

# TECHNICAL FEASIBILITY FOR THE EXPLOITATION OF METHANE HYDRATES

STEFANIA MASSARI (\*)

---

## Abstract

Methane hydrates have been largely studied in the last years as a potential energy source and many international projects are focused on this topic, but numerous technical problems still need to be solved. In this paper the most recent findings in gas hydrates discovering, investigating, recovery and producing techniques have been analysed. Particular attention has been put on the possible ways of exploiting gas hydrates even as a means of gas transportation and ocean carbon storage.

## Riassunto

In questi ultimi anni, molti studi e numerosi progetti di ricerca a livello internazionale si sono focalizzati sugli idrati di metano come possibile fonte energetica; purtroppo a tutt'oggi si presentano ancora molte difficoltà tecniche che necessitano di essere risolte, prima di poter sfruttare commercialmente questa risorsa.

Nel presente lavoro vengono analizzate le più recenti tecniche per la ricerca, l'identificazione ed il recupero degli idrati e la successiva produzione di metano da essi. In particolare, ci si concentra sui possibili modi di sfruttare gli idrati di metano, tra i quali appaiono decisamente interessanti l'utilizzo dei depositi oceanici per lo stoccaggio della CO<sub>2</sub> e l'uso degli idrati come nuova modalità di trasporto del gas naturale.

**Keywords:** methane hydrates formation, recovery, CO<sub>2</sub> injection, NGH chain

---

(\*) Dipartimento di Studi Aziendali, Giuridici ed Ambientali – Università del Salento, Italy.

## Introduction

The ever-increasing global demand of energy is challenging us to find more and more additional sources of clean, abundant, economic fuels, while most capital is invested worldwide in exploring for high-cost and non conventional fuel reserves.

Natural gas is at the moment the cleanest and most widely used of all fossil fuels. It is used as fuel and feedstock, so its secure and economic supply is vital for industry, electric power generation and homeowners in most of the countries of the world.

Methane hydrates represent a very attractive alternative source of energy for the future, since tremendous amount of gas has been demonstrated to be stored within and below hydrated sediments, in the oceans and in the continental areas of Arctic regions. Estimates of the inventory of total methane in gas hydrates range from 700 to 10,000 Gigatons of carbon (1).

Even if gas hydrates caught the attention of industry since 1930's, when they were found within long distance oil and gas pipelines, only in the last 10 years hydrate science has advanced significantly (2). Laboratory experiments, computer modeling, field expeditions and development of specific technical tools have enabled a much more confident assessment of methane hydrates in natural environment, in order to exploit their energy potential.

## Structure and origin of methane hydrates

Hydrates or clathrates are ice-like compounds, constituted by crystalline polyhedral cages of water molecules, containing various "guest" gases, such as  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{N}_2$ ... The amount of a guest gas stored in  $1\text{m}_3$  of hydrate may be over  $160\text{ m}^3$ . Depending on the chemical species of the guest molecules, different cage structures may be formed: I, II and H, studied by X-ray diffraction. The H-structure forms with two different guest molecules, one of which is a small molecule as methane, and the other one is a larger molecule as methylcyclohexane. H-structure hydrates usually form under milder thermodynamics conditions (equilibrium pressure and temperature) than structures I, II (3). Pure methane hydrates form Type I structure, with a methane-to-water ratio of 1:6, in an ideally saturated compound (See Fig.1).

Methane hydrate is the most abundant form of natural clathrates, found in sediments of the ocean floor, and there are some evidences of their presence also in outer regions of the solar system (4).

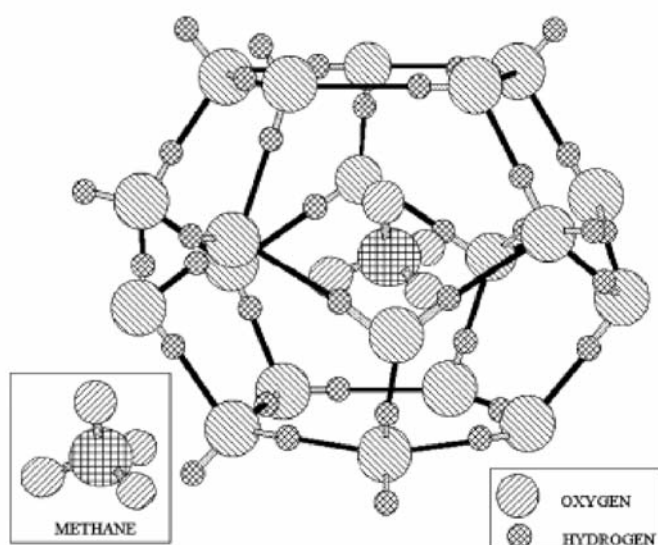


Fig 1 - Schematic of methane hydrate structure I.

