The Oil Drum: Europe
DISCUSSIONS ABOUT ENERGY AND OUR FUTURE

Hydrates updated

Posted by Luis de Sousa on April 17, 2008 - 12:00am in The Oil Drum: Europe
Topic: Geology/Exploration
Tags: gas hydrates, jean laherrère, methane hydrates [list all tags]

This is a guest post by Jean Laherrère.

I was asked recently by e-mail, referring to a 2002 paper on hydrates:

> I read your excellent questions. Do you have any answers posted?

I decided to update my past papers on hydrates.

Core sample of massive gas hydrate (courtesy NGHP Expedition 01)

Previous papers

- Laherrère J.H. 2002 *Hydrates: some questions from an independent O&G explorer* Introduction as chairman of RFP 9 "Economic use of hydrates: dream or reality?" WPC Rio, Sept 5.
- Laherrère J.H. 2000 *The uncertainties of oceanic hydrates* Tomorrow's Oil Dec. p11-16
- Laherrère J.H. 2000 *Oceanic hydrates: more questions than answers* Energy Exploration & Exploitation, Special issue on hydrates Nov-Dec vol 18 n°4 p349-383
- Laherrère J.H. 1999 *Gas Hydrates* *Uncertain resource size enigma* & *The SOFAR channel: what and why* Offshore Magazine Part 1 August, p140-141,160-162, *Data shows oceanic methane hydrate resource over-estimated* Part 2 September p156-158

2002 notes

My 2002 paper as Chairman of the World Petroleum Congress panel on hydrates was short, coming from the following notes:

> In assessing a new oil prospect, the oil industry evaluates the necessary parameters including:
>
> - Source rock
> - Maturation
> - Expulsion
> - Migration
> - Reservoir
> - Trap
> - Seal
>
> But in the case of hydrates, the source, reservoir and seal are the same, comprising the

500 metres of unconsolidated sediment beneath the seabed. Since the hydrate is solid, there is no possibility of migration.

Furthermore, hydrates being only about 1% of the porosity, the rest is 99% water, so, the gas hydrate stability zone (GHSZ) does not correspond to a seal. Free gas stays because it is in this state in the zone where hydrates are converted into gas. Leg 164 in the Blake Ridge found that the percentage of methane is about the same above and below the bottom simulating reflector (BSR).

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

Time factor

We have also to take into account the geological time factor. It is hard to believe that hydrates contained in the first 600 metres of oceanic sediments covering a period of less than 10 million years could hold two times more carbon than the fossil fuels from 6,000 metres of sediments covering a period of more than 500 million 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 4 - Neue estimates

Methane sources	Location	Tg/year or Mt/year
Natural	wetlands	120
	lakes, rivers	20
	oceans	10
	termites	10
	total	160
Anthropogenic	mining and petroleum	100
	enteric fermentation(cattle)	80
	flooded rice fields	50
	biomass burning	30
	landfills	30
	animal waste	30
	domestic sewage	20
	total man-made	340
Grand Total		500

The methane hydrates accumulated in the Blake Ridge at 5 kt/yr, representing 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 ten times that in oceanic methane 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 1300 Tcf attributed to the Blake Ridge hydrates by the USGS, which is obviously a much more reliable

> resource.
>
> The fact is that there is no commercial interest in oceanic hydrates. Chevron, testifying to a US Senate Committee in 1998, correctly stating 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 facing the growing cost of fossil fuels imports.

2002 Russian presentation to the WPC hydrates panel

In *Natural Gas Hydrates as a Potential Mineral Resource* by Georgy A. Cherkashev and Valery A. from the Soloviev Research Institute for Geology and Mineral Resources of the Ocean "VNIIOkeangeologia", St.Petersburg, Russia, the abstract reads as follows:

> Abstract : The study of natural gas hydrates is of big importance as gas hydrates provide a large potential energy source. About 70 areas with gas hydrate evidences are known in the World Ocean. Gas hydrates have been directly evidenced by visually observation in 20 of the above areas. In the other 50 sites gas hydrates related reflector (BSR) or specific seismic signatures like VAMP's were recorded. BSR is only an indirect evidence of hydrates and gas immediately above and below the reflector. Attempts to seismically determine gas hydrates in sediments gave no reliable results yet.
>
> Extensive theoretical and experimental studies including global and regional assessments of gas volume in gas hydrates have been carried out. The global gas hydrate reservoir has been estimated to an amount as much as $7.6 \cdot 10^{18} m^3$ of gas, but published assessments differ by 3 orders of magnitude. The various projects of gas extraction from gas hydrates have been proposed. At the same time the following problems have still to be cleared up: what do the accumulations of natural gas hydrates represent; what are the deposits dimensions and configuration; what are their 3D parameters; how big volume of gas contain in separate hydrate accumulation. It is up to the nearest future investigations to solve these problems.
>
> During the last 10 years VNIIOkeangeologia has carried out investigations on gas hydrates around the world. It was established that: submarine gas hydrate formation represents a global physical and geological event; the amount of gas hydrates in the sea basins is more determined by concentrated gas hydrate occurrences (gas hydrate accumulations) than by uniform distribution of gas hydrates in sediments; the location of gas hydrate accumulations is controlled by special geological conditions; the major role in formation of submarine gas hydrate accumulations belongs to fluid filtration as well as to diffusion processes. Estimation of the total gas quantity concentrated in gas hydrate accumulations of the Ocean based on our results is almost 100 times smaller than previous estimates. However, the estimation is still in the same order of magnitude as the total remaining conventional natural gas.

