part 1

Hydrates Everywhere

Hydrates are everywhere. Indeed we eat lots of them in the form of carbohydrates as in sugar and starch as found in fruit, vegetables and cereals.

Methane hydrate is different because methane is held inside the lattice of the molecular structure of water in the proportion of 1/5.75. It is also known as clathrates from the Latin word for lattice. Methane hydrate can occur in a high-pressure environment as found in gas pipelines or oceanic sediments. When broken down, one unit volume of hydrate gives a 150 units of methane and 0.85 of water.

The study of hydrate has a long history. H. Davy discovered it in 1811, and M. Faraday established the chemical formula of hydrate of chlorine in 1823. During the 1930s several gas pipelines were put into operation in cold climates, and it was found that methane hydrate than ice formed in them, clogging the flow.

Methane hydrates were found in Siberia in 1964, and it was reported that they were being produced in the Messoyakha Field from 1970 to 1978. They were also reported in the Mackenzie delta (Bily 1974) and on the North Slope of Alaska (Collett 1983).

Oceanic Surveys

The Deep Sea Drilling Program (DSDP), which was extended in 1985 as the Ocean Drilling Program (ODP), stimulated an interest in hydrates. Russian research suggested that they could occur at a depth of a few hundred meters below the seabed in deep water areas. Geophysicists simultaneously identified what was known as the Bottom Simulating Reflector (BSR) on deepwater seismic surveys (Markl 1970, Shipley 1979). It was soon assumed that the BSR marked the occurrence of hydrates, trapping free gas below, and several Joides sites were designed to investigate them. These sites were planned by universities not oilmen, although the latter were called in to advise on safety on the PPSP panel (I was one of them during the first half of the 80s). A total of 625 sites were drilled by the Glomar Challenger between 1963 and 1983 under the auspices of the DSDP, (see Figure 1), but it was ruled not to drill through the BSR to avoid any blow out.

Figure 1
and a further 500 sites have been drilled up to now by the drillship Joides Resolution (see Figure 2).

Figure 2
Together, these programs have investigated a large number of sites in water depths up to 7000 m, the average being 3500 m. The ODP program concentrated in shallower waters but took more cores and, thanks to a safer drillship, penetrated the BSR. The details are as follows:

<table>
<thead>
<tr>
<th>legs</th>
<th>number</th>
<th>average water depth (m)</th>
<th>cores number</th>
<th>core/hole</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSDP 1968-1983</td>
<td>1-96</td>
<td>1092</td>
<td>3527 m</td>
<td>92</td>
</tr>
<tr>
<td>ODP 1985-1998</td>
<td>100-177</td>
<td>1247</td>
<td>2624 m</td>
<td>161</td>
</tr>
</tbody>
</table>

Together, as much as 250 km of cores have been recovered with an average recovery of about 60%. Accordingly, it can be said that the first few hundred meters of the seabed in oceanic areas, covering some 360 M.km² have been thoroughly explored. Continental shelves and the Slope (200-3000 m) cover respectively 7.5 and 15 percent of the oceanic area, together comprising some 80 M.km²

Publications

The cynic might say that the study of hydrates is tailor made for academic research insofar it can continue for a very long time.
long time without providing conclusive evidence. It is furthermore a wide subject covering such matters as fuel resources, transport, environmental hazards, global warming, turbidites formation, submarine slides and eruptions, drilling hazards, and even the Bermuda triangle mystery. One of the reasons for the inconclusive results is that hydrates decompose into water and methane on being brought to the surface so it is difficult to study them in their original state.

Literally hundreds of papers have been written, with some authors contributing in abundance, but they are characterized by generalizations, speculations, quotations and references, rarely supported by useful facts. In fact, many such papers are designed to attract funding for still further research, often repeating what has already been done.

The Blake Ridge investigations are a case in point. It commenced with Leg 11 (Sites 102, 103 and 104). Then Leg 76 allegedly found hydrate at Site 533, followed up by Leg 164. A new 3D seismic survey is now proposed to reinvestigate the area. Also, the JNOC program will drill this fall a borehole in 950 m of water in the Nankai Trough, which was already investigated by Leg 87 with the BSR and no sign of hydrates. The research goes on and on but never seems to deliver a concrete answer.

On land in permafrost, Ginsburg, the Russian expert, disputed in 1993 the claims that the Messoyakha Field was producing natural hydrates, as quoted in US papers. The 1974 paper on hydrates in the MacKenzie Delta reported that they were interbedded with gas and water, especially in borehole Mallik L-38. Another borehole at the same site was drilled in 1998 finding hydrates between 897 and 1110 m beneath the base of the permafrost at 640 m. It confirmed the early report, adding nothing new, outside cores. But it is interesting to investigate the difference between land hydrates and oceanic hydrates.