Source: C. E. Taylor, Topics in Catalysis, Vol 32, Nos 3-4, March 2005

Methane hydrates are common constituents of the shallow marine geosphere, probably formed by migration of the gas from depth along geological faults followed by crystallization (5). There are essentially two ways through which hydrates can create energy gas deposits: by binding gas into hydrates within the sediments and by forming a trap for free gas beneath this layer, using hydrate-cemented sediments as seal (1).

Many studies, as computational methods, NMR, Raman Spectroscopy, have been conducted in order to understand the structure and the dynamics of methane hydrates (6,7). Methane molecules may be originated through two different pathways: thermogenic way and biogenic way. The majority of hydrate deposits on Earth are composed of biogenic methane, as indicated by its isotopic composition and the lack of other hydrocarbons such as ethane (8). Biogenic methane is formed by bacterial degradation of organic matter, either in fresh water or seawater, once  $\text{SO}_4^{2-}$

is depleted, being the production of methane from decaying organic matter inhibited by the presence of dissolved sulphate (9). Sulphate is removed from pore waters deeper in sediments by reaction with methane, preventing in this way the coexistence of the two molecules at high concentrations in sediments pore waters (10). Thermogenic methane, usually associated with fossil carbon, is instead produced abiologically from organic matter when temperature increases to about 110°C and it is often accompanied by other organic compounds as ethane (11).

Once methane is formed, it can move within the sediment column by diffusion, pore water flow or migration of bubbles and there are some evidences that the gas may also move through the hydrate stability zone without freezing into hydrate (8).

Methane hydrates are thermodynamically stable at low temperatures and high pressures. It has been observed that methane hydrates form at 0°C where the pressure is equivalent to that of 250 m of water; at 10°C they form at a pressure corresponding to 1000 m of water (12). Even methane hydrates can persist metastably several degrees above its thermodynamic melting temperature, it is very difficult to maintain hydrate structures during core samples retrieval, due to the occurring of rapid depressurization which melts them (13).

The appropriate conditions for hydrates formation may be found under the permafrost of Siberia and Alaska as well as under seabeds deeper than 500 meters in marine environment. The total amount of hydrates in marine sediments seems to be orders of magnitude greater than the one in permafrost, but hydrates in the permafrost often occur in higher concentrations and in more accessible locations (See Fig.2).

In marine sediments, methane hydrates are restricted to areas where the required pressure and temperature conditions are met and where the abundance of methane is sufficient to exceed the local solubility (14).

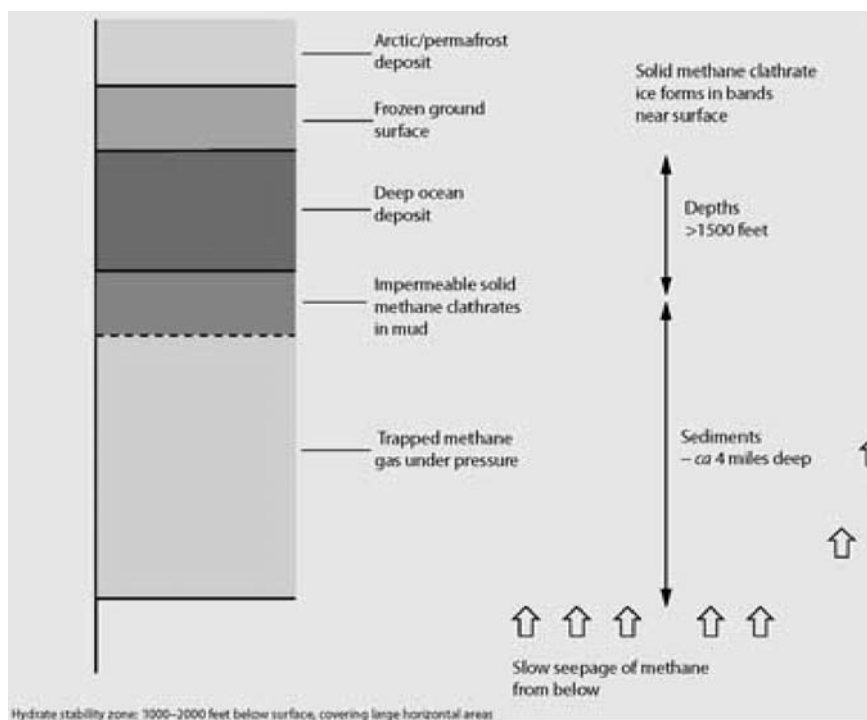


Fig 2 - Distribution of Methane Hydrates

Source: Royal Society of Chemistry, [www.rsc.org](http://www.rsc.org)

Inside the hydrate stability zone, methane hydrate phase coexists with liquid water phase and no free gas is found. At the base of hydrate stability zone, pressure and temperature conditions match those of P-T conditions for three-phase equilibrium between water, hydrate and free gas (See Fig.3). Understanding the P-T condition for the three phase equilibrium in marine sediments is very important for exploring and exploiting hydrates resource (15). The formation and the occurrence of gas hydrates is controlled by formation temperature, formation pore pressure, gas chemistry, pore water salinity, availability of gas and water, gas and water migration pathways and presence of the reservoir rocks and seals (16).