The presentation (35 slides) displays many pictures of hydrates in particular of Lake Baikal. They believe that accumulations related to fluid discharge areas near the sea floor are renewable.

My papers after 2002

Since 2002 I often include a paragraph on hydrates in my oil and gas production papers, as in the last one in English:

Laherrère J.H. 2007 *Uncertainty of data and forecasts for fossil fuels* with *annex on climate change* Universidad de Castilla-La Mancha, Ciudad Real, 24 April

> **myth 7 :oceanic hydrates represents more resources than all fossil fuels**
>
> Hydrates of methane (a solid which contains 160 times more methane in volume than Natural Gas) are reported by some as representing more reserves than all other fossil fuels combined. Thid is completely wrong because oceanic hydrates in sediments of less than few millions years (Ma) cannot match fossils fuels issued by sediments during a period of more than 600 Ma. These unrealistic estimates have been divided by 100 (Soloviev V.A. 2004 "On gas hydrate mythology" IGC).
>
> Out of thousands of holes drilled by JOIDES only 3 found hydrates thicker than 15 cm and the last thick occurrence (leg 164) has shown no continuity in a hole drilled 20m apart. Oceanic hydrates are heterogeneous and of limited extent : few millimetres vertically and few meters horizontally. No methods are known to produce them. Japan and India have drilled many wells since 1999 to core oceanic hydrates, and despite their needs of gas, there is no plan to produce them. There is no known technology to produce oceanic hydrates. Continental hydrates in permafrost have been found, but they are accumulated in conventional gas fields which were trapped as free gas before the glaciations 2 millions years ago. Now in permafrost they do not add anything to conventional reserves except problems!

Recent hydrates recovery

The knowledge of oceanic hydrates occurrence comes mostly from proxy data and few direct proof or pictures of hydrates in cores exist. The drilling for hydrates by the Japanese in 1999 in Nankin was reported for years as having found hydrates, but a few years later it was recognized that no hydrates was cored, only proxy data (seismic, logs, chlorine concentration). It is difficult to find pictures of cores with large hydrate occurrence. What is published must be the best ones!

Japan

After the drilling of several wells in Nankai in 1999 failing to recover any hydrate in the cores, Japan went back to the permaforst in Mallik, where hydrates had been found already in 1972, in order to core real hydrates. After the lack of success in production in Mallik, Japan went back again to Nankai and drilled many wells. NETL (The gas hydrates resource pyramid) published a core showing sand and disseminated hydrates.

Example of disseminated gas hydrate (white specks) within porous and permeable marine sandstone from the Nankai Trough, offshore Japan (from Fujii, et al, 2005 ICGH Proceedings)

Figure 1 - A core drilled in Nankai, offshore Japan, showing sand and disseminated hydrates.

There is a rumour of a production test for 2009. But Japan needs gas and should be the first country to invest in hydrates if there are enough reserves and technology to produce it.

US offshore Oregon: 2006 Cascadia

The Integrated Ocean Drilling program leg 311 took place in Cascadia in 2006 where 1216 m of cores were recovered; it is stated:

> at Sites U1326 and U1327, where gas hydrate was observed in sections several tens of meters thick at a shallow depth of ~100 meters below seafloor (mbsf); concentrations exceed 80% of the pore volume. Another site of very high gas hydrate concentrations was the cold vent Site U1328, where beds containing massive forms of gas hydrate occurred within the uppermost ~40 m with concentrations exceeding 80% of the pore space as a result of focused fluid/gas migration from underneath.

But the picture is less appealing.

Figure F24. Images of pore-filling gas hydrate within coarse-grained sands. **A–C.** Interval (44.85 mbsf). **D.** Interval 311-U1326C-7X-3, 77–85 cm (53.27 mbsf).