Papers commonly state that it is impossible to assess the size of hydrate resources, but then go on to make estimates based on uncertain parameters to several significant digits. Previously it was assumed that the porosity in the oceanic hydrate sequences were almost completely filled by hydrate, but then Leg 164 found that only 1-2% were filled. The range of uncertainty is very great.

The Department of Energy supported research from 1982 to 1991 to develop a full understanding of hydrates, which resulted in establishing the presence of hydrates in Alaska; studies of fifteen offshore hydrate basins; development of production models for de-pressuring and thermal extraction and development of a Test Lab Instrument.

This funding ceased in 1992, but work continued through a number of other institutions, including the USGS. Still another project has now been unveiled 1998 by the US Department of Energy - Office of Fossil Fuels (DOE/FE-0378), with identical objectives of 1982.

The research goes ever onward but seems incapable of answering the basic questions. A sort of momentum is propelled by many vested interests who have staked their reputations on the elusive hydrate.

Direct evidence of hydrates from cores

It is reasonable to expect that the many thousands of boreholes that have been drilled and cored in the oceanic seabed would have encountered ample indications of hydrates. But in fact there are only three major known occurrences of massive hydrates:

- 14 cm at Site 498 (Leg 67 Guatemala)
- 105 cm were recovered at Site 570 (Leg 84 Guatemala not far from an exploratory well) but hydrate was not expected as there was no BSR. On logs the body is 3-4 m thick with an unknown extent as there is no corresponding seismic reflection.
- 5-7-14 cm at Site 997A (Leg 164 Blake Ridge), but no hydrates were found at same depth 20 m away at Site 997B

Massive hydrates are connected with faults and the presence of a deep source of methane.
At many sites where hydrates were found, they consist of a few dispersed grains or thin laminae, which are interpreted as biogenic, resulting from microbial methane production.

Ginsburg has widely sampled the seabed off Russia, finding numerous hydrate occurrences in millimeter to centimeter thick layers. Photographs of these occurrences are often used to illustrate hydrates as in Figure 4 (from 708 meters in the Sea of Okhostsk, Ginsburg, 1993)

**Figure 3:** see Offshore August page 140

So the truth is that there is no evidence from all the worldwide research and extensive coring for any massive hydrate deposits. Undeterred by this negative evidence, the hydrate proponents are forced to seek indirect evidence.

**Proxy (indirect) evidence of hydrates**

They find it in abundance from a great variety of angles, including gas analysis: the gas from the Pressure Core Sampler (PCS) being assumed to come from hydrates; water analysis: interstitial water chloride being assumed to correlate with hydrates; seismic analysis: the BSR being assumed to come from hydrates and/or freegas; log analysis: resistivity and density being assumed to infer hydrates.

**BSR (bottom simulating reflector)**

As already mentioned, the so-called BSR event typically occurs at a depth of between 200 and 600 m beneath the seabed reflector, which it parallels, cutting across other reflectors. It has been interpreted as the base of the zone at which hydrates form. Theoretically it deepens with water depth. The "BSR" reflector has been variously explained as being due to the higher velocity of hydrates or to the velocity contrast been hydrates and free gas or the free gas only.

There are discrepancies between velocities given by VSP (recorded with a geophone in the well) which is not very accurate and the Sonic log which is commonly disturbed by cavings (as most of the calipers shows that the diameter very often exceeds the maximum range of the caliper).

Velocities of Leg 164 are a good example of poor quality and disagreements between VSP, Sonic and seismic surveys. Site 994 was drilled at a location lacking BSR but close to Sites 995 and 997 with strong BSR. The three holes are similar and it is difficult to explain why the BSR dissapears and to calibrate exactly the origin of the reflection.

There are BSR without hydrates and hydrates without BSR.

Previously, it had been assumed that the hydrate cemented the sediments above the BSR, with free gas filling the pore-space below. The concentration of hydrate and the so-called free gas in mainly unconsolidated clays (with as much as 60% porosity) is assumed now to be about 1% of the porosity. In fact the presence of only a few percent of gas in a reservoir can drastically lower its seismic velocity (Domenico 1976), so it is impossible to determine gas saturation by seismic means. Hydrates at such low concentration are unlikely to seal any gas. Freegas is in fact bubbles in water.

