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Oil & Gas Science and Technology – Rev. IFP, Vol. 55 (2000), No. 6, pp. 611-616

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V. Lachet[1] and E. Béhar[1]

1 Institut français du pétrole, Division Chimie et Physico-Chimie appliquées,
1 et 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France
e-mail: veronique.lachet@ifp.fr - emmanuel.behar@ifp.fr

* Paper presented at the *Third International Conference on Gas Hydrates* (Salt Lake City, Utah, USA, July 18-22, 1999)

Résumé — Perspectives industrielles des hydrates de gaz naturel — Les hydrates de gaz naturel sont habituellement considérés comme des sources de nuisances possibles lors du développement de champs de pétrole ou de gaz, en particulier dans les opérations de forage en eau profonde et si les technologies du transport polyphasique sont à examiner. Néanmoins, ils représentent un potentiel énergétique important, si des procédés économiques de récupération des énormes quantités de méthane piégées dans les hydrates se trouvant naturellement dans la croûte terrestre (« charbon blanc ») sont mis au point.

D'autre part, les hydrates peuvent être utilisés pour le stockage du gaz naturel d'une manière satisfaisante, tant sur les plans de l'économie que de la sécurité, en particulier dans les pays froids.

Dans les sites éloignés en mer, l'utilisation des hydrates pour le transport du gaz naturel est également considérée actuellement comme une alternative économique aux procédés basés soit sur la liquéfaction, soit sur la compression.

Cet article présente quelques perspectives industrielles envisageables à moyen terme, soit pour réduire les nuisances liées aux hydrates, soit pour exploiter leurs applications potentielles.
Mots-clés : hydrates, gaz naturel, ressources, stockage, transport.

Abstract — Industrial Perspective on Natural Gas Hydrates — *Natural gas hydrates are usually considered as possible nuisances in the development of oil and gas fields, mainly in deepwater drilling operations and if multiphase transport technologies are to be examined. However they have an energetic potential value if economic recovery schemes are found for the enormous amounts of methane trapped in the hydrates naturally occurring in the earth crust ("white coal").*

On another side, hydrates can be used for the safe and economic storage of natural gas, mainly in cold countries.

In remote offshore areas, the use of hydrates for natural gas transportation is also presently considered as an economic alternative to the processes based either on liquefaction or on compression.

This paper presents some possible medium-term industrial perspectives, either to reduce the nuisance of hydrates or to exploit their potential applications.
Keywords: hydrates, natural gas, resources, storage, transportation.

INTRODUCTION

The main hydrocarbon industry current concerns related to natural gas hydrates are presented in this paper. Attractive possible industrial uses of gas hydrates are introduced while the different problems encountered in the oil and gas industry due to hydrates are discussed. In the following, four items will be especially developed:

– *hydrates in the earth*: naturally occurring gas hydrates in the earth crust represent a considerable energy resource. A reasonable estimate of the amount of methane stored in *in-situ* gas hydrates is 10^{16} m^3 (Englezos, 1993). Such gas resources are regarded as the energy of the future ("white coal") provided economic recovery schemes are found;
– *hydrates in well drilling*: decomposition of the naturally occurring hydrates due to drilling through the hydrates zones and gas hydrates formation in the drilling fluids are two major problems for drilling operations. Drilling through hydrates zones, either for gas production from these naturally occurring hydratess or for oil and gas production from reservoirs located below the *in-situ* hydrates may cause serious problems: uncontrolled gas release, blowouts, fires, casing damage and gas leakage through and outside the casing. Hydrates formation in drilling muds during deepwater operations induces plugging of subsea equipment causing difficulties in subsequent field procedures. Barker and Gomez (1989) reported that the formation of gas hydrates during drilling operations has caused the plugging of the choke line and kill line, the blocking of the opening and closing of blowout preventers, the sealing of the wellbore annuli and the immobilization of the drill string;
– *hydrates in gas storage and transportation*: natural gas hydrates formation can be used for the storage and transportation of natural gas as volumetric gains can reach almost 155, meaning the hydrates volume can be about 155 times smaller than the corresponding gas volume under standard conditions;
– *hydrates in pipelines*: natural gas hydrates formation and deposition in wells and pipelines within a cold environment or in subsea flowlines and pipelines carrying (monophasic or multiphasic) gas, condensate or oil can cause severe problems, mainly during shutdowns and the following startups.