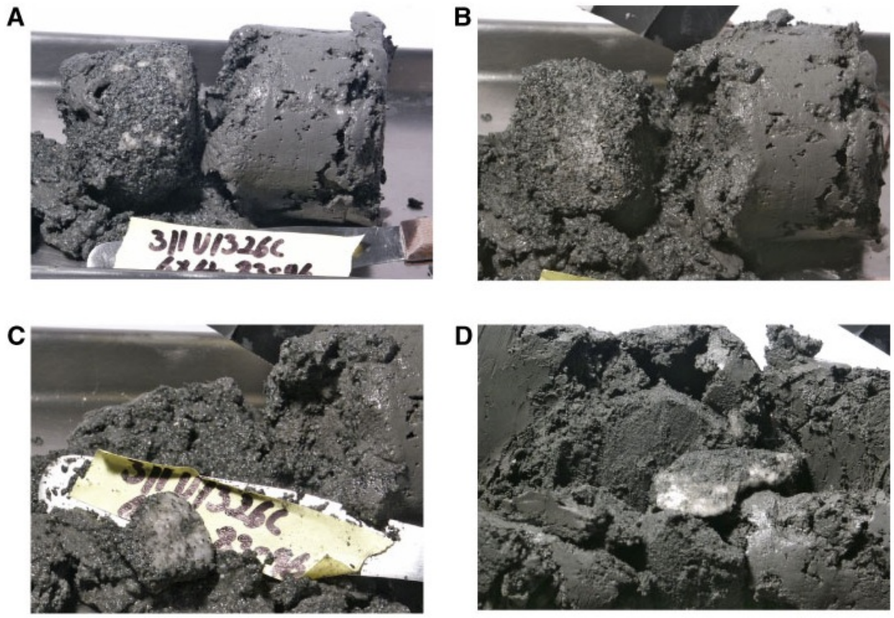


Figure 2 - Cores drilled at the Site U1326 in Cascadia. Click for large version.

Expedition 311 Preliminary Report

Figure F25. Images of gas hydrate samples recovered at cold vent Site U1328. A, B. Interval 311-U1328E-2X-2, 80–90 cm (8.69 mbsf). C. Section 311-U1328E-2X-CC.

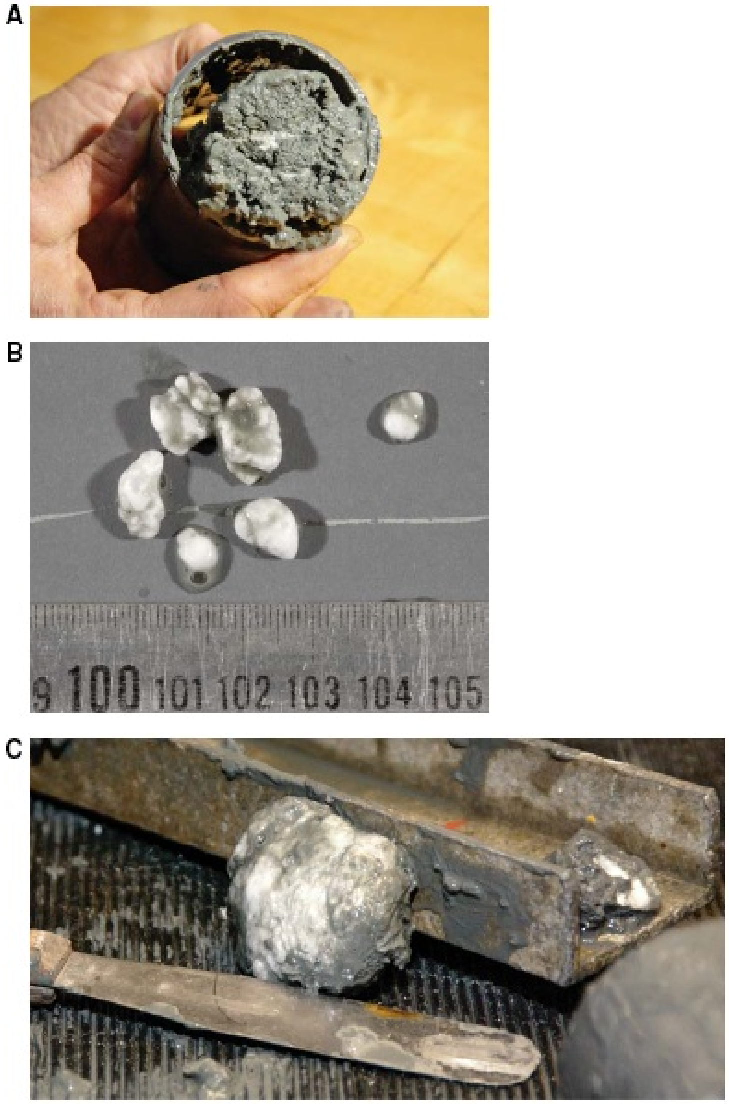


Figure 3 - Cores drilled at the Site U1328 in Cascadia.