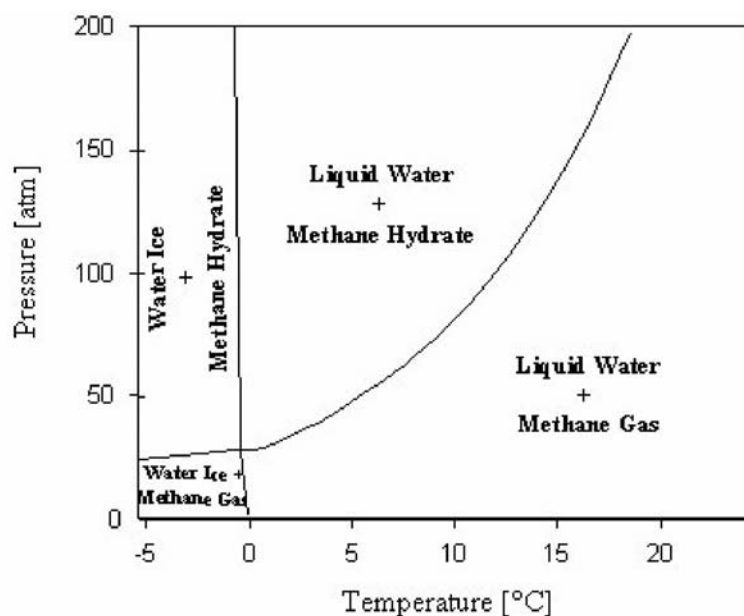


Fig. 3 - Methane Hydrate Stability Zone.

Source: Gas HyDyn Centre, [www.emse.fr](http://www.emse.fr)

Although information, for marine sediments, on the pore size-distribution, the size of the pores filled with methane and the variation of pore size on a regional scale are very limited, it seems that marine sediments bearing methane hydrate have a broad size-distribution, from few nanometers to tens of microns. In addition, from recent studies, it results that the decomposition conditions are mainly affected by the pore sizes, while the surface textures and mineral components have less influence (17). All these findings are very important for a better comprehension of methane hydrates distribution in nature and their possible use as gas methane source.

### Detection and recovery techniques

At present, the methane gas abundance has been detected by multiple techniques, such as seismic reflection profiles, vertical seismic profiles, sonic logs, pore water analyses, resistivity logs, pressure core

samplings and temperature probes (18). Until recently, the most reliable remote sensing tool for the location and characterization of methane hydrates was the detection of Bottom-Simulating Seismic Reflectors or BSRs. A BSR is a subsurface reflection that appears on seismic cross-sections and parallels the sea bottom while crossing sedimentary boundaries, as it should be where an accumulation of methane hydrates is (See Fig.4). Actually the prominence of this reflector, caused by a contrast in the seismic properties above and below the phase boundary, depends on the presence of a small amount of free gas immediately beneath the phase boundary. So, in areas where hydrates are not in contact with gas, no BSR would be shown; on the other hand, a BSR usually indicates the presence of hydrates, but it doesn't say anything about their quantity (19).

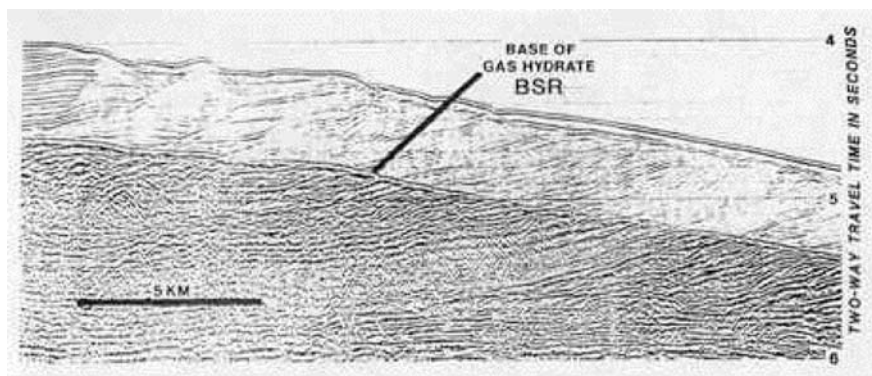


Fig. 4 - Bottom-Simulating Seismic Reflection.

