane hydrates are believed to be the motherlode of hydrocarbon deposits and current estimates consider them vast enough to constitute the largest untapped natural gas reserves on Earth. The considerable amount of methane that can be contained within clathrate structures, combined with their vast geographical distribution in shallow subsurface depths, often trapping reservoirs of free-gas below, are factors in favour of the economic exploitation of these gas hydrates.

Marine sediments, thousands of meters under water, contain most of the known occurrences of methane hydrate and good deposits have been identified along the coasts of many countries (Table 1). In India, the east coast in particular, offers great potential for hydrate deposits in the Bay of Bengal, where gas has been struck along the Andhra Pradesh coastal margin. In Siberia, Alaska and Canada, they are known to occur below permanently frozen ice (permafrost). If gas hydrates have not been exploited so far, it is because they decompose during recovery of the drill cores eluding evaluation, a prerequisite for any economic exploitation. Also, since they occur under high

pressure, the risk of damaging drilling equipment while drilling through must have desisted petroleum explorers from hydrate-prospecting for a long time. Such hazards in drilling pressurized pockets were soon overcome by adopting slow drilling under carefully controlled mud-weight and temperature<sup>4</sup>. Further, the success of the International Ocean Drilling Programme (ODP) in safely drilling through pressurized pockets of hydrate fields, soon encouraged systematic prospecting and development of techniques for hydrocarbon recovery to enable proper evaluation. A few countries have even ventured now to exploit their hydrate deposits by depressurizing and elevating their temperature by hot water circulation.

Geophysical methods employed in identifying and delineating the hydrate deposits include wire line well logs in combination with seismic data, caliper, gamma ray, spontaneous potential, resistivity, neutron porosity and a widely employed acoustic technique whereby the undersea hydrate/gas phase transition is demarcated by seismic reflections. The latter boundary usually parallels the sea-floor bottom topography and hence this technique is referred to as bottom simulating reflector or BSR<sup>4</sup>. Detection of deposits using BSR has been an established procedure during the early periods of prospecting, but this was felt inadequate for quantitative estimation, particularly in spotting deposits within sediments which sometimes lack a reflective layer. According to Ian R. MacDonald<sup>8</sup> at the College of Geosciences, Texas A&M University, the pitfalls in mapping and estimating reserves may result from the following: (1) Difficulties in determining how much methane, free or as hydrate will produce the detectable reflection; (2) Hydrates brought up for study often dissociate and calculations of their concentrations prior to their dissociation is not easy; (3) BSR-like seismic signatures are also produced by sediments having no connection to hydrate; (4) Most BSRs are higher up than the theoretical depth of phase boundary or in other words the

Table 1. Gas hydrate locations (Source: ref. 4)

Country	Type	Location
USA	Oceanic	Gulf of Mexico, Blake Ridge promontory off SE coast, Eel River basin off California, Continental ridge off eastern coast.
	Continental	North slopes, off Alaska.
Canada	Oceanic	Beaufort Sea, Labrador Shelf, Sverdup Basin.
	Continental	Makenzie Delta, Arctic Islands.
USSR	Oceanic	Black Sea, Caspian Sea
	Continental	Timan-Pechora Province, NE & E Siberian Coast, Kamchatka.
Norway	Oceanic	Continental slope of western coast.
Costa Rica	Oceanic	
Nicaragua	Oceanic	Middle American Trench
Guatemala	Oceanic	
Mexico	Oceanic	
Barbados	Oceanic	Barbados Ridge Complex
Panama and Columbia	Oceanic	Pacific area off Panama, Colombian basin.
Peru	Oceanic	Peru-Chile trench.
Japan	Oceanic	Nankai trough.
Australia	Oceanic	Timor trough.
New Zealand	Oceanic	Hikurangi trough.
Australia	Oceanic	Wilkes Land margin and Western Ross Sea.
SW Africa	Oceanic	Continental slope of SW Africa.
Oman	Oceanic	Makran margin, Gulf of Oman.
India	Oceanic	Off east coast (Bay of Bengal).

deposits could have formed deeper than where it is actually found, if they had migrated; (5) Calculations assuming uniform hydrate distribution over the entire area, may lead to unreliable estimation; also, methane contents in methane hydrate are variable and controlled by clathrate geometry; for example, shallow reservoirs (<1.5 km below) carry more methane per unit volume than can be contained as free gas in the same space<sup>3</sup>.

The ambiguities in estimation of hydrate deposits by BSR technique are illustrated in one of the recent explorations undertaken in the Atlantic Ocean, 350 km off the South Carolina coast of the United States along a submerged promontory called Blake Ridge<sup>2</sup>. This is a sediment drift deposit on the continental rise of North America. Steven Holbrook and colleagues (Woodhole Oceanographic Institution, USA), using seismic reflection techniques (BSR) identified at depths of 2800 m below

sea-level, a layer of gas hydrate and thicker layer of free gas immediately below. Vertical seismic velocity data in a series of holes made at this site have revealed that hydrate fills up to 7% of pore volume in hydrate layer and, free gas 1% beneath<sup>2</sup> and they estimated a reserve of 30 billion tons of methane hydrate over an area of 100,000 km<sup>2</sup>. However, Gerald Dickens<sup>9</sup> (formerly of University of Michigan) and his colleagues took direct measurements of sample using specially-developed pressure core sampler (PCS). This device can recover 1320 cc cylindrical sediment at *in situ* pressure for later laboratory study under controlled condition without disturbing the original concentration. They found that hydrate occupies much larger volume – up to 9% and, gas 12% of pore volume. Their calculations for Blake Ridge deposit of hydrate and free gas spread over 26,000 km<sup>2</sup> gave a figure of  $4.7 \times 10^{16}$  g

CH<sub>4</sub> which is about three times the earlier estimates by Holbrook *et al.*<sup>2</sup>.

During the last few years, surveys using bottom-simulating reflections have located a number of potential sites around the world and these new finds should swell the global estimate of gas hydrate and associated free gas resources<sup>3,10</sup>. While, indeed, these hydrocarbons appear to hold great promise as an alternate energy source, the technological problems in their production at reasonable market price overcoming the geological hazards like the uncontrolled gas release or site subsidence may prove to be serious obstacles, at least for some time to come. In this connection, the present global concern to restrict release into atmosphere climate damaging 'green-house' gases, like methane, is a serious aspect to be noted and future attempts to exploit the hydrate deposits should have suitable safeguards.

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