Gulf of Mexico Chevron JIP

The Gulf of Mexico gas hydrates Joint Industry Project (JIP) leaded by Chevron gathered several oil companies: ConocoPhillips, Total, Schlumberger, Halliburton, Reliance (India), JOGMEC (Japan) together with the USDOE/MMS to investigate possible problem with hydrates drilling. They concluded that hydrates pose a minimal drilling hazard.

India

The 2006 Indian expedition uncovered richest known hydrate accumulation, described later in the
Report to Congress An Assessment of the Methane Hydrate Research Program and An Assessment of the 5-Year Research Plan of the Department of Energy prepared by the Federal Methane Hydrate Advisory Committee in June of 2007.
In The World's Largest Potential Energy Resource published by the USGS in the 7th of February of 2008, it is stated:

- one of the richest marine gas hydrate accumulations ever discovered was delineated and sampled in the Krishna-Godavari Basin;

- penetrated more than 9,250 meters of sedimentary section, and recovered nearly 2,850 meters of core. 494 cores Collected about 140 gas-hydrate-bearing sediment samples for storage in liquid nitrogen;
- discovered gas hydrate in numerous complex geologic settings and collected an unprecedented number of gas hydrate cores.
- Most of the recovered gas hydrate was characterized as either pore-filling grains or particles disseminated in coarser grain sediments or as a fracture-filling material in clay dominated sediments.

This last description matches what happens in most oceanic hydrates cores; this discovery is of limited extent due to hydrates being in the middle of impermeable clay. How to get in the energy needed to make a hydrate fluid and how to get out this moveable converted hydrate?

On the 18th of February the Oil & Gas Journal published an article by Sam Fletcher entitled *US-India study discovers large gas hydrate presence*. It confirms the statement of an unprecedented number of hydrate cores but portraits this only picture of a core where the hydrates ar millimetric!

Gas hydrates are an ice-like combination of natural gas and water formed by high pressure and low temperatures. The expedition collected an "unprecedented" number of gas hydrate cores. Photo from USGS.

Figure 4 - Core drilled during the 2006 US-India expedition that supposedly uncovered the largest hydrate reserves known today.

Fourtunatelly the NETL Methane Hydrate Newsletter (excellent Fire in the ice) from the Fall of 2006 publishes a better picture in the article *International team completes landmark Gas Hydrate expedition in the offshore of India*. Instead of being millimetric, the hydrate concentration is centimetric to decimetric, but far from representing huge reserves. More likely, as for Leg 164, the extension must be metric (as seen also on the seafloor).

Core sample of massive gas hydrate (courtesy NGHP Expedition 01)

Figure 5 - Another core drilled during the 2006 US-India expedition, this time published by the NETL Methane Hydrate Newsletter.

In the same newsletter the article *The gas hydrates resource pyramid* includes this picture of the seafloor showing that a massive hydrate is vertically decimetric and horizontally metric.

Example of massive sea-floor mound from Offshore Vancouver Island (courtesy Ross Chapman, U.Victoria)

Figure 6 - Picture of large hydrate in the seafloor published by the NETL Methane Hydrate Newsletter.

It is intriguing to know that the denstiy of methane hydrates in these depths is lower than water, hence pieces of hydrates should go up in the water column, except if glued to the seafloor. If huge amounts of hydrates are present they should push up the sediments: nothing like that is shown.

The scattered occurrences of hydrates on the seafloor is well seen on what is collected in the trawl of fishing vessels, as shown by Cherkashev & Soloviev. But why do they stay on the bottom if their density is lower than water?