Source: Natural Resource Canada, [www.nrcan.gc.ca](http://www.nrcan.gc.ca)

Recently some large-scale deposits of methane hydrates have been discovered without any evidence of a BSR and in some sites BSRs have been located and found to be devoid of hydrates.

A recent study made in the Sverdrup Basin in Canada has shown that in situations where detected gas hydrates occur exclusively in the hydrate stability zone, the existence of a BSR is unlikely, while in situations where hydrates are in contact with gas, such seismic evidence of the gas hydrate base may occur (20). At the moment, the most promising technique for the detection and characterization of gas hydrate deposits, in permafrost or in deep ocean, is the integration of acoustic data with well log data. In addition to seismic data, DOE (US Department of Energy) is

developing an electro-magnetic resistivity technology to deep water hydrate detection and in the meantime it is working on the combined application of seismic surveys, geochemical analyses of piston core pore-waters and heatflow probes (21).

According to these and combined data regarding specific sites, such as the Blake Ridge (a large drift deposit south east of US), it seems that methane is distributed below the seafloor in different forms. Specific horizons, going from top to bottom, can be detected: a sulphate reduction zone without  $\text{CH}_4$ , a dissolved gas zone without gas hydrate, a gas hydrate zone, a free gas zone and a lower dissolved gas zone (22).

Below the seafloor, the two equilibrium curves ( $\text{CH}_4$  hydrate-pore water partial saturation curve and the free  $\text{CH}_4$  gas-pore water saturation curve) intersect at a certain point; this crossing point determines the limit in pore space above which methane occurs dissolved in water or in solid gas hydrate and below which it is dissolved in water or as free gas bubbles (18). So potential gas hydrate volumes should be carefully distinguished from gas concentrations and gas hydrate abundances, in order to evaluate the exploitable amounts of methane hydrates and the appropriate recovery methods.

The process of recovering methane from hydrates is quite difficult and risky, due to possible dissociation of gas from the clathrates and subsequent release of gas to the sea surface and into the atmosphere, and the destabilization of sedimentary hydrates deposits, followed by probable submarine landslides (23).

Methane hydrates deposits are much deeper than underwater oil or natural gas fields and the difficulties for their recovery are numerous due to the necessity of developing special vessels.

Good drilling practices that guarantee wellbore stability are essential for safe and cost effective exploitation of gas hydrates reserves. In comparison with other hydrocarbons, the drilling of methane hydrates presents some specific drilling hazards, such as: loss of well control due to dissociation of gas generated by drilling operation; borehole failure caused by the loss of formation competence which accompanies dissociation; loss of well control when drilling into the overpressured gas below the hydrate stability zone. It is then very important to undertake extensive pre-drilling planning in order to locate the overpressured zones and the conditions under which gas hydrate would dissociate during drilling. It seems that controlling the circulation rate during drilling is the key to minimize the thermal disturbance caused by drilling (24).



At present there is no suitable technology for recovery of methane from oceans, but many methods have been proposed and are under development. The three most commonly used methods for methane recovery are: depressurization, thermal fluxing and salts injection, either individually or in combination. All these methods cause decomposition of hydrates and release of the methane-bound gas, so they are very risky; in addition how much methane can be practically recovered at reasonable costs is however highly uncertain (25).

The depressurization method (the most promising and economic one) works by decreasing the reservoir pressure below hydrate equilibrium, through a hole drilled into the layer, in order to make hydrate dissociate and the gas flow up. This is an endothermic reaction and the extraction of gas by this in-situ technique may be hampered by the formation of ice and/or the reformation of methane hydrate.

The thermal stimulation method consists of in-situ heating using steam or hot gas/liquid injection and down-hole combustion; an alternative option is the use of electrical heating. The problem of this technique is that it requires nearly as much energy as it is ultimately produced, due to high loss of heat during the transfer from the surface to the hydrate layer (26). The energy required to dissociate hydrates ranges from 50 to 130 kJ/mol; without any heat loss, the injected energy is about 10% of the recovered one, while taking into account the heat loss to reservoir rock and water, the injected energy would exceed the heating energy or the recovered gas (27). Commercial dissociation seems to be most feasible for reservoirs that are near the hydrate/free gas phase boundary; as distance from this boundary increases, higher temperatures and/or greater depressurization would be required for dissociation, meaning a strong impact on the economics of gas recovery.

The recovery of methane gas is also possible by methanol or other gas hydrate inhibitors injection, but the cost associated with the use of large volumes of chemicals would be very high, either economically or environmentally.