There are other possible explanations for the BSR reflector which may:

- be an artefact of the recording equipment related to automatic gain control;
- represent a formation boundary, with the crossing events being artefacts caused by diffraction from faults or the seabed;
- represent diagenetic contrasts or compaction;
- represent opalisation;
- be one of multiples of a thermocline (sharp contrast of temperatures inside the oceans) or the Sofar Channel (minimum of sound velocity in waters around 1000 m)
The literature contains much evidence for such alternative explanations or questionable picks for the BSR:

- A Barents Sea Bright Spot (Andreassen et al 1990, Laberg et al 1998) could be due to opal conversion which is known to affect velocity (Tribble 1992; Westbrook, 1994; Lee 1996; Pecher 1997)
- Slides illustrated by Mienert 1998 fig 12 showing two BSRs; and Neben 1998 fig 8: short reflection lacking any BSR characteristic;
- Base of blanking (Schmuck 1993 fig 4&5);
- Discomformites and sedimentary changes as at Site 184 Leg 19 Bering Sea (Makogon 1981 fig 56);
- Diffraction, as on the USGS survey on Leg 164 (Blake Ridge) related to a nearby diapir as shown on figure 4 where the BSR could be a diffraction

Figure 4

- Thermoclines (there are strong currents as the Gulf Stream or El Nino) within the ocean which can cause multiples, as seen for example on Leg 112 off Peru (Pecher et al 1996). However, thermocline is probably an explanation only in special cases. It is worth mentioning in this connection the remarkable so-called SOFAR oceanic acoustic layer, used by dolphins and whales and later the military to communicate. The Sofar channel will be studied in annex part 3.

A detailed evaluation of all the many alternative explanations of the BSR is beyond the scope of this paper, but it can be said with assurance that there is virtually no concrete evidence to equate this phenomenon with the occurrence of methane hydrates. It seems due more to the freegas (1% of porosity) low velocity below the hydrates zone.

Solubility of methane in seawater

Minshull.1989 wrote: ""The stability of gas hydrate depends not only on the pressure and temperature conditions but also on the concentration of natural gas present in the sediment, which must exceed the solubility of gas in seawater"". Many graphs have been published on the stability of hydrates versus pressure and temperature, but complete graph of the solubility of methane in deepwater is lacking, save one graph of solubility of methane in water sediments in Bonham (1978) (figure 5). It shows a drastic increase of solubility of methane with pressure explaining the lack of giant gasfields in HPHT conditions.

Figure 5:
Du Rouchet 1980 mentioned that Makogon has drawn in 1971 a graph where the solubility of methane of 2L gas /L water for 70 bars decreases sharply to 0.4 L/L when converting into hydrate, but this theory of discontinuity of solubility was not kept in recent articles.

The Louisiana State University (http://www.pete.lsu.edu/perttl), in an article on leak detection in deepwater pipeline, reports that the solubility of methane can increase up to 150 times, from from 0.68 cf/bw (0.12 L/L) in shallow water to 24-100 cf/bw under deepwater pressures and temperatures. These values are in agreement with Bonham which gives 50 cf/bw (8L/L) for 5000 m. It is in agreement with the values given on geopressed gas brines of the Gulf Coast which have produced around 30 cf/bw (5 L/L).

So there is a drastic discrepancy (over 1 to 10) between the solubility of methane in seawater given by the hydrates experts who say that this value determine the hydrates stability and the solubility given by the gas experts as Bonham and the gaspipelines experts who say that 0.5 Tcf can be dissolved in a cubic mile of deepwater. Site 994 found at 569 m a concentration of 5 L methane/ L water, reported as too high to be true, but corresponding to the solubility of Bonham in these conditions.

Global Warming and submarine landslides
The proponents of hydrates have not been slow to join in the debate about global warming. It is claimed that changes in sea-level during past glaciations led to the release of methane from hydrates causing global warming. However, it has to be recognized that hydrates take time to decompose and their input has to be related with other causes of climate change. Raynaud (1998) found no evidence for catastrophic hydrate release.

Blow out
Many floating drilling plateforms have been lost in shallow water when a gas pocket was penetrated before the blow out preventer was installed. The gas arriving quickly at the surface creates a very low density fluid and the floating platforms sink (Archimede law). It explains why now a shallow seismic survey is carried out to avoid any shallow gas. This hazard is considered when drilling hydrates in deepwater, but it has to be dismissed for two reasons. First decomposition of hydrates takes time and energy (as it is not a gas pocket); second decomposed methane or freegas dissolves before reaching the surface.

Pockmarks, gas plumes and hydrate outcroops
Craterlike depressions were found in 1985 in the Barents Sea (Solheim 1993) in a waterdepth around 300m. They are about 10 to 25 m wide and 1 m deep, and were interpreted as gas eruptions associated with hydrates but without any proof. It is normal to have gas eruptions or mud volcanoes in the oceans as on land.