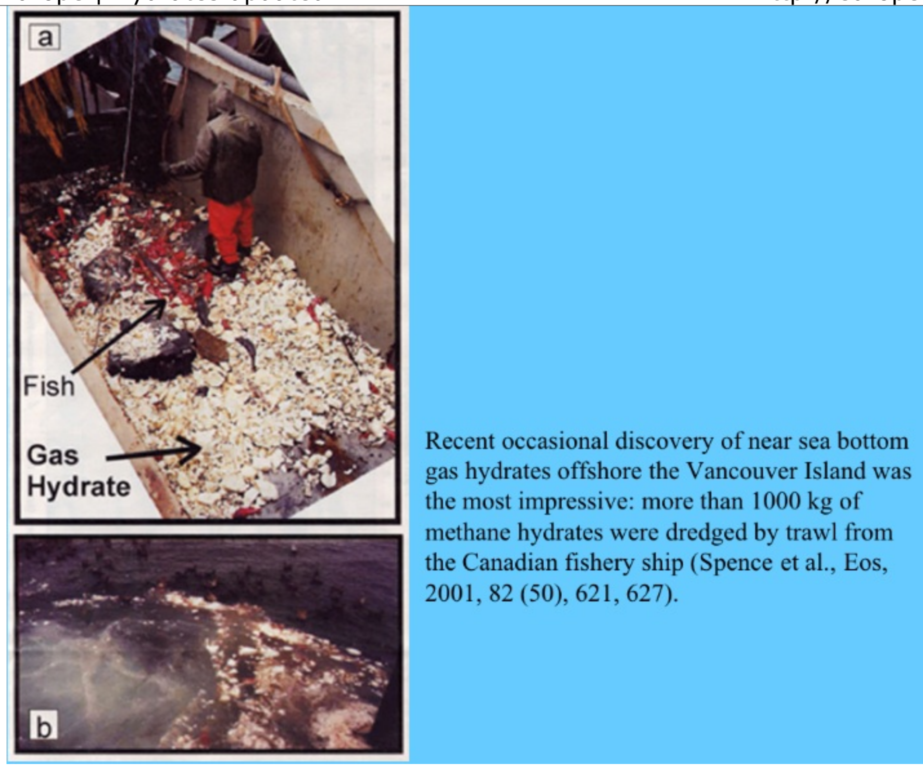


Figure 7 - Methane dredged by the trawl of a Canadian fishing ship. Click for large version

The NETL HMNews Spring-Summer of 2007 confirms that hydrates are just thin filling in fractured clays, clearly seen in this X-ray of a core.

Figure 4: An example longitudinal X-ray image of a one-meter-long pressure core obtained from offshore India containing gas-hydrate bearing fractured clay-dominated sediments. Gas hydrate (lightest shading) occurs primarily as thin, high-angle features filling apparent fractures (photo courtesy of NGHP Expedition 01).

Figure 8 - X-ray image of a core drilled offshore in India.

On the 13th of December of 2007 Der Spiegel featured an article by Gerald Traufetter entitled *Warning Signs On The Ocean Floor*, with the subtitle *China and India Exploit Icy Energy Reserves*. It reads:

> China and India have reported massive finds of frozen methane gas off their coasts, which they hope will satisfy their energy needs.
> Indian researchers discovered a 132-meter (433-foot) thick layer of methane hydrate in the Krishna-Godavari Basin. "One of the thickest that's ever been found in the world," says Malcolm Lall, the director of the Indian gas hydrate program. The team has also been successful in the Andaman Islands, were they discovered, 600 meters (984 feet) beneath the ocean floor, a layer of frozen methane embedded in ash sediments from prehistoric volcanic eruptions. "This too is a first," says Lall.

I doubt that India succeeds in producing these hydrates and I am absolutely sure that they will not satisfy their needs.

China

NETL reported in in 2007 that hydrates had been found in China (Shenhu area of South China sea) with an unusual CH_4 concentration of 20-40% (how reliable?) of pore volume in clay sediments. But no pictures of cores where provided.

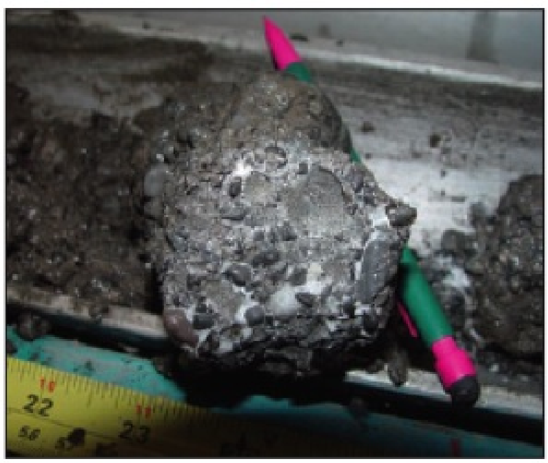
South Korea

In 2007 South Korea found some hydrates under 6500 ft of water (not far from Donghae gasfield). But no indication on the cores and no picture that I can find.

Permafrost

The Messoyakha and Mallik gasfields have some layers of hydrates above other layers of conventional gas. Glaciations started few millions years ago and former conventional gasfields now in permafrost. In these fields some layers of gas inside sandy reservoirs converted into hydrates layers. This means that the trapping is completely different from oceanic hydrates within clay.