A very promising method is the injection of CO<sub>2</sub> into the hydrate formation with the effect of displacing methane, with the added value of CO<sub>2</sub> sequestration. As demonstrated in many experiments, chemicals such as CO<sub>2</sub> promote the hydrate dissociation by shifting the hydrate/free gas boundary towards lower pressure and lower temperatures. In this way CO<sub>2</sub> could stimulate methane hydrate dissociation with its contemporary storage and the recovery of methane gas (28) (See Fig.5).

It has been demonstrated that  $\text{CO}_2$  hydrates form in porous media at higher temperature than the one needed for the dissociation of methane hydrate, so an initial external thermal source would help to start the process (29).

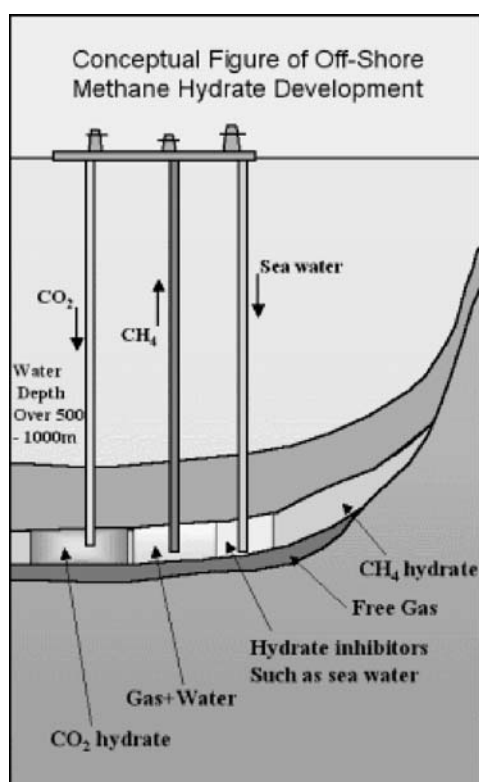


Fig. 5 - Methane Recovery through  $\text{CO}_2$  injection.

Source: R. C. Hendricks, Report NASA/TM-2007-214816

Even  $\text{CO}_2$  seems to be a relatively poor guest molecule for the cage structure of Type I hydrate, it appears to be a very efficient guest for the cage in structure II hydrate and it may also act as a helpgas for Type H structure hydrate (7).

$\text{CO}_2$  hydrates have been recently studied as a means of reducing greenhouse gas emissions to the atmosphere through ocean capture in form of hydrates. Some international projects have already planned to carry out

field and laboratory investigations on ocean sequestration, focusing on CO<sub>2</sub> hydrates behaviour and issues related to pipeline and injector blockage phenomena, due to the formation of CO<sub>2</sub> hydrates under deep ocean conditions, which may interfere with CO<sub>2</sub> droplet dissolution (30).

An innovative thermal stimulation method for contemporary methane recovery and carbon sequestration has been proposed recently; it is based on the location of an in situ point heat source, via combustion of liquid fuel and oxidant, directly within the hydrate layer. If the pumped oxidant is composed of oxygen and CO<sub>2</sub> instead of air, it is possible to reduce the required methane fuel usage, boosting energy efficiency, and sequester significantly more carbon (31).

### **Methane Hydrate Research Programs and Project**

Even if methane hydrates are unanimously considered a strategic source of energy, numerous technical, economic and environmental issues still need to be solved before starting their exploitation. In the last ten years, many countries have established own Research Programs on methane hydrates and some Governmental Projects have also started to involve industrial companies.

The first known production of natural gas from hydrates, by methanol and CaCl<sub>2</sub> injection, occurred in the Soviet Union in the Messoyaka gas field, which, according to estimations, contains billions of cubic meters of methane hydrates. The Soviets extracted gas for 13 years, but the project has been an economic failure due to the high cost of the chemicals (32).

Japan was, instead, the first country to establish a national hydrate research program in 1995 and set up the first drilling campaign in 1997, while the Oil Industry Development Board of India started a gas hydrate research program in 1996, focused on the Bay of Bengal and the Arabian Sea, off the continental shelf of India (33).

The first national program in the U.S. was established through the Methane Hydrate Research Act of 2000, a public law, as amended by the Energy Policy Act of 2005. The first arctic exploratory test well was drilled by the U.S. in February 2007 (34).

U.S. have maintained for a long period of time a strategic advantage towards other countries in terms of science knowledge base on

methane hydrates, but other countries such as Japan, China, India and South Korea have started to outspend the U.S. on hydrates-related research. Japan is one of the most active countries in methane hydrate research; the Japan Oil, Gas and Metal National Corporation has been experimenting methane hydrate reserves in Canada and has recently started undersea experiments in Japanese waters. Commercial production has been targeted for 2010 (35).

In 2006 an U.S. Interagency Roadmap for Methane Hydrate Research and Development established a context of research and long-term goals to be achieved through 2025.