Gas plumes has been identified acoustically on the Blake Ridge (Paull 1995) from a pockmark around 2000 m deep (corresponding to a fault), but the plume dissappears around 100 m above sea floor, being dissolved in the water. It is likely that this gas comes from the freegas escaping from the fault.

Outcroops of hydrate on the sea floor have been found too as seen on figure 6 (Louisiana State University), where bubbles do not go far. It is normal that seeping gas, being in the stability of hydrates, convert into hydrates. The outcrops means that hydrates are stable and do not decompose into gas when in contact with seawater giving gas plume, it seems to be the contrary, freegas reaching the seafloor is converted into hydrate.

It is strange that most of the legs on hydrates did not find any evidence of hydrates in the first 200 meters of sediments.

Figure 6:
Bermuda triangle

McIver 1982 proposed that the hydrate can decompose at the sea floor and emit a gas plume, causing turbidites flow, or a gliding plane for massive slides and even the disappearance of ships and aircrafts. This explanation received much media cover in connection with the Bermuda triangle mystery. Dillon called this story a fairy tale on the basis of insurance company data showing no special hazard in this area and on laboratory instrument simulating the conditions under which the "pock-mark" eruptions are believed to occur. Even with many variations, he was unable to produce any conditions likely to prove hazardous.

This conclusion is better confirmed by the studies of the Louisiana State University (see above) which say on the web: "Unlike shallow water, potentially large volumes of natural gas can be dissolved in seawater at the pressures and temperatures surrounding these deepwater flowlines. For example, from 392 to 526 billion cubic feet of natural gas can be dissolved in one cubic mile of seawater at deepwater conditions. The Gulf of Mexico (GOM) contains about 700 000 cubic miles of seawater and can accommodate very significant amounts of dissolved gas before the pollution is detected at the surface."

However this Bermuda mystery from hydrate is still proposed by Gruy 1998 and by Fischer (WO June) 1999.

Part 2

Origins of oceanic gas

Methane is continuously produced at the surface of the earth from the fermentation of a range of organic material including termites, bovine digestion, rice paddies, marshes. It also comes from hydrocarbon source rocks during their chemical evolution from organic deposits on the sea-bed to deeply buried oil and gas deposits. It also escapes from imperfectly sealed deeply buried hydrocarbon source-rocks and reservoirs. The so called "eternal flames" which were worshiped in antiquity in several areas around the Middle East are fuelled by methane.

The generation of gas from hydrocarbon source-rocks may be due to bacterial action giving what is termed biogenic gas, which may be distinguished by its isotopic signature from thermogenic gas, which due to the heating of the source-rock on burial. It is widely accepted that most oceanic methane is of biogenic origin (Monasterksy, 1998). It is likely that the occurrences of hydrates in the form of a few small dispersed gains or lamina as found in several of the boreholes are of this origin. In addition some massive hydrate deposits are associated with sea-bed disturbances, suggesting faults and fractures, and are probably formed from the escape of gas from depth. Kvenvolden, 1993, has
described the environment of hydrate formation in many different areas, finding methane with a thermogenic signature only in three places: the Gulf of Mexico, the Caspian Sea and the Mid-Atlantic Trench.

It is important to recognize that the methane in hydrates is held in the molecular structure as a solid as soon it is generated in the zone of hydrate stability. It cannot therefore migrate and accumulate in large deposits. It follows that true biogenic hydrates are represented only by the minor occurrences of dispersed grains and laminae as found in many of the boreholes. The so-called free gas (it is just bubbles in water) which is commonly observed below is also the same biogenic gas out of the stability of hydrates, being either not converted into hydrates or decomposed from hydrates. It may, in some cases, come from deep-seated thermogenic gas.

Resources

Estimates of the size of marine methane hydrate deposits range greatly, highlighted the extreme uncertainty that surrounds the subject (Prensky 1995).