Messoyakha gas production from hydrate is controversial because the deeper free gas layers were producing at the same time (Ginsburg's personal information). Mallik hydrates were found in 1973 and re-drilled later to get good cores:



Example of disseminated gas hydrate (white) within porous and permeable Arctic sandstone from the Mallik site, Northwest Canada (courtesy Mallik 2002 Gas Hydrate Project)

Figure 9 - A permaforst hydrate core drilled in Mallik.

The production test in Mallik is confidential, financed by oil companies, but it is rumored to be producing about 1500 cubic meters per day: were it a conventional gasfield, in such remote place, it would be considered to be dry!

Despite the assumed production of gas hydrate in Messoyakha and the pilot test of Mallik, where a small amount of gas was produced by injecting stream, the volumes produced are so low that could have been negligible or considered dry in any appraisal of conventional gas discovery in such remote places.

The 2007 report to the US Congress states:

> Currently, there is no commercially proven way to recover methane gas from hydrates

> in permafrost, the most easily accessible location where hydrate is found.
>
> While there is no standard, proven method of hydrated gas production, it is believed that simple depressurization may cost less than thermal stimulation or inhibitor injection strategies

The Hot Ice n°1 hydrate well drilled by Anadarko in 2003-2004 did not recover any hydrate. BP drilled in 2007 a well in the Alaska North Slope to evaluate hydrate at 4 miles south of the Milne B-pad, in the Milne Point oil field, Northwest of BP's Prudhoe Bay oil field. In the 2007 report to the US Congress they confirmed gas production through depressurization. But the US Congress report said also that it is not commercial. Furthermore, the 30 Tcf of the Prudhoe Bay field is still stranded 40 years after its discovery.

Fresh water lake : Baikal

The NETL HMNews of the Fall of 2007 publishes a good picture of two centimetric hydrate layers in a 1.5 m core taken by 1330 m deep, in September of 2007 in Lake Baikal:

Figure 10 - A core drilled in September of 2007 in Lake Baikal showing two clear centrimetic hydrate layers.

More cores deeper and at same depth few meters away should be quite interesting.

The excellent book *Submarine gas hydrates* by Ginsburg & Soloviev published in 1994 (with a translation sponsored by Statoil published in 1998) contains many many core pictures and quotes lake Baikal with hydrates occurrences because after BSR : Hutchinson et al 1991.

Cherkashev & Soloviev WPC 2002 did show some pictures of dospersed hydrate occurrences.

Gas hydrates recovered from near bottom sediments, Lake Baikal, Siberia. Subbottom depth of 25 cm. Plastic tube was disturbed during core sampling. Photo by J.Klerkx.

Gas hydrates in sediments of Lake Baikal, subbottom depth of 1 m. Fresh core - left, the same core cut in two - right. Photo by V.Kaulio

Figure 11 - Dispersed hydrates in cores drilled in Lake Baikal, as pictured in Cherkashev & Soloviev WPC 2002. Click for large versions.

Hydrate in gaspipeline

Hydrates are well known by gas engineers because they deposit in gas pipes as tubing or pipelines, as it is sometimes found in the permafrost by the Russians. Methanol is used to prevent the deposit of hydrates.

When I met Gabriel Ginsburg, the best hydrate specialist in AAPG 1993, I asked him about the production of Messoyakha from hydrate using methanol to dissolve it. He answered that production from hydrate layers is not certain, because there is also production from free gas layers and the use of methanol was essentially for preventing the formation of hydrate.