A specific effort has been made by the representatives of seven U.S. federal agencies by setting a five-year plan (2007-2011) for methane hydrate research and development, with particular focus on demonstrating the technical and economic viability of methane recovery from hydrate deposits. Funds addressed to the program are \$40M for the fiscal year 2009 and \$50M for the fiscal year 2010. The Department of Energy (DOE) is also collaborating with oil companies in two big projects: with BP, focused on permafrost issues, and with Chevron JIP, focused on the Gulf of Mexico (36).

At international level, two important campaigns of explorations comprehend the Mallik well in the McKenzie River Delta in Canada and a well in the Nankai Trough off the southeast coast of Japan.

Currently, the analyses of methane hydrate reservoirs are based on well logging and collection, handling and analysis of conventional cores which rely heavily on technologies developed about twenty years ago; during the last few years an advance pressure coring has been tested which has become an indispensable technique for offshore gas hydrate expeditions (37).

This new tool has been developed under the European Projects HYACE (1998-2001) and HYACINTH (2001-2004); since 1997 other two projects have been funded by the European Commission: HYDRATECH (2001-2004) and ANAXIMANDER (2002-2005).

In particular, the Anaximander project has the aim of performing delicate sampling of sediments containing methane hydrates in the Anaximander Eastern Mediterranean Sea Mountain, east of Rhodes Island, at the average depth of 2000 m below the sea level (38).

**Natural gas hydrate as a means of methane transportation**

In addition to the promising exploitation of natural methane hydrates reservoirs, the studies focused on hydrates stability, dissociation and conditions of formation are very important even to prevent pipelines blockage, during oil and gas transportation, and also for a novel way of transporting natural gas.

Methane gas hydrates, in fact, present particular properties which have started to be considered very useful for methane transportation and storage: 1) natural gas hydrates (NGH) contain about 170 times as much gas as their volume, i.e. hydrate yields up to 160 m<sup>3</sup> of natural gas per tonne of hydrate at standard conditions; 2) they can be safely (being made of solid crystalline bulk with water molecules) transported at about -20°C under atmospheric pressure.

The NGH chain consists of four serial steps: formation of hydrate, processing of the formed hydrate, storage and transportation of the processed hydrate and its dissociation (39). The technologies related to each of these steps are being investigated in order to improve the overall efficiency of the process and evaluate the economic viability of gas transportation via NGH.

In particular, the formation rate and the stability of the formed hydrate are vital for long distance and period transportations, so some recent studies have focused on substances able to control the dissociation rate. It has been demonstrated that sodium dodecyl sulphate (SDS) is a good hydrate promoter, with the side effect of decreasing the hydrate stability below ice point; adding substances such as Xanthan gum and starch decreases the dissociation rate of methane hydrates formed in SDS solution (40).

Several studies have already demonstrated the economic convenience of gas transportation via NGH in comparison with LNG, in situations such as small markets i.e. islands where pipelines and LNG are not economical, or where the gas production is too variable and may drop below a certain level to be economical for LNG, or for sites where associated gas (on- or off-shore) cannot be flared or re-injected and other infrastructures haven't built yet. So a profitable and successful small volume gas transport market could be developed worldwide using NGH in all those situations where LNG is too expensive. Actually, the NGH process is simpler, safer, and cheaper than LNG for production and transportation; requires smaller investments and payback times for equivalent gas sales

and has the advantage of better regulating the gas quantities, which can be designed for the specific needs of a particular power station (41). The international interest for gas transportation via NGH is demonstrated by numerous studies made by academic and industrial researchers around the world. Marathon Oil Corporation and Mitsui Engineering & Shipbuilding Co., Ltd. are particularly involved in the development of the NGH total system and over 2002-2003 a Process Development Unit, the first demonstrational operation large-scale experimental plant, was constructed for the production of 600kg of NGH per day in form of pellet (42). As the latest achievement, Mitsui and MES are executing an up-to-date feasibility study on natural gas supply chain through NGH, in collaboration with Japan Oil, Gas and Metals National Corporation (JOGMEC) and other 6 Japanese leader companies related to natural gas business (43).

## **Conclusions**

According to many studies, it seems that the total amount of energy content of gas hydrates is about twice that of total fossil fuel reserves. Even if hydrate occurrence would be lower of a factor of 10, compared to the most positive estimations (60 instead of 800 ZJ), and even if only a small percentage of the detected hydrates would be exploitable, they would still offer the potential for a radical change in the global energy scenarios. Under favourable conditions, with competitive extraction costs of below some 50 US\$/bbl (oil equivalent), the estimated market value for methane hydrates would be of about 1 trillion US\$ in 2050 (44).