Gas hydrates also have some worth mentioning applications outside the fields of the hydrocarbon industry. The literature (Englezos, 1993) reports some interesting uses of hydrates formation for the development of innovative separation methods. For instance, they can be used in order to recover water from an aqueous solution by forming hydrates, separating the crystals from the concentrated solution and then decomposing the hydrates. Such a procedure is possible because gas hydrates contain only pure water and the hydrate-forming gases. Several applications based on this separation method have been thought of:

– concentration of aqueous organic solutions: fruit juices (Huang *et al.*, 1966), coffee extract (Werezak, 1969), sugar, etc.;
– processes for the desalination of seawater (Knox *et al.*, 1961; Barduhn *et al.*, 1962), etc.

1 *IN-SITU* GAS HYDRATES

Sediments in large areas of the permafrost and on the outer continental margins of the oceans occur within appropriate pressure and temperature conditions for hydrates to be stable. Temperature and pressure increase with depth, thus these two factors are working against each other for hydrates stability so that there are limited reservoirs where hydrates are stable. Seismic reflection profiles across continental margins indicate the frequent occurrence of natural gas hydrates within the few hundred meters of seafloor sediments, overlying deeper zones containing free gas or oil, as natural gas hydrates reservoirs form impermeable seals under which the hydrocarbons can accumulate. Natural gas hydrates zones are thus viable exploration targets. However, drilling through this naturally occurring hydrates reservoir may cause serious problems due to the potential for the catastrophic release of gases, resulting in the alteration of sedimentary geotechnical properties. Such difficulties will be discussed in Section 2.1.

At present, approximately 50 locations worldwide have been identified where geophysical and geochemical evidence indicates the occurrence of natural gas hydrates (Kelland, 1994). Quantification of the amount of gas, mostly methane, stored in hydrates reservoirs is difficult since only a few of the sites have been drilled and tested for their hydrates content. Estimates of the methane content of these reservoirs obtained by several researchers are summarized in Table 1 (Kelland, 1994). Gas hydrates in oceanic sediments may comprise the earth's largest fossil fuel reservoir.

TABLE 1

Gas and gas hydrates reserves (from Kelland, 1994)

In-situ gas hydrates estimate range	
Onshore, continental	$14 – 34\,000 \times 10^{12}$ m^3
Offshore, oceanic	$3100 – 7\,600\,000 \times 10^{12}$ m^3
Unexploited conventional gas reserves	260×10^{12} m^3

Problems now are in determining which gas hydrates reservoirs are economically exploitable and in developing the technology for their production. Possible production methods of such naturally occurring hydrates reservoirs are:

– reducing the pressure;
– increasing the temperature;

– adding a substance, such as methanol, which decomposes the hydrates.

This last method has been used in the production of natural gas from hydrates reserves at Messoiakh in Russia (Makogon, 1974).

The current situation can be summarized by the *Shell* Gas Hydrate Team reflections (Krason, 1999): “There do not appear to be any major technical ‘show-stoppers’ to hydrate-associated gas production, if suitable accumulations can be found.” The team also asserts that “The economics of drilling, completing and producing deepwater gas-only wells could well be the major hurdle yet to be resolved.”

2 HYDRATES AND DRILLING

With the increase in deepwater exploration, two major problems can be encountered:
– problems due to the dissociation of *in-situ* hydrates when drilling through naturally occurring hydrates zones;
– problems due to the formation of hydrates in the drilling fluids when drilling a new well.

2.1 Drilling through Hydrate Zones

Gas hydrates that naturally exist in the earth may pose serious problems to drilling operations. Two techniques have been used to tackle these problems.