<table>
<thead>
<tr>
<th>Methane gas</th>
<th>Methane gas</th>
<th>Methane carbon</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1015 m³</td>
<td>Pcf (1015 cf)</td>
<td>Tt (1018 g)</td>
<td></td>
</tr>
<tr>
<td><strong>Oceanic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-25</td>
<td>180-880</td>
<td>2.7-13.7</td>
<td>Trofimuk et al. (1977)</td>
</tr>
<tr>
<td>3.1</td>
<td>110</td>
<td>1.7</td>
<td>McIver (1981)</td>
</tr>
<tr>
<td>7,600</td>
<td>270,000</td>
<td>4100</td>
<td>Dobrynin et al. (1981)</td>
</tr>
<tr>
<td>17.6</td>
<td>620</td>
<td>11</td>
<td>Kvenvolden (1988)</td>
</tr>
<tr>
<td>19.5</td>
<td>690</td>
<td>11</td>
<td>MacDonald (1990)</td>
</tr>
<tr>
<td>26-139</td>
<td>930-4</td>
<td>910</td>
<td>Gornitz and Fung (1994)</td>
</tr>
</tbody>
</table>

| **Continental** | | | |
| 0.057         | 2           | 0.03           | Trofimuk et al. (1977) |
| 0.014         | 0.5         | 0.008          | Meyer (1981) |
| 0.031         | 1.1         | 0.02           | McIver (1981) |
| 34            | 1200        | 18             | Dobrynin et al. (1981) |

(We corrected the obviously wrong values of continental methane carbon).

All of these estimates are extremely unreliable, most failing to indicate the area, thickness and concentration of the alleged deposits.

The estimates of Kvenvolden and MacDonald are given below (Kvenvolden 1998). It is noteworthy that MacDonald was obliged by recent data to reduce the hydrate saturation in the pore space from 10% to 1% and to obtain the same order he multiplied by 2.5 the area, demonstrating again the wild speculation that attaches to the subject.

<table>
<thead>
<tr>
<th>author</th>
<th>area</th>
<th>thickness</th>
<th>% pore</th>
<th>amount</th>
<th>carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kvenvolden &amp; Claypool 1988</td>
<td>10</td>
<td>500</td>
<td>10</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>MacDonald 1990</td>
<td>25</td>
<td>500</td>
<td>1</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

It would be much more realistic to greatly reduce the thickness estimate because there is no evidence from the thousands of boreholes throughout the world's oceans of anything approaching 500 m. Furthermore, as in the oil
industry, it is important to distinguish net from gross thickness, given especially the real occurrence in the form of dispersed grains.

The claim by the USGS that "the worldwide amounts 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" is preposterous, especially since it is widely reported in the media.

Kvenvolden estimates the distribution of organic carbon, excluding dispersed carbon in rocks and sediments (which equals nearly 1000 times the total amount), as follows in gigatons (Gt):

- gas hydrates: 10 000
- fossil fuels: 5 000
- soil: 1 400
- dissolved organic matter in water: 980
- land biota: 830
- peat: 830
- detrital organic matter: 60
- atmosphere: 4
- marine biota: 3

The comparison is greatly flawed. The amount of hydrocarbons in oil and gas fields is estimated only about one percent of the generated hydrocarbons. Since the reported hydrate volumes cover disseminated deposits, it is necessary to multiply the corresponding oil deposits by at least a hundred to obtain a comparable disseminated value.

A recent estimate of the hydrocarbon endowment (Perrodon, Laherrere & Campbell, 1998) giving proper ranges for the ultimate recoverable resource, being a small part of the resources

- liquids in Gb:
  - conventional oil: min 1700, mean 1800, max 2200
  - conventional gas liquids: min 200, mean 250, max 400
  - non-conventional HC: min 300, mean 700, max 1500
  - total liquids: min 2300, mean 2750, max 4000

- gas in Tcf:
  - conventional gas: min 9000, mean 10000, max 13000
  - non-conventional gas: min 1000, mean 2500, max 8000
  - total gas: min 10000, mean 12500, max 20000

The most optimistic (and unrealistic) estimate of ultimate oil is 10 000 Gb (1.500 Gt) compared with the above mean of 2750 Gb for oil. The maximum hydrocarbon amount, including gas is about 3000 Gt, which with a further 2000 Gt from coal, gives a total for fossil fuels of about 5000 Gt. But fuels reserves have to be compared to hydrate recoverable resources and not to carbon disseminated in the sediments.

Combaz (1991) estimated that the total fossil organic matter in its scattered state weighs up to $10^{16}$ tons (10 000 000 Gt) of organic carbon, when the fossil fuels concentrated stock reaches about $10^{14}$ tons (100 000 Gt) of carbon.
oceans produce annually 23 Gt/a of organic matter compared to 0.7 Gt/a for land. The 10 000 Gt estimate by Kvenvolden for hydrates is only one tenth of Combaz's estimate of the fossil fuels.