Unfortunately there are still several technical problems in detecting, extracting and producing gas from methane-hydrates at the moment and only through a concerted effort at global scale this resource potential could be exploited.

More information is urgently needed about hydrates potential as energy source, their influence on the sea floor stability and their effect on global climate change. Studies on methane hydrates in nature could also provide useful data for carbon sequestration in the oceans and the development of an alternative way to LNG for methane transportation.

To transform the long-term potential of gas hydrates in an economically feasible energy source, cooperation between governmental institutions and industry is needed, as well as more investments and suitable research strategies are required.

Received July 31, 2009

Accepted September 21, 2009

## REFERENCES

- (1) E. Desa, "Submarine methane hydrates – Potential fuel resource of the 21st Century", *Proc. of AP Akademi of Sciences 2001*, 5(2), 101-114.
- (2) L. Morel, "Near term energy potential realization of domestic methane hydrate deposits. The need for funding and industry participation", Report of 2006 WISE Intern, The University of Kansas, August 3 2006
- (3) T. Kozaki et al., "Phase equilibrium and crystallographic structures of clathrate hydrates formed in methane + 2,2-dimethylpentane + water system", *Journal of Chemical and Engineering Data 2008*, 53, 2820-2823
- (4) A. Li et al., "Modelling the infrared emission from the  $\epsilon$ -Eridani disk", *Astrophysica. Journal 2003*, 598, L51-54.
- (5) J.M. Hermida-Ramón et al., "Structural study of methane hydrate", *Journal of Structural Chemistry 2007*, 18, 649-652
- (6) A.K. Sum et al., "Measurements of Clathrate Hydrates via Raman Spectroscopy," *Journal of Physical Chemistry B 1991*, 101 (38), 7371-7377
- (7) J.A. Ripmeester, C. I. Ratcliffe, "The Diverse Nature of Dodecahedral Cages in Clathrate Hydrates As Revealed by  $^{129}\text{Xe}$  and  $^{13}\text{C}$  NMR Spectroscopy:  $\text{CO}_2$  as a Small-Cage Guest", *Energy Fuels 1998*, 12 (2), 197–200.
- (8) D. Archer, "Methane hydrate stability and anthropogenic climate change", *Biogeosciences 2007*, 4, 521-544
- (9) T.M. Hoeler et al., "Acetogenesis from  $\text{CO}_2$  in an anoxic marine sediment", *Limnology and. Oceanography 1999*, 44 (3), 662-667
- (10) W.S. Borowski et al., "Marine pore-water sulphate profiles indicate in situ methane flux from underling gas hydrate", *Geology 1996*, 24 (7), 655-658
- (11) A.V. Milkov, "Molecular and stable isotope compositions of natural gas hydrates: a revised global dataset and basic interpretations in the context of geological settings", *Org. Geochem. 2005*, 36 (5), 681-702

- 
- (12) K. Nath, "Methane Hydrate: little known energy resource of the future", *Journal of Surface Science and Technology* 2007, 23 (1-2), 59-72.
  - (13) S. Circone et al, "Methane hydrate dissociation rates at 0.1 MPa and temperatures above 272 K", in *Gas Hydrates: Challenges for the Future*, 2000, Edited by Holder and Bishnoi, P.R., 545-555.
  - (14) K.A. Kvenvolden "Methane hydrate - a major reservoir of carbon in the shallow geosphere?", *Chemical Geology* 1998, 71, 41-51
  - (15) R. Sun and D. Zhenhao, "An accurate model to predict the thermodynamic stability of methane hydrate and methane solubility in marine environments", *Chemical Geology* 2007, 244, 248-262
  - (16) R. Norris and U. Rohl, "Carbon cycling and chronology of climate warming during the Palaeocene/Eocene transition", *Nature* 1999, 401, 775-778
  - (17) T. Uchida et al., "Decomposition of methane hydrates in sand, sandstone, clays, and glass beads", *Journal of Geophysical Research* 2004, 109, B05206
  - (18) C. K. Paull et al, Increased continental margin slumping frequency during low stands above gas hydrate bearing sediments", *Geology* 1996, 24, 143-146
  - (19) Hydratec Project, "Techniques for the quantification of methane hydrate in European Continental Margins", 2004, [www.hydratech.bham.ac.uk](http://www.hydratech.bham.ac.uk)
  - (20) J.A. Majorowicz et al., "Study of the natural gas "Trap Zone" and the methane hydrate potential in the Sverdrup Basin, Canada", *Natural Resources Research* 2002, 11 (2), 79-96.
  - (21) The Technical Coordination Team of the National Methane Hydrate R&D Program (US DOE), "An interagency five-year plan for methane hydrate research and development FY2007-FY 2011", Technical Report, April 2007, 1-37
  - (22) G.R. Dickens, "The potential volume of oceanic methane hydrates with variable external conditions", *Organic Geochemistry* 2001, 32, 1179-1193.
  - (23) B.C. Chakoumakos, " Preface to the Clathrate Hydrates special issue", *American Mineralogist* 2004, 89, 1153-1154