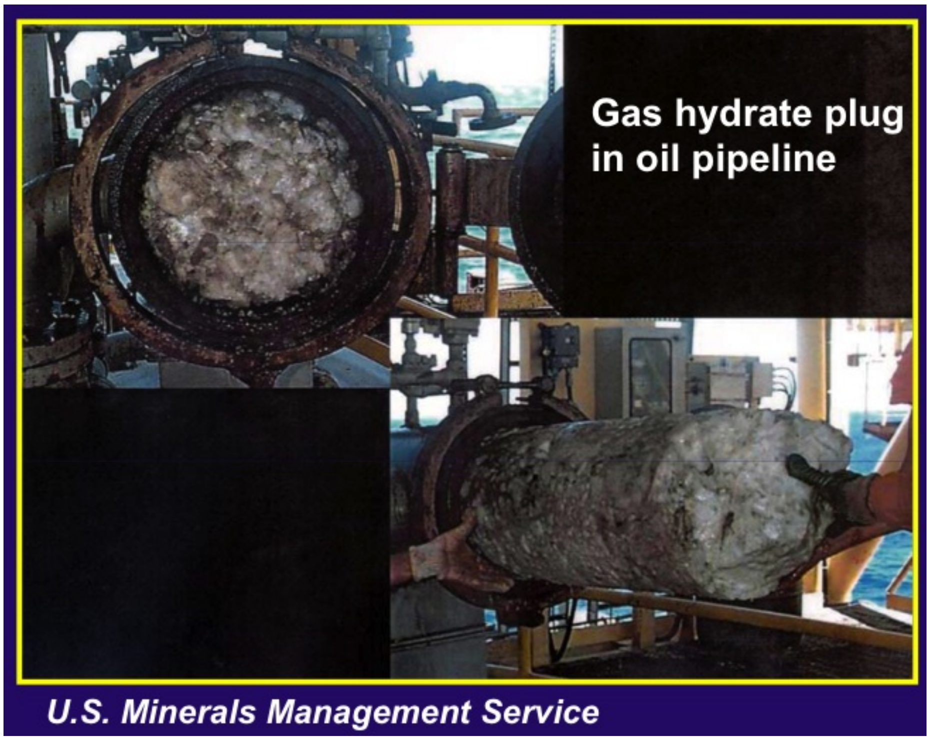


Figure 12 - Hydrate plug from a scrapper in a gas pipeline from Carolyn Ruppel . Click for large version.

Organic carbon in the Earth

Alexei Milkov in *Gas Hydrate Resource Potential in the Gulf of Mexico* (Rice University, November 12, 2003) estimates global hydrate reserves between 500 and 2500 Gt, to compare with 10 000 Gt by Kvenvolden in 1988 (which is unrealistic looking at the geological time involved for hydrates, compared to the fossil fuels).

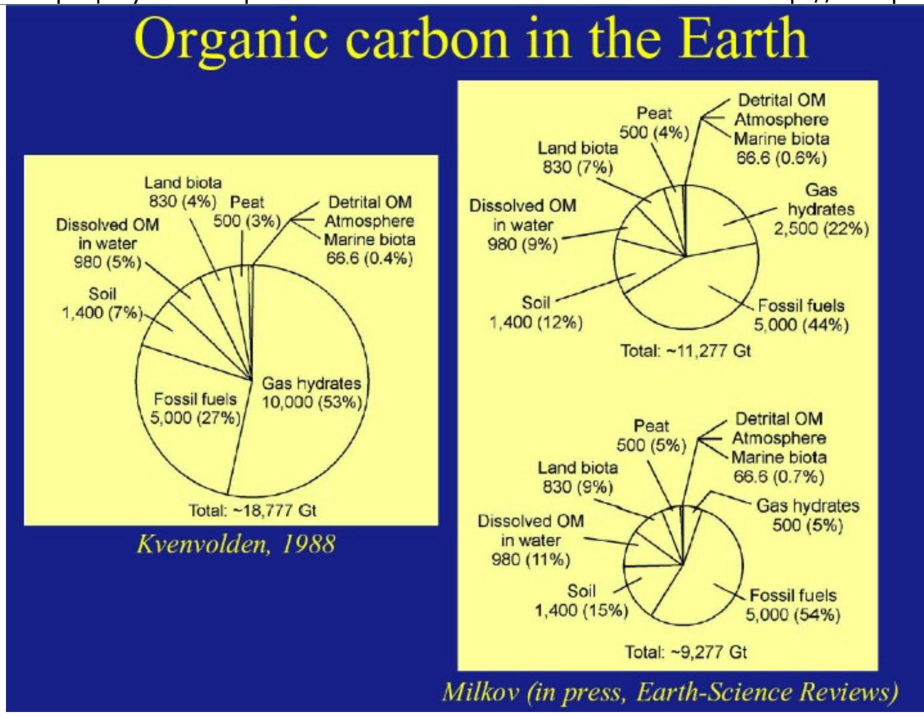


Figure 13 - Organic carbon in the Earth by Kvenvolden (1998) compared to Milkov (2003). Click for large version.

With 500 Gt, hydrates are lower than dissolved methane in geo-pressured water (50 000 Tcf in the Gulf Coast) which 30 years ago were described as the energy source of future, just as hydrates are now. But production pilots in US and Japan were abandoned mainly for environmental problems: what to do with brines? No one is talking any more of producing these huge dissolved methane resources!

Milkov shows that hydrates estimates have been in decline since 1973 divided by a ratio of more than 1000, being now about the volume of conventional gas, but without any technique to produce them.