The first solution is to prevent the dissociation of hydrates by:
– reducing the temperature of the drilling mud;
– increasing the mud density;
– decreasing the penetration rate.

The second technique, proposed by Franklin (1983), is to induce a controlled hydrates decomposition process instead of trying to prevent this dissociation. Such controlled dissociation can be encouraged by:
– increasing the temperature of the drilling mud;
– decreasing the mud weight;
– decreasing the penetration rate;
– maintaining laminar mud circulation in the well annulus.

2.2 Hydrates Formation in Drilling Muds

The risk of hydrates formation in drilling muds has become today a major concern in drilling operations. The higher sea-floor hydrostatic pressures and the lower environmental temperatures encountered in deepwater drilling increase the likelihood of hydrates formation. At the same time, the move towards the use of environmentally favored water-based over oil-based drilling fluids has made the problem even more worrying.

Surprisingly, the literature reports very few cases of hydrates formation in drilling fluids. According to Barker and Gomez (1989), possible explanations for this absence of reports are that:
– the industry deepwater well drilling experience is limited;
– the likelihood of gathering favorable conditions (sufficient quantities of gas and water, high pressure and low temperature) for hydrates formation is relatively low;
– some well difficulties might have been attributed to other causes because of a lack of understanding and recognition of hydrates.

One can also add that hydrates problems in drilling operations are not necessarily disclosed outside the company that encountered such difficulties.

Barker and Gomez (1989) cite two hydrates experiences with drilling muds in deepwater offshore Santa Barbara (1977) and in the Green Canyon of the Gulf of Mexico (1985). Well choke lines, kill lines and blowout preventers were plugged. This plugging of the well control equipment has led to both safety and economic problems. Losses in drill times has reached up to 70 days (Barker, 1988).

The following simple rules of thumb described by Sloan (1998) may be used to estimate risks of hydrates formation at various water depths:
– for water depth below 300 m, a hydrates problem will probably not occur;
– for water depth in between 300 and 460 m, without inhibition a hydrates problem may occur;
– for water depth in between 460 and 600 m, without inhibition a hydrates problem will occur;
– for water depth above 900 m, experience is insufficient.

3 USE OF HYDRATES FOR NATURAL GAS STORAGE AND TRANSPORTATION

3.1 Advantages in Using Hydrates for Gas Storage and Transportation

There are three advantages in employing hydrates formation as a means for storage and transportation. First, a much lower space is needed, second, costs are reduced and third, safety is improved.

3.1.1 Volumetric Gains

An estimation of the gas storage capacity of hydrates has been proposed by Berner (1992). The theoretical storage capacity of Structure II hydrate crystals, with complete filling of all cavities, and with no impurities nor inclusions, is approximately 191 m^3 of gas per 1 m^3 of hydrates. 5 vol% of impurities or inclusions within the crystals together with 96% occupation of cavities will result in an effective storage capacity of approximately 174 m^3 of gas per 1 m^3 of hydrate crystals. “Help” gases such as ethane, propane and iso-butane are often added to natural gases in order to improve hydrates stability. Assuming that these supplemental gases account for approximately 8% of the gas volume, this lowers the volume reduction factor to approximately 160. This 160 m^3 value for the crystals together with a 0.97 packing factor leads to a final volumetric gain of approximately 155.

As a consequence, ships designed to carry natural gas as hydrates do not have to be larger than insulated bulk carriers.

3.1.2 Cost Reduction

In the literature (Kelland, 1994; Gudmundsson, 1996), comparisons are made between the storage of natural gas as gas hydrates and the storage of natural gas as liquefied natural gas (LNG) or compressed natural gas (CNG). Figure 1, proposed by Kelland (1994), gives an overview of the potential of these three techniques.