- 
- (24) R. Birchwood et al., "Safe drilling in gas-hydrate prone sediments: findings from 2005 drilling campaign of the Gulf of Mexico Gas Hydrate Joint Industry Project (JIP)", *Fire in the Ice Winter 2008*, 1-4
  - (25) R.C. Hendrics, "Methane hydrates: more than a viable aviation fuel feed-stock option", Technical Report NASA/TM-2007-214816, 2007, 1-14
  - (26) Y. Zhou et al., "Experimental investigation of methane gas production from methane hydrate", *Industrial and Engineering Chemistry Research* 2009, 48, 3142-3149
  - (27) S.-Y. Lee, "Methane hydrates potential as a future energy source", *Fuel processing Technology* 2001, 71, 181-186
  - (28) L.J. Pacelli Zitha et al., "Gas hydrates as energy resource: will they deliver?", *Proceedings of the Vulnerability and Opportunity of Methane Hydrate Workshop*, 13-14 March 2008, Laxenburg, Austria
  - (29) D.H. Smith et al., "Assessing the thermodynamic feasibility of the conversion of methane hydrate into carbon dioxide hydrate in porous media", *Proceedings of the First National Conference on Carbon Sequestration*, 2001, National Energy Technology Laboratory
  - (30) S.M. Masutani, R.B. Coffin., "Research Activities on Marine Methane Hydrates and CO<sub>2</sub> Sequestration", *Proceedings of the 24th Meeting of the Marine Facilities Panel of the U.S.-Japan Cooperative Program in Natural Resources (UJNR)*, U.S. Dept. of the Navy, Carderock Division, NSWC, (2001), Washington, DC
  - (31) M.J. Castaldi et al., "Down-hole combustion method for gas production from methane hydrates", *Journal of petroleum Science and Engineering* 2007, 56, 176-185
  - (32) N. Nakicenovic et P. Canadell, *Draft Meeting Proposal for the Global Carbon Project and IIASA Vulnerability and Opportunity of Methane Hydrates Workshop*, 13-14 March 2008, Laxenburg, Austria
  - (33) P. Jauhari, "Methane hydrates in marine sediments - untapped source of energy", *Journal of Indian Ocean Studies* 2001, 9 (1)
  - (34) Federal Methane Hydrate Advisory Committee, "An assessment of Methane Hydrate Research Program and an assessment of the 5-year Research Plan of the Department of Energy", Report to Congress, June 2007

- 
- (35) L. Lewis, "Japan Arctic methane hydrate haul raises environment fears", *The Times* 2008, April 14, [www.timesonline.co.uk](http://www.timesonline.co.uk)
  - (36) The Technical Coordination Team of the National Methane Hydrate R&D Program, "An Interagency Five-Year Plan For Methane Hydrate Research And Development", Technical Report, April 2007
  - (37) E.C. Anders and M. Rothfuss, "Advanced Pressure Coring", Proceeding of the AAPG International Conference and Exhibition Cape Town, October 26-29 2008
  - (38) D. Marinakis et al., "The effect on the stability of deep sea sediment, caused by dissociation of the contained gas hydrate: The case of Anaximander mud volcano seabed", Proceedings of the 32<sup>o</sup> International Geological Congress, Firenze, 20-28 agosto 2004
  - (39) H. Wefeng et al. "Evaluation and analysis method for natural gas hydrate storage and transportation processes", *Energy Conversion and Management* 2008, 49, 2546-2553
  - (40) H. Ganji et al., "Effect of mixed compounds on methane hydrate formation and dissociation rates and storage capacity", *Fuel Processing Technology* 2007, 88, 891-895
  - (41) T. Sydeny and R.A. Dawe, "Review of ways to transport natural gas energy from countries which do not need the gas for domestic use", *Energy* 2003, 28, 1461-1477
  - (42) H. Kanda, "Economic study on natural gas transportation with natural gas hydrate (NGH) pellets", Proceedings of the 23rd World Gas Conference, Amsterdam 2006
  - (43) T. Nogami et al, "Development of natural gas ocean transportation chain by means of natural gas hydrate (NGH)", Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008), Vancouver, July 6-10, 2008
  - (44) K. Volker, "Implications of methane hydrate availability for future energy systems: a model-based scenario sensitivity analysis", *Proceedings of the Vulnerability and Opportunity of Methane Hydrate Workshop*, 13-14 March 2008, Laxenberg, Austria