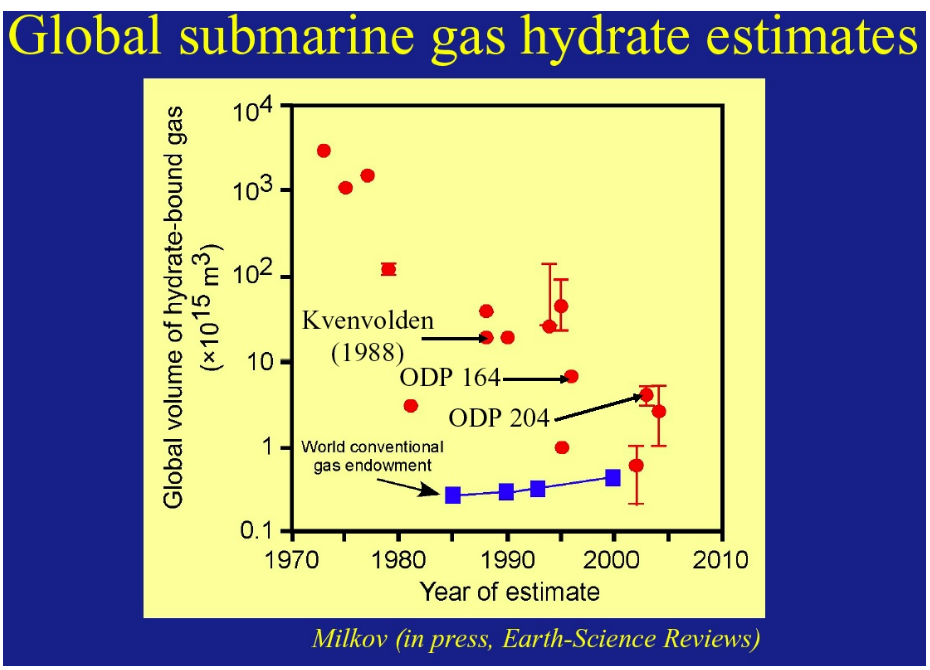


Figure 14 - Submarine Gas hydrates estimates through time, after Milkov (2003). Click for large version.

Alexei Milkov, a bright young Russian geologist, has worked on hydrates in Russia and in the US, Texas A&M University, with Sassen and with BP. I met him in Houston in 2003. He knows more than anyone on hydrates resources, but now being a scholar in the Woods Hole Oceanographic Institution, I was disappointed to find () that [a recent study](#) refers to this obsolete 10 000 Gt in order to justify the importance of studying hydrates.

The [UNEP yearbook 2008](#) is referring to this 10 000 Gt obsolete estimate saying that sediments in oceans continue to accumulate for centuries and millenia (but even this would not be enough to get 10 000 Gt!).

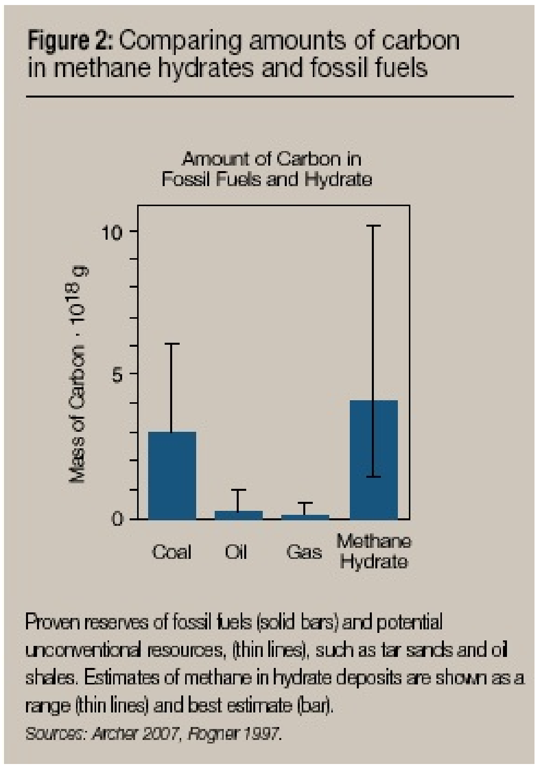


Figure 15 - Carbon sources as reported by UNEP.

Conclusion

Since 2002 many hydrates discoveries have been made in countries eager to get domestic methane production as in Japan, India, China and South Korea. But as in previous discoveries in US Cascadia and Blake Ridge, hydrates are of limited extent, quite dispersed and mainly in clay sediments in deepwater. Permafrost drilling finds different hydrate types, being frozen from former conventional gasfields.

Estimates of methane hydrates have been divided by a factor of 1000 but old estimates are still quoted in order to get financing.

An offical report to the US Congress states that there is no commercial hydrate production technique available. Oceanic hydrate methane will stay unproduced as marsh gas or methane in cows or termites.

My only unanswered question is: why hydrates being lighter than water are not popping up to the sea surface?

Previously at The Oil Drum : Europe:

Arctic Oil and Gas Ultimates

Interview with Jean Laherrère