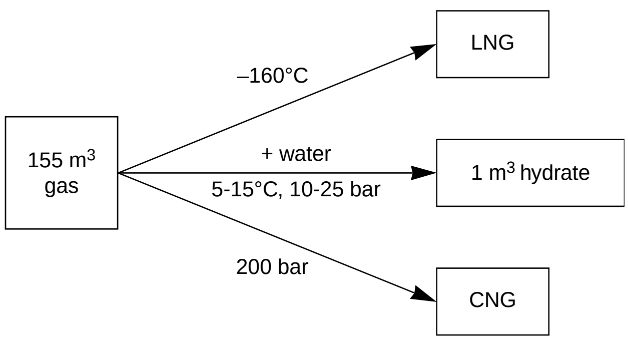

Figure 1

Technical advantages of gas hydrates compared to LNG and CNG (from Kelland, 1994).

The process for generating natural gas hydrates has the advantage of operating at temperatures and pressures near ambient conditions avoiding the use of very low temperatures (LNG) or very high pressures (CNG), leading to cost reduction for refrigeration or compression.

Experimental studies in Norway and Russia have shown that natural gas hydrates are stable for up to two years when stored in the range –5° to –15°C at atmospheric pressure. The addition of “help” gases can be used to increase this stability leading to significantly lower pressures and/or higher temperatures. Consequently, the equipment needed for the formation, the storage, as well as the transportation of the natural gas as hydrates is simpler and cheaper. For instance, ships designed to carry frozen hydrates do not need to be refrigerated and will thus be substantially less expensive than LNG ships. Berner (1992) reports the example of a gas field in the Barents Sea located in remote offshore where the pipelines used for conventional transport account for as much as 75% to 80% of the initial development cost of the project. In such offshore remote locations, the use of hydrates for gas transportation will exhibit considerable advantages.

Gudmundsson (1996) has estimated that the total capital cost of the natural gas hydrates technology, including hydrates production, shipping and melting processes, is approximately one quarter less than the LNG equivalent liquefaction, shipping and regasification.

3.1.3 Positive Safety Aspects

The use of natural gas hydrates for storage and transportation is an alternative that maintains high degree of safety. Unlike LNG or CNG, the explosive release of gas during an accident is inherently inhibited in a hydrates system because the crystals matrix, that has a high latent energy, must melt before gases are released. If a hydrates mass is ignited, it will burn slowly and will not explode. Concerning gas transportation, the use of hydrates has the following advantage: in case the wall of a hydrates carrier is breached, the natural gas hydrates will not readily flow out of the ship as is the case for LNG.

3.2 Production of Gas from Hydrates

As shown above, there are many advantages in using hydrates for gas storage and transportation. The question, however, is to develop economic methods for the production of the gas from the hydrates. The methane released from hydrates is expected to be saturated with water. For the utilization of this water-saturated methane, two product options are proposed by Wegrzyn *et al.* (1997).

Option 1 involves liquid-gas separation followed by pipeline transportation of the gas to customers, allowing methane to be used directly as a gaseous fuel.

Option 2 consists in converting methane into liquid fuels to avoid pipeline transport of gas from permafrost or offshore locations. Liquid fuels are produced *via* an indirect route where synthesis gas is first produced from the water-saturated methane using steam reforming, followed by catalytic conversion of this synthesis gas to products such as methanol and dimethylether. This selected process for synthesis of liquid fuels is highly energy efficient and selective, thus needing a minimum input of energy.

4 GAS HYDRATES FORMATION IN MULTIPHASE PIPELINES

The coexistence in multiphase wells and lines of natural or associated gas, condensate or crude, as well as condensed or formation water at relatively low temperatures under relatively high pressures can lead to hydrates formation which after agglomeration plugs the equipment.

The normal practice for avoiding such accidents is to add thermodynamic inhibitors, such as methanol, glycols or electrolytes at concentrations in the water phase within the range 10 to 50 wt%. Electrolytes injection is not a preferred option because the aqueous salt solutions are corrosive. Methanol, despite its toxicity for the environment, is the most commonly used inhibitor. The cost to the petroleum industry to inhibit the formation of gas hydrates is estimated to represent 5% to 8% of the total production plant cost (Sloan, 1991).