**Volumetric Flaws**

In assessing a new oil prospect, the oil industry evaluates the necessary parameters including: the occurrence of source-rock; maturation; migration; reservoir development; trap and seal. But in the case of hydrates, the source, reservoir and seal are the same, comprising the 500 m of unconsolidated sediment beneath the seabed. Since hydrate is a solid, there is no possibility of migration. Furthermore hydrate being only about 1% of the porosity, the rest is 99% water, so the hydrates do not correspond to a seal. Free gas stays there as it is the equivalent of hydrate in zone where hydrate is unstable. Leg 164 in the Blake Ridge found that the percentage of methane is about the same above and below the BSR.

The estimates of volume of hydrates assume that most of the available organic material is converted into hydrate as the percentage of total organic carbon (TOC) is around 1% when the percentage of hydrate is around 1% of porosity or 0.5% of the total volume.

We have also to take into account the time factor.

It is hard to believe that hydrates contained in the first 600 m of oceanic sediments covering a period of less than 10 millions years could hold twice more carbon than the fossil fuels from 6000 m of sediments covering a period of more than 500 millions years.

Holbrook 1996 estimated in the Blake Ridge study that 30 Gt of methane hydrate (23 Gt of carbon) occurred in deposits laid down over six million years, namely at the rate of 5 kt/year. This compares with the following estimates from other sources of methane (Neue, 1993)

<table>
<thead>
<tr>
<th>sources of methane</th>
<th>in Tg/year or Mt/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>natural</td>
<td></td>
</tr>
<tr>
<td>wetlands</td>
<td>120</td>
</tr>
<tr>
<td>lakes, rivers</td>
<td>20</td>
</tr>
<tr>
<td>oceans</td>
<td>10</td>
</tr>
<tr>
<td>termites</td>
<td>10</td>
</tr>
<tr>
<td>total</td>
<td>160</td>
</tr>
<tr>
<td>anthropogenic</td>
<td></td>
</tr>
<tr>
<td>mining and petroleum</td>
<td>100</td>
</tr>
<tr>
<td>enteric fermentation=cattle</td>
<td>80</td>
</tr>
<tr>
<td>flooded ricefields</td>
<td>50</td>
</tr>
<tr>
<td>biomass burning</td>
<td>30</td>
</tr>
<tr>
<td>landfills</td>
<td>30</td>
</tr>
<tr>
<td>animal waste</td>
<td>30</td>
</tr>
<tr>
<td>domestic sewage</td>
<td>20</td>
</tr>
<tr>
<td>total man-made</td>
<td>340</td>
</tr>
<tr>
<td>total</td>
<td>500</td>
</tr>
</tbody>
</table>

The hydrate methane accumulated in the Blake Ridge of 5kt/yr represents about half the present methane coming from all the oceans.

It is noteworthy that the amount of biogenic marsh gas (wetlands) or bovine methane (enteric fermentation) is about

http://www.oilcrisis.com/olaherrere/hydrates/ (11 of 19) [27.02.2001 16:33:00]
ten times that in oceanic methane hydrates.

**US estimates of hydrates**

In 1995, the U.S. Geological Survey (USGS) completed its most detailed assessment of U.S. gas hydrate resources, with the in-place gas resource from 112,000 Tcf to 676,000 Tcf, with a mean value of 320,000 Tcf (more accurate and different values are even given!). Subsequent refinements of the data in 1997 have suggested that the mean should be adjusted slightly downward, to around 200,000 Tcf. In fact from the graph figure 7 it seems that 200,000 Tcf is closer the most likely (probability around 65%) than the mean (probability around 40%) which is still 300,000 Tcf.

**Figure 7:**

![Figure 7:](http://www.fe.doe.gov/oil_gas/methanehydrates/hydrates_intro.html)

But the comparison with the US proved conventional gas reserves of 1,400 Tcf is unrealistic. Some authors claim that about only one percent recovery is enough to give huge reserves, but it has to be a significant recovery or nothing.
Comparison with other non-conventional gas sources

There several other sources of non-conventional gas, which are much better known and accessible than hydrates. For example, Bonham (1982) estimated that there was as much as 50 000 Tcf in geo-pressured brines in the Gulf Coast. This is much larger than the 1 300 Tcf attributed to the Blake Ridge hydrates by the USGS, and is obviously a much more reliable resource. There is more in Russia. Zor'kin & Stadnik (1975) estimated the amount of gas dissolved in water at around 35 000 Tcf for West Siberia and as much again for Caspian. That said, there remain technical difficulties in producing gas from these sources, including the disposal of the brines, but they must be small compared with those of oceanic hydrates. Geo-pressured brines have been tested in the Gulf Coast and found uneconomic and full of problems.

Prospects for future production

So far there is no commercial hydrate production and none is planned. The reports of production in the Messoyakha Field have been challenged, as already noted. To produce hydrates it would be necessary to first find a concentrated deposit and then apply thermal or depressuring energy or solvents to release the gas. Many wild ideas have been voiced. For example, Iseux, 1991 proposed hydraulic fracturing, ignoring the unconsolidated nature of the sediments, and the injection of hot solvent. Islam, 1994 proposed electromagnetic heating of hydrates in permafrost. The absurdity of such is evident for oceanic hydrates when deepwater conventional oilfields require presently flow rates per well of around 10 000 b/d to be economic. The only valid interest seems to be in ideas for transporting the methane from the remote gasfields in the form of hydrates, if cheaper than LNG.

The fact is that there is no commercial interest in the oceanic hydrates (any more than there is in the oceanic dissolved gold, despite being the largest gold resource in the world). Chevron testifying to a US Senate Committee in 1998 correctly stated that hydrates occur in low concentrations and have no commercial potential. Gazprom likewise dismissed submarine hydrates (Krason, 1999), on the strength of substantial Russian research. Oil companies are involved in hydrate projects only in Japan and India, which are countries with limited indigenous oil and gas who face the growing cost of imports.

Conclusions

Methane hydrates are well known to the oil industry as a material that clogs pipelines and casing. They are also present in permafrost areas and in the oceans where the necessary temperature and pressure conditions for stability occur. Oceanic hydrates are mainly biogenic and different from thermogenic hydrates.

Claims for the widespread occurrence in thick oceanic deposits are unfounded. The thickest interval recovered from a total of 250 000 m of core from 2300 ODP/DSDP boreholes was one meter with an unknown extent. Mostly, they occur as dispersed grains and laminae. Indirect evidence from seismic reflectors (BSR), seismic direct hydrocarbon indicators, logs and free gas samples is unreliable and highly speculative.

BSR can have several origins, the most likely being the so-called freegas below the hydrate stability zone where gas is not trapped but has the same concentration as hydrate i.e. 1% of the porosity. Such dispersed hydrate cannot seal free gas as the porosity is 99% water.

Being a solid, methane in oceanic hydrates cannot migrate and accumulate in deposits sufficiently large to be commercially exploited. The published estimates of the size of the resource are highly unreliable and give flawed comparisons with conventional fossil fuels. There are other non-conventional sources of gas which are infinitely more reliably known and accessible than hydrates, yet remain uneconomic for the time being. The prospects for the commercial production of oceanic hydrates in foreseeable future are negligible. In short, they are a chimera.

The academic research dedicated to hydrates has brought more questions than answers. Hopefully the oil industry with the deepwater exploration will start to look more into the realities of oceanic hydrates outside their impact as a nuisance clogging pipelines.
Part 3: Annex

SOFAR channel

Most of seismic studies fail to record the events within the water section. The oceans contain layers of waters of
different temperature as wells as strong currents such as the Gulf Stream or El Nino which affect drastically the
weather. Oceans present different structures: thermocline (temperature), halocline (salinity), pycnocline (pressure),
lysocline (dissolution of calcium carbonate), and a minimum sound velocity speed layer called the SOFAR channel
which is a strong path for communication used by dolphins, whales and submarines. Submarines communications
were a confidential subject (military secret) up to 1991 and very few papers have been published. More data are now
being released. The SOFAR (sound fixing and ranging) channel, was discovered during WW II and used by the U.S.
Navy to locate downed aircraft pilots. The aviator released a small explosive device that sank to the SOFAR channel
before detonating; hydrophones cabled to shore received the signals and determined the pilot's position by
triangulation. Acoustic waves can propagate thousands of kilometers with relatively little attenuation.

In a 1960 experiment, 130 kilograms of TNT were detonated off the coast of Perth, Australia. Hydrophone
(underwater microphone) receivers detected sounds generated by the detonation 3.7 hours later near Bermuda, 20,000 kilometers away. A proposal by Dr. Munk resulted in the Heard Island Feasibility Test (HIFT), to assess the feasibility of acoustic thermometry for long-range monitoring of ocean temperatures. HIFT was conducted from 26-30 January 1991, off the coast of Heard Island. This uninhabited volcanic island is located near Antarctica, midway between Africa and Australia. The location was selected because of the sound channel's close proximity to the surface (175 meters), as well as the multiple, unimpeded paths to receiving stations on both U.S. coasts, 18,000 kilometers away. The HIFT signal was of sufficient strength to be detected, after computer processing, by 17 of 19 monitoring stations in all five oceans, including along both the East and West U.S. coasts.

The speed of sound decreases with decreasing temperature (4 m/s for °C) and increases with increasing pressure (or depth = 1 m/s for 100 m) and increasing salinity (1 m/s for 1%). Temperature in the ocean is primarily controlled by the absorption of sunlight. 99% of light is absorbed in the upper 100 meters of the oceans. The relationship of these factors results in a zone of minimum sound velocity in the ocean referred to as the SOFAR channel.

The figure 1 (from Matthias Tomcsak The Flinders University of South Australia. http://www.es.flinders.edu.au/~mattom) displays the various curves of sound velocity for different oceans as Wedell sea with no Sofar channel (as the temperature starts low and has no effect), North Pacific with Sofar around 600 m, Sargasso sea with Sofar around 1200 m and the Mediterranean sea with Sofar around 200 m.

Figure 1:
It is easy to reconstruct such curves with the rules on temperature (4m/s for °C) and depth (1m/s for 100 m) and with the temperature data. For Pacific sea at equator there is 27°C at surface, 25°C at 100m, 8°C at 500m, 4.5°C at 1000m and 1.7°C at 3000m. With such data the speed of sound is as figure 2. The minimum of velocity is around 1000m depth.

**Figure 2:**
This channel is important for a variety of reasons. Sound is used by a variety of marine organisms to communicate. Acoustic Thermometry is the field of study that relies on sound to measure the temperature of the oceans. Scientists have proposed using sound to assess global warming. This field experiment has generated quite a bit of controversy. In order to move forward with the experiment, additional studies were needed to determine the potential impact on marine mammals. But now Sofar channel is used to measure the temperature of ocean and global warming in the Acoustic Thermometry of Ocean Climate program (http://atoc.ucsd.edu). The ATOC program began transmitting acoustic signals in late 1995 from a low-frequency acoustic source installed on Pioneer Seamount off central California. The signals were recorded on horizontal receiving arrays at 11 U.S. Navy SOSUS stations in the northeast Pacific, and on two vertical receiving arrays, one near the Big Island of Hawaii and the other near Kiritimati (Christmas) Island, just north of the equator in the central Pacific. They were also recorded by a single receiver off New Zealand. ATOC, is an international program involving 11 institutions in seven nations.

Howard 1998 reports that the scientists were able to detect variations as small as 20 milliseconds in the hour-long time it took pulses to travel some 3,000 miles (4,800 km) between the underwater speakers and receivers. Those subtle shifts allowed the scientists to estimate average ocean temperatures along the signals' pathways to within .006°C. They also were able to detect an expected seasonal swing in upper ocean temperatures of about 2°C.

Figure 8 (http://atoc.ucsd.edu/Explorations_f98/Atoc.html) display the ATOC experiment from the source to receivers around the Pacific.

Figure 3:
This Sofar channel used to transmit sound on horizontal path should be seen also as a reflector on a vertical path. Very few seismic studies have been recorded on the water section as it is omitted in all surveys as no interest. I found only one by Gonella & Michon 1988 on a 100 km track by CGG in Atlantic west of the Gibraltar Straight, near the Goringe Ridge. Acoustic reflectors are clearly detected within the water in the 600-1500 m depth range (around 1 second) as seen in figure 8. These reflectors seem to correspond to the Sofar channel but also to the strong water current coming from the Mediterranean Sea, explaining the dipping of the current over the flank of the Goringe Ridge. Unfortunately no BSR could be seen on the sediment reflections as they are parallel and weak.

Figure 4: see Offshore August page 162

The study of the Sofar channel is in its infancy. It should be interesting for the deepwater oil industry to try to record seismic events around waterdepth of 600-1000 m in order to evaluate its influence in seismic recordings.

References
8. Durouchet J. 1980 "Une explication paleoclimatique des grands gisements superficiels de gaz sec du nord dxe la Siberie occidentale " BCREDP 4 p 119-142


16. Howard J 1998 "Listening to the Ocean's Temperature" Explorations, Vol 5, nº2, Fall


22. McIver R.D. 1982 "Role of naturally occurring gas hydrates in sediment transport" AAPG 66/6 June p789-792


28. Pecher 1997 http://www.ig.utexas.edu/staff/ingo/hygeoph/node5.html

38. Prensky S. 1995 "Hydrate Resources Estimation"
   http://www.aist.go.jp/GSJ/dMG/hydrate/hydrate.resources.html
44. Tribble J.S. et al 1992 "Effects of biogenic silica on acoustic and physical properties of clay-rich marine sediments" AAPG 76/6 June 1992 p792-804

from
Part 1: "Gas Hydrate, Uncertain resource size enigma"
Offshore, August 1999, p140-141,160-162,
Part 2: "Data shows oceanic methane hydrate resource over-estimated"
Offshore, September 1999, p156-158