In order to reduce investment and operating costs, new additives that can be used at much lower concentrations have been developed. Such substances are usually classified as either dispersant additives or kinetic additives. With the first ones, sizable crystals growth and/or agglomeration are inhibited while with the second ones, nucleation is delayed and growth is maintained below a critical level. The replacement of methanol with such inhibitors can reduce the treating cost by 50% or more (Notz *et al.*, 1995), as the latter are effective at less than 1 wt% in the aqueous phase. Substantial progress is currently being made to validate kinetic and dispersant inhibitors on some pilot fields, but it may take several years before such methods are commonly used in many pipeline applications.

Notz *et al.* (1995) have shown some limits of kinetic inhibitors leading to the general conclusion that such additives should be considered when the reservoir fluids are not too far into the hydrates region (*i.e.* small subcooling) and/or if the residence time in the well, the flowline or the pipeline is relatively short.

Dispersant additives are efficient if a liquid hydrocarbon phase, condensate or crude, is available and if the water cut (or the Water Oil Ratio) is kept small (Béhar *et al.*, 1995).

5 POSSIBLE MEDIUM-TERM INDUSTRIAL PERSPECTIVES

Here are some perspectives that might be industrially used in a relatively near future in the oil and gas production, either to reduce the nuisance of hydrates or to exploit their potential applications.

5.1 Dissociation of Hydrates

Dissociation of hydrates, either for producing natural gas or for melting plugs (in drilling muds and in production wells or multiphase transport lines), could be induced by a highly exothermic chemical reaction (Rojey and Jaffret, 1997). Examples of such reactions are:

$$NaNO_2 + NH_4NO_3 \rightarrow N_2 + 2H_2O + NaNO_3$$

or:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

5.2 Hydrates in Drilling Fluids

Planning of deepwater wells should incorporate an awareness that gas hydrates can form: the likelihood of hydrates formation in the wellhead, the blowout preventers, the choke line and the kill line must be assessed before the well is drilled. Such planning should also consider long shutdown periods.

Heat maintenance of near-mudline well-control equipment by external heat-transfer systems is a potential method for reducing the risk of hydrates.

Mud formulations should be designed to inhibit hydrates (*i.e.* high salinity plus glycerol content) while achieving a correct balance of mud weight and viscosity. The compatibility of the chemicals added to inhibit hydrates with both the drilling fluid and the cementing operations should be considered, as well as the resultant mud toxicity.

5.3 Hydrates in Multiphase Production and Transport

Development of new and better kinetic or dispersant additives does not appear to be the favored option chosen by many operating companies at the present time, since in most cases methanol is used to avoid hydrates problems, even though its toxicity is well known.

However, for covering the whole range of applications in crudes and natural gases multiphase production and transport, mixtures of a kinetic additive with a thermodynamic inhibitor or even with a dispersant additive should be considered. No quantification of the effectiveness of such combinations is found in the literature.

Devices able to detect the formation of hydrates, especially for subsea applications, should be an effective feedback monitoring system which will make any inhibition program more efficient and cost effective.

To conclude, the emphasis will be put on the new industrial opportunities which arise from the use of hydrates, either naturally or artificially formed and further decomposed.

5.4 Use of Hydrates for Gas Transportation

The use of marine transport for natural gas in hydrates form could be a potentially safe and reliable means of transporting large volumes of natural gas across the ocean with a bulk storage capacity within the natural gas hydrates carrier of about 155 m^3 of gas per 1 m^3 of ship storage space.

Also, large-scale and long-distance transport of natural gas at atmospheric pressure in hydrates form should be possible in a relatively near future.

5.5 *In-Situ* Gas Hydrates

Natural gas hydrates represent a huge untapped potential source of energy for the 21st century.

If the technological challenges for the catalytic conversion of natural gas hydrates in liquid fuels are met, a vast source of clean energy will become more easily available in the 21st century.

ACKNOWLEDGEMENTS

Special thanks are addressed to all organizing committee members of the *Third International Conference on Gas Hydrates* for their invitation to present this paper.

We thank the *United Engineering Foundation* for its financial support.

Pr. Gerald Holder is gratefully acknowledged for his help.

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Final manuscript received in